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(54) **A dispensing device for a detergent tablet**

(57) A combination of a detergent tablet (1) and of a device (2) to disperse the tablet (1) in an aqueous medium, the device (2) containing the tablet (1), the device (2) being at least partially formed from a flexible water permeable material (3).

The device is also partially formed from a flexible water impermeable material (40, 41).

In another aspect, a process of dispersing a detergent tablet (1) in an aqueous medium in a washing machine comprising the first step of providing a detergent tablet (1) and a device (2) being at least partially formed from a flexible water permeable material (3), a second step of inserting the tablet (1) in the device (2), and a third step of inserting the device (2) containing the tablet (1) into the washing machine, the device (2) being also partially formed from a flexible water impermeable material (40, 41).

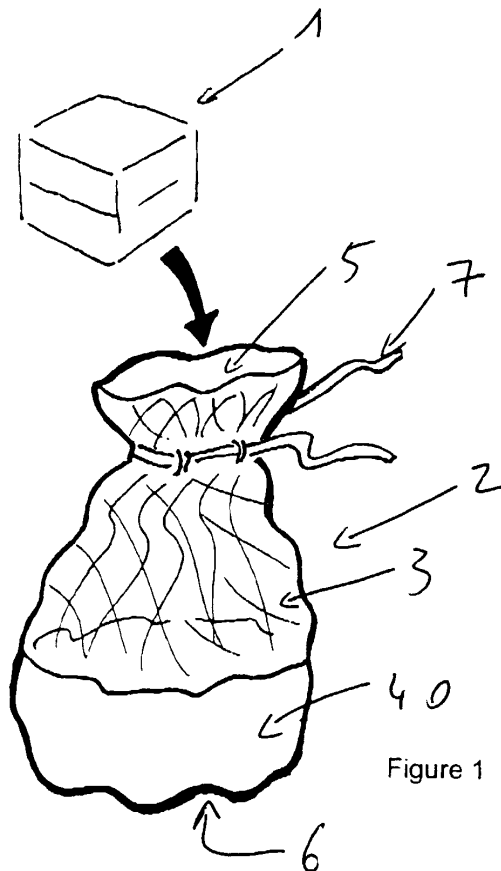


Figure 1

DescriptionTechnical field

5 **[0001]** The present invention relates to devices for delivering a detergent composition in tablet form.

Background of the invention

10 **[0002]** Tablets are used in particular in the field of automatic dish washing or in the field of machine washing of laundry to facilitate handling of a detergent composition compared to alternative forms such as powder, granules, liquids or paste. However, in order to maintain the dispersion characteristics of a detergent composition in tablet form when compared to the alternative forms listed above, it is preferred to use a specific device for delivering the detergent composition in tablet form.

15 **[0003]** It is known for instance from GB 2 327 093 A to combine a detergent tablet and a device to disperse the tablet in an aqueous medium, the device containing the tablet, the device being at least partially formed from a flexible water permeable material.

20 **[0004]** Also known is a process of dispersing a detergent tablet in an aqueous medium in a washing machine comprising the first step of providing a detergent tablet and a device being at least partially formed from a flexible water permeable material, a second step of inserting the tablet in the device, and a third step of inserting the device containing the tablet into the washing machine.

[0005] Among the advantages of devices to disperse a tablet is their ability to improve the dispersion characteristics of the tablet, which may result from an increase of mechanical disintegration.

25 **[0006]** While having this and other advantages, devices to disperse a tablet have disadvantages. For example, the flexible water permeable material may let through, prior to use in the wash medium, dry powder which is usually produced by the tablet by friction. In addition, the flexible permeable material typically comprises apertures of a size such that the fingers of a user will be in contact with the tablet itself through such apertures once the tablet is inserted into the device and prior to use in the wash medium.

30 **[0007]** The invention seeks to provide a combination and a process of the above mentioned type, which avoids at least some of the above mentioned disadvantages.

Summary of the invention

35 **[0008]** In accordance with the invention, this object is accomplished in the first and second aspects of the invention in a combination or process of the above mentioned kind characterised in that the device is also partially formed from a flexible water impermeable material.

40 **[0009]** A combination or process in accordance with the invention has a number of advantages. Since the device is also partially formed from a flexible water impermeable material, contact between fingers of a user and the tablet may be prevented by having the user catching the device in its part formed from the water impermeable material. Indeed, such water impermeable material would a fortiori prevent contact between the tablet and the fingers. Further, the part of the device formed from the flexible water permeable material would also prevent any dry powder produced by the tablet by friction to be let through. Due to the flexibility of the water impermeable material, the improvement in dispersion characteristics of the tablet which may result from an increase of mechanical disintegration is maintained.

Detailed description of the invention

45 **[0010]** The invention relates to the combination of a detergent tablet and of a device to disperse the tablet in an aqueous medium.

By a device to disperse a tablet it should be understood a device which is used for dispensing the tablet in an aqueous medium, whereby the dispensing is usually facilitated by the use of the dispensing device. Dispensing devices already exist for detergent powder, as proposed example in EP-A-343069 or EP-A-343070. Dispensing devices also exist for liquid detergent, as proposed for example in FR-A-2563250. Depending on the form of the detergent, the dispensing devices have different specifics. An aqueous medium is typically formed mainly of water, and typically applies here to the washing medium for laundry.

50 The invention relates to the combination of a detergent tablet and of a device. A detergent tablet is typically obtained by compression of a detergent powder. A detergent tablet may be coated or not, and have one or more layers. Detergent tablets are being sold currently. Typical detergent tablets are described for example in EP-A-846755.

55 The device of the invention is at least partially formed from a flexible water permeable material. By flexible, it should be understood that the material is not rigid. Such a characteristic of the material normally leads to improved tablet

disintegration due to the mechanical squeezing effect incurred by the deformation of the flexible material during a normal wash, such deformation being for example due to collisions between the device and the laundry to be washed, or to collisions between the device a wall of a washing machine. Typically flexible material include for example synthetic polymeric (nylon, polyolefin) materials or vegetal (cotton, cellulosic) materials. The flexible material is also water permeable. This should be understood as meaning that liquid water is not prevented from flowing through the material. This characteristic allows to facilitate dispersion of a tablet by allowing ingress or egress of the aqueous medium in which the tablet disperses.

[0011] Tablet dispersion is used here as a generic wording encompassing equivalent expressions such as tablet disintegration or tablet dissolution for example.

[0012] According to the invention, the device contains the tablet. Indeed, the device is used as a mean for controlling the dispersion characteristics of the tablet, so that the device defines a first region which is inside the device and contains the tablet, as well as a second region which is outside the device, the characteristics of the device itself allowing to control dispersion of the tablet by means of the characteristics of the separation between the first and the second region. typically, such separation is achieved partly by the flexible water permeable material. The characteristics of the separation between the first and the second region depend normally also on the flexible water impermeable material.

Typically, a material is hereby considered as flexible when it collapses when submitted to its own weight.

[0013] Indeed, the device is also partially formed from a flexible water impermeable material. A water impermeable material is sift-proof such that liquid water cannot pass through such a material. The presence of such a sift-proof material allows to prevent passage of even the thinnest solid particles which may be separated from the tablet for example by friction. Thus, when a user is catching such a device by placing the fingers onto the sift-proof material, contact between such solid particles or even direct skin contact with the tablet is avoided.

[0014] In a preferred embodiment, the device has an opening and a part opposed to the opening, whereby the part opposed to the opening is formed from the flexible water impermeable material. By a part opposed to the opening, it should be understood a part which is on the bottom of the device if the opening is on the top of the device. It is preferred that the part opposed to the opening is formed from the flexible water impermeable material in order to prevent the thinnest solid particles which may be separated from the tablet for example by friction to sieve through and to be deposited on a support for the device prior to inserting the device in a washing machine. Indeed, typically, a user will put the empty device onto a supporting surface, the part opposed to the opening being in contact with the supporting surface, and insert a tablet into the device through the opening, whereby the tablet may be inserted together with solid particles which may be separated from the tablet by friction for example, such solid particles being prevented from soiling the supporting surface by means of the impermeable material forming the part opposed to the opening.

[0015] In another preferred embodiment, the part of the device being formed from flexible water impermeable material is in the form of a band. Typically, such a band is placed around the device allowing a potential user to place the fingers onto the band when holding the device, thus in particular minimising potential direct skin contact with the detergent tablet.

[0016] The device is at least partially formed from a flexible water permeable material and also partially formed from a flexible water impermeable material. Substantially, the device is preferably completely formed of the addition of the flexible water permeable material and of the flexible water impermeable material, although it may comprise addition optional elements such as closing means or such as structural means. The flexible material forming the device, has a total surface area. The total surface area of the flexible material is preferably formed of more than 50% of the permeable material and of less than 50% of the impermeable material. More preferably, the total surface area of the flexible material is formed of more than 60% of the permeable material and of less than 40% of the impermeable material. Even more preferably, the total surface area of the flexible material is formed of more than 75% of the permeable material and of less than 25% of the impermeable material. Most preferably, the total surface area of the flexible material is formed of more than 90% of the permeable material and of less than 10% of the impermeable material. Further, the flexible impermeable material should preferably cover a surface area of at least half of the total external surface of a laundry detergent tablet. Typically, the flexible impermeable material should have a surface area of at least 10 cm², more preferably of at least 15 cm², even more preferably of at least 20 cm² and most preferably of at least 30 cm².

[0017] Preferably, the device comprises at least one wall, but may also comprises more than one wall, in order to be made more resistant, for example.

[0018] In a preferred embodiment, the flexible water permeable material is a net material. Such material may be woven, extruded or non-woven for example. Preferably, the material should be resistant to the high temperature of machine washing, to detergent compositions, and to use through several cycles. Further, it is preferred that the material is not abrasive to avoid damaging fabrics.

[0019] In a preferred embodiment, the device comprises a sleeve. Typically a sleeve is a piece of material in the shape of a tube having two ends. The sleeve has at least one opening to insert the tablet. What is meant by "opening to insert the tablet" is an opening which has dimensions allowing insertion of a tablet without involving permanent

deformation of the device.

In a most preferred embodiment, the sleeve has only one opening to insert the tablet. It should be noted that this preferred device may also comprise other apertures, whereby such other apertures are typically smaller than the opening to insert the tablet, so that the other apertures are not openings as far as the tablet itself is concerned. Preferably, this opening is simply located on one end of the sleeve, the other end of the sleeve being closed as far as a tablet is concerned.

In a further preferred embodiment, the sleeve has two openings for a tablet. Typically, each of these two openings is located on each of both ends of the sleeve. The advantage of such a device is that manufacture is rendered extremely simple as the device simply consists of a sleeve without need for closing one of the ends of such sleeve.

The sleeve may have a length and a flexibility allowing to prevent that the tablet escapes from the sleeve during a normal wash operation. Indeed, the combination of the length and of the flexibility of the sleeve is such that the egress of a tablet inserted in the sleeve is hindered. Preferably, the sleeve should have a length and a flexibility allowing to wrap the tablet in the sleeve. More preferably, the length and flexibility of the sleeve allows to wrap the sleeve around the tablet so that the wrapping part of the sleeve goes all around the tablet at least ones.

In the specific case where the sleeve has only one opening to insert the tablet, the part of the sleeve used to wrap the tablet is typically the part of the sleeve which comprises the opening, the tablet being normally sitting in the other part opposed to the opening.

In an other specific case where the sleeve comprises two openings, one at each end of the sleeve, the tablet would typically sit roughly in the middle of the sleeve, each of the free ends of the sleeve being thereby wrapped around the tablet.

[0020] It should be noted that wrapping may be obtained directly by the user prior to inserting the device together with the tablet into a laundry washing machine, or could also be produced within the washing machine due the interaction of the device with the laundry itself, in combination with the movement induced by the washing machine.

In a preferred embodiment, the sleeve has a length of at least 10 cm, more preferably of at least 17 cm, even more preferably of at least 22 cm and most preferably of at least 30 cm.

Preferably, the sleeve is of such a flexibility that it is freely pliant or pliable.

An opening to insert a tablet may be provided with alternative closing means such as a string, a velcro band or an elastic string or rubber band which allows insertion of the tablet when stretch and prevents egress of a tablet when in normal position.

[0021] Preferably the tablet fits loosely in the device, so that the tablet is not closely constrained by the wall of the sleeve, so that the tablet may move relatively freely within the device. This facilitates insertion of the tablet in the device, and may also favour disintegration of the tablet.

[0022] The invention is particularly advantageous with a tablet having a tensile strength of at least 30 KPa. Indeed, it was found that a tablet having a high tensile strength will require improved dispersion by means of a device when compared to a tablet having a low tensile strength. More preferably, the invention applies to a tablet having a tensile strength of at least 40 KPa, even more preferably of at least 50KPa.

[0023] In another aspect, the invention also relates to a process of dispersing a detergent tablet in an aqueous medium in a washing machine comprising the first step of providing a detergent tablet and a device being at least partially formed from a flexible water permeable material, a second step of inserting the tablet in the device, and a third step of inserting the device containing the tablet into the washing machine, the process being characterised in that the device is also partially formed from a flexible water impermeable material.

[0024] The detergent tablet and the device of the process are preferably according to the first aspect of the invention.

[0025] It should be noted that the process is preferred when two or more tablets are inserted into the device. Indeed, the insertion of more than one tablet may increase disintegration due to mechanical friction between the different tablets. Further, at equivalent total product quantity, the surface activity of two tablets will normally be higher than the surface activity of one tablet only.

[0026] The invention also relates to a kit comprising a device and a plurality of detergent tablets according to the first aspect of the invention, the device and the plurality of detergent tablets being provided in a package. Typically, the package is a carton box, the carton box containing the detergent tablets which may be contained into secondary packages such as flow-wraps, the device being preferably collapsible and placed on the top part of the box.

[0027] Specific information on detergent tablets are given in the following paragraphs.

[0028] The tablets may comprise components such as fragrance, surfactants, enzymes, detergent etc.... Typical tablet compositions for the preferred embodiment of the present invention are disclosed in the pending European applications of the Applicant n° 96203471.6, 96203462.5, 96203473.2 and 96203464.1 for example. Elements typically entering in the composition of detergent tablets or of other forms of detergents such as liquids or granules are detailed in the following paragraphs.

Highly soluble Compounds

[0029] The tablet may comprise a highly soluble compound. Such a compound could be formed from a mixture or from a single compound. A highly soluble compound is defined as follow:

A solution is prepared as follows comprising de-ionised water as well as 20 grams per litre of a specific compound:

1- 20 g of the specific compound is placed in a Sotax Beaker. This beaker is placed in a constant temperature bath set at 10°C. A stirrer with a marine propeller is placed in the beaker so that the bottom of the stirrer is at 5 mm above the bottom of the Sotax beaker. The mixer is set at a rotation speed of 200 turns per minute.

2- 980 g of the de-ionised water is introduced into the Sotax beaker.

3- 10 s after the water introduction, the conductivity of the solution is measured, using a conductivity meter.

4- Step 3 is repeated after 20, 30, 40, 50, 1min, 2 min, 5 min and 10 min after step 2.

5- The measurement taken at 10 min is used as the plateau value or maximum value.

The specific compound is highly soluble according to the invention when the conductivity of the solution reaches 80% of its maximum value in less than 10 seconds, starting from the complete addition of the de-ionised water to the compound. Indeed, when monitoring the conductivity in such a manner, the conductivity reaches a plateau after a certain period of time, this plateau being considered as the maximum value. Such a compound is preferably in the form of a flowable material constituted of solid particles at temperatures comprised between 10 and 80°Celsius for ease of handling, but other forms may be used such as a paste or a liquid.

Example of highly soluble compounds include Sodium di isoalkylbenzene sulphonate (DIBS) or Sodium toluene sulphonate for example.

Cohesive Effect

[0030] The tablet may comprise a compound having a Cohesive Effect on the particulate material of a detergent matrix forming the tablet. The Cohesive Effect on the particulate material of a detergent matrix forming the tablet or a layer of the tablet is characterised by the force required to break a tablet or layer based on the examined detergent matrix pressed under controlled compression conditions. For a given compression force, a high tablet or layer strength indicates that the granules stuck highly together when they were compressed, so that a strong cohesive effect is taking place. Means to assess tablet or layer strength (also refer to diametrical fracture stress) are given in Pharmaceutical dosage forms : tablets volume 1 Ed. H.A. Lieberman et al, published in 1989.

The cohesive effect is measured by comparing the tablet or layer strength of the original base powder without compound having a cohesive effect with the tablet or layer strength of a powder mix which comprises 97 parts of the original base powder and 3 parts of the compound having a cohesive effect. The compound having a cohesive effect is preferably added to the matrix in a form in which it is substantially free of water (water content below 10% (pref. below 5%)). The temperature of the addition is between 10 and 80C, more pref. between 10 and 40C.

A compound is defined as having a cohesive effect on the particulate material according to the invention when at a given compacting force of 3000N, tablets with a weight of 50g of detergent particulate material and a diameter of 55mm have their tablet tensile strength increased by over 30% (preferably 60 and more preferably 100%) by means of the presence of 3% of the compound having a cohesive effect in the base particulate material.

An example of a compound having a cohesive effect is Sodium di isoalkylbenzene sulphonate.

When integrating a highly soluble compound having also a cohesive effect on the particulate material used for a tablet or layer formed by compressing a particulate material comprising a surfactant, the dissolution of the tablet or layer in an aqueous medium or solution is significantly increased. In a preferred embodiment, at least 0.5% per weight of a tablet or layer is formed from the highly soluble compound, more preferably at least 0.75%, even more preferably at least 2% and most preferably at least 4% per weight of the tablet or layer being formed from the highly soluble compound having a cohesive effect on the particulate material.

It should be noted that a composition comprising a highly soluble compound as well as a surfactant is disclosed in EP-A-0 524 075, this composition being a liquid composition.

A highly soluble compound having a cohesive effect on the particulate material allows to obtain a tablet having a higher tensile strength at constant compacting force or an equal tensile strength at lower compacting force when compared to traditional tablets. Typically, a whole tablet will have a tensile strength of more than 5kPa, preferably of more than 10kPa, more preferably, in particular for use in laundry applications, of more than 15kPa, even more preferably of more than 30 kPa and most preferably of more than 50 kPa, in particular for use in dish washing or auto dish washing applications; and a tensile strength of less than 300 kPa, preferably of less than 200 kPa, more preferably of less than 100 kPa, even more preferably of less than 80 kPa and most preferably of less than 60 kPa. Indeed, in case of laundry application, the tablets should be less compressed than in case of auto dish washing applications for example, whereby

the dissolution is more readily achieved, so that in a laundry application, the tensile strength is preferably of less than 30 kPa.

This allows to produce tablets or layers which have a solidity and mechanical resistance comparable to the solidity or mechanical resistance of traditional tablets while having a less compact tablet or layer thus dissolving more readily. Furthermore, as the compound is highly soluble, the dissolution of the tablet or layer is further facilitated, resulting in a synergy leading to facilitated dissolution for a tablet according to the invention.

Tablet Manufacture

[0031] The tablet may comprise several layers. For the purpose of manufacture of a single layer, the layer may be considered as a tablet itself.

Detergent tablets can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients, in particular gelling surfactants, are used in particulate form. Any liquid ingredients, for example surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients.

In particular for laundry tablets, the ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure. Preferably, the tablets according to the invention are compressed using a force of less than 100000N, more preferably of less than 50000N, even more preferably of less than 5000N and most preferably of less than 3000 N. Indeed, the most preferred embodiment is a tablet suitable for laundry compressed using a force of less than 2500N, but tablets for auto dish washing may also be considered for example, whereby such auto dish washing tablets are usually more compressed than laundry tablets.

The particulate material used for making a tablet can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 600g/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear batch mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige® CB and/or Lodige® KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation sentering, etc. Individual particles can also be any other particle, granule, sphere or grain.

The components of the particulate material may be mixed together by any conventional means. Batch is suitable in, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum (s) or mixer(s). Non-gelling binder can be sprayed on to the mix of some, or all of, the components of the particulate material. Other liquid ingredients may also be sprayed on to the mix of components either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate material after spraying the binder, preferably towards the end of the process, to make the mix less sticky.

The tablets may be manufactured by using any compacting process, such as tableting, briquetting, or extrusion, preferably tableting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy®, Korch®, Manesty®, or Bonals®). The tablets prepared according to this invention preferably have a diameter of between 20mm and 60mm, preferably of at least 35 and up to 55 mm, and a weight between 25 and 100 g. The ratio of height to diameter (or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. In another preferred embodiment, the tablets have a square cross-section of 45 mm by 45 mm and are 25 mm high. The compaction pressure used for preparing these tablets need not exceed 100000 kN/m², preferably not exceed 30000 kN/m², more preferably not exceed 5000 kN/m², even more preferably not exceed 3000kN/m² and most preferably not exceed 1000kN/m². In a preferred embodiment according to the invention, the tablet has a density of at least 0.9 g/cc, more preferably of at least 1.0 g/cc, and preferably of less than 2.0 g/cc, more preferably of less than 1.5 g/cc, even more preferably of less than 1.25 g/cc and most preferably of less than 1.15 g/cc.

Multi layered tablets are typically formed in rotating presses by placing the particulate material of each layer, one after the other in force feeding flasks. As the process continues, the particulate material layers are then pressed together in the pre-compression and compression stages stations to form the multilayer tablet. With some rotating presses it is also possible to compress the first feed layer before compressing the whole tablet.

Hydrotrope compound

[0032] A highly soluble compound having a cohesive effect may be integrated to a detergent tablet, whereby this compound is also a hydrotrope compound. Such hydrotrope compound may be generally used to favour surfactant dissolution by avoiding gelling. A specific compound is defined as being hydrotrope as follows (see S.E. Friberg and M. Chiu, J. Dispersion Science and Technology, 9(5&6), pages 443 to 457, (1988-1989)):

EP 1 072 716 A1

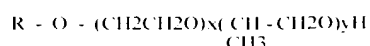
1. A solution is prepared comprising 25% by weight of the specific compound and 75% by weight of water.
2. Octanoic Acid is thereafter added to the solution in a proportion of 1.6 times the weight of the specific compound in solution, the solution being at a temperature of 20° Celsius. The solution is mixed in a Sotax beaker with a stirrer with a marine propeller, the propeller being situated at about 5mm above the bottom of the beaker, the mixer being set at a rotation speed of 200 rounds per minute.
3. The specific compound is hydrotrope if the the Octanoic Acid is completely solubilised, i.e . if the solution comprises only one phase, the phase being a liquid phase.

It should be noted that in a preferred embodiment of the invention, the hydrotrope compound is a flowable material made of solid particles at operating conditions between 15 and 60° Celsius.

Hydrotrope compounds include the compounds listed thereafter:

A list of commercial hydrotropes could be found in McCutcheon's Emulsifiers and Detergents published by the McCutcheon division of Manufacturing Confectioners Company. Compounds of interest also include:

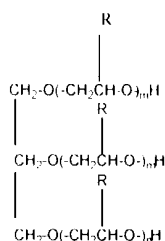
1. Nonionic hydrotrope with the following structure:



where R is a C8-C10 alkyl chain, x ranges from 1 to 15, y from 3 to 10.

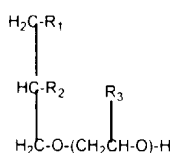
2. Anionic hydrotropes such as alkali metal aryl sulfonates. This includes alkali metal salts of benzoic acid, salicylic acid, benzenesulfonic acid and its many derivatives, naphthoic acid and various hydroaromatic acids. Examples of these are sodium, potassium and ammonium benzene sulfonate salts derived from toluene sulfonic acid, xylene sulfonic acid, cumene sulfonic acid, tetralin sulfonic acid, naphthalene sulfonic acid, methyl- naphthalene sulfonic acid, dimethyl naphthalene sulfonic acid, trimethyl naphthalene sulfonic acid= Other examples include salts of dialkyl benzene sulfonic acid such as salts of di-isopropyl benzene sulfonic acid, ethyl methyl benzene sulfonic acid, alkyl benzene sulfonic acid with an alkyl chain length with 3 to 10, (pref. 4 to 9), linear or branched alkyl sulfonates with an alkyl chain with 1 to 18 carbons.

3. Solvent hydrotropes such as alkoxyated glycerines and alkoxyated glycerides, esters slakoxyated glycerines, alkoxyated fatty acids, esters of glycerin, polyglycerol esters. Preferred alkoxyated glycerines have the following structure:



where l, m and n are each a number from 0 to about 20, with l+m+n = from about 2 to about 60, preferably from about 10 to about 45 and R represents H, CH₃ or C₂H₅

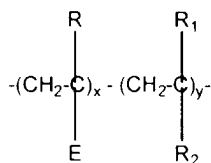
Preferred alkoxyated glycerides have the following structure



where R₁ and R₂ are each C_nCOO or -(CH₂CHR₃-O)_l-H where R₃ = H, CH₃ or C₂H₅ and l is a number from 1 to about 60, n is a number from about 6 to about 24.

4. Polymeric hydrotropes such as those described in EP636687:

EP 1 072 716 A1



where

E is a hydrophilic functional group,
R is H or a C1-C10 alkyl group or is a hydrophilic functional group;
R1 is H a lower alkyl group or an aromatic group,
R2 is H or a cyclic alkyl or aromatic group.

The polymer typically has a molecular weight of between about 1000 and 1000000.

5. Hydrotrope of unusual structure such as 5-carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid (Diacid®)

Use of such compound in the invention would further increase the dissolution rate of the tablet, as a hydrotrope compound facilitates dissolution of surfactants, for example. Such a compound could be formed from a mixture or from a single compound.

Tensile Strength

[0033] For the purpose of measuring tensile strength of a layer, the layer may be considered as a tablet itself.

Depending on the composition of the starting material, and the shape of the tablets, the used compacting force may be adjusted to not affect the tensile strength, and the disintegration time in the washing machine. This process may be used to prepare homogenous or layered tablets of any size or shape.

For a cylindrical tablet, the tensile strength corresponds to the diametrical fracture stress (DFS) which is a way to express the strength of a tablet or layer, and is determined by the following equation :

$$\text{Tensile strength} = 2 F / \pi D t$$

Where F is the maximum force (Newton) to cause tensile failure (fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell industries, Inc. D is the diameter of the tablet or layer, and t the thickness of the tablet or layer. For a non round tablet, πD may simply be replaced by the perimeter of the tablet.

(Method Pharmaceutical Dosage Forms : Tablets Volume 2 Page 213 to 217). A tablet having a diametral fracture stress of less than 20 kPa is considered to be fragile and is likely to result in some broken tablets being delivered to the consumer. A diametral fracture stress of at least 25 kPa is preferred.

This applies similarly to non cylindrical tablets, to define the tensile strength, whereby the cross section normal to the height of the tablet is non round, and whereby the force is applied along a direction perpendicular to the direction of the height of the tablet and normal to the side of the tablet, the side being perpendicular to the non round cross section.

Tablet Dispensing

[0034] The rate of dispensing of a detergent tablet can be determined in the following way:

Two tablets, nominally 50 grams each, are weighed, and then placed in the dispenser of a Baucknecht® WA9850 washing machine. The water supply to the washing machine is set to a temperature of 20 °C and a hardness of 21 grains per gallon, the dispenser water inlet flow-rate being set to 8 l/min. The level of tablet residues left in the dispenser is checked by switching the washing on and the wash cycle set to wash program 4 (white/colors, short cycle). The dispensing percentage residue is determined as follows:

$$\% \text{ dispensing} = \text{residue weight} \times 100 / \text{original tablet weight}$$

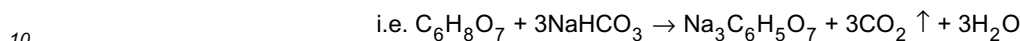
The level of residues is determined by repeating the procedure 10 times and an average residue level is calculated based on the ten individual measurements. In this stressed test a residue of 40 % of the starting tablet weight is considered to be acceptable. A residue of less than 30% is preferred, and less than 25% is more preferred.

It should be noted that the measure of water hardness is given in the traditional "grain per gallon" unit, whereby 0.001

mole per litre = 7.0 grain per gallon, representing the concentration of Ca^{2+} ions in solution.

Effervescent

- 5 **[0035]** Detergent tablets may further comprise an effervescent. Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas,



Further examples of acid and carbonate sources and other effervescent systems may be found in : (Pharmaceutical Dosage Forms : Tablets Volume 1 Page 287 to 291).

- 15 An effervescent may be added to the tablet mix in addition to the detergent ingredients. The addition of this effervescent to the detergent tablet improves the disintegration time of the tablet. The amount will preferably be between 5 and 20 % and most preferably between 10 and 20% by weight of the tablet. Preferably the effervescent should be added as an agglomerate of the different particles or as a compact, and not as separated particles.

- 20 Due to the gas created by the effervescency in the tablet, the tablet can have a higher D.F.S. and still have the same disintegration time as a tablet without effervescency. When the D.F.S. of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

Further dissolution aid could be provided by using compounds such as sodium acetate or urea. A list of suitable dissolution aid may also be found in Pharmaceutical Dosage Forms: Tablets, Volume 1, Second edition, Edited by H.A. Lieberman et al, ISBN 0-8247-8044-2.

25 Coating

[0036] Solidity of a tablet may be improved by making a coated tablet, the coating covering a non-coated tablet, thereby improving the mechanical characteristics of the tablet.

- 30 This very advantageously applies to multi-layer tablets, whereby the mechanical characteristics of a more elastic layer can be transmitted via the coating to the rest of the tablet, thus combining the advantage of the coating with the advantage of the more elastic layer. Indeed, mechanical constraints will be transmitted through the coating, thus improving mechanical integrity of the tablet.

- 35 In one embodiment of the present invention, the tablets may then be coated so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in no more than very low levels of breakage or attrition. Finally the coating is preferably brittle so that the tablet breaks up quickly when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dissolved under alkaline conditions, or is readily emulsified by surfactants. This contributes to avoiding the problem of visible residue in the window of a front-loading washing machine during the wash cycle, and also avoids deposition of undissolved particles or lumps of coating material on the laundry load.

Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

The coating material has a melting point preferably of from 40 °C to 200 °C.

- 45 The coating can be applied in a number of ways. Two preferred coating methods are a) coating with a molten material and b) coating with a solution of the material.

- In a), the coating material is applied at a temperature above its melting point, and solidifies on the tablet. In b), the coating is applied as a solution, the solvent being dried to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Normally when the molten material is sprayed on to the tablet, it will rapidly solidify to form a coherent coating. When tablets are dipped into the molten material and then removed, the rapid cooling again causes rapid solidification of the coating material. During the solidification phase, the coating undergoes some internal stress (e.g. shrinkage upon cooling) and external stress (e.g. tablet relaxation). This will likely cause some cracks in the structure such as edge splitting if the coating material is too brittle to withstand these mechanical stress, which is often the case when a coating is solely made from components solid at 25°C. Indeed, it is preferred that the coating comprises a component which is liquid at 25°C. It is believed that this liquid component will allow the coating to better withstand and absorb mechanical stress by rendering the coating structure more flexible. The component which is liquid at 25°C is preferably added to the coating materials in proportions of less than 10% by weight of the coating, more preferably less than 5% by weight, and most preferably of less than 3% by weight. The component which is liquid at 25°C is preferably added to the coating materials in proportions of more than 0.1% by

weight of the coating, more preferably more than 0.3% by weight, and most preferably of more than 0.5% by weight. Further preferred is the addition of reinforcing fibres to the coating in order to further reinforce the structure.

Preferably, the coating comprises a crystallised structure. By crystallised, it should be understood that the coating comprises a material which is solid at ambient temperature (25°C) and has a structure exhibiting some order. This can be detected typically by usual crystallography techniques e.g. X-ray analysis, on the material itself. In a more preferred embodiment, the material forming the crystallised structure does not co-crystallise or only partially with the optional component which is liquid at 25°C mentioned above. Indeed, it is preferred that the optional component remains in the liquid state at 25°C in the coating crystalline structure in order to provide flexibility to the structure and resistance to mechanical stress. In another embodiment, the optional component which is liquid at 25°C may advantageously have a functionality in the washing of laundry, for example silicone oil which provides suds suppression benefits or perfume oil.

The coating may also comprise other optional components. Suitable coating materials are for example dicarboxylic acids. Particularly suitable dicarboxylic acids are selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof. Most preferred is adipic acid.

Clearly substantially insoluble materials having a melting point below 40 °C are often not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 200 °C are not practicable to use. Preferably, an acid having a melting point of more than 90°C such as azelaic, sebacic acid, dodecanedioic acid is used. It is even more preferred to use an acid having a melting point of more than 145°C such as adipic acid.

By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid.

A coating of any desired thickness can be applied according to the present invention. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

Tablet coatings are very hard and provide extra strength to the tablet.

Examples of optional components which are liquid at 25° are including PolyEthylene Glycols, thermal oil, silicon oil, esters of dicarboxylic acids, mono carboxylic acids, paraffin, triacetin, perfumes or alkaline solutions. It is preferred that the structure of the components which is liquid at 25°C is close to the material forming the crystallised structure, so that the structure is not excessively disrupted. In a most preferred embodiment, the crystallised structure is made of adipic acid, the component which is liquid at 25°C being available under the name Coasol™ from Chemoxy International, being a blend of the di-isobutyl esters of the glutaric, succinic and adipic acid. The advantage of the use of this component being the good dispersion in the adipic acid to provide flexibility. It should be noted that disintegration of the adipic acid is further improved by the adipate content of Coasol™.

Fracture of the coating in the wash can be improved by adding a disintegrant in the coating. This disintegrant will swell once in contact with water and break the coating in small pieces. This will improve the dissolution of the coating in the wash solution. The disintegrant is suspended in the coating melt at a level of up to 30%, preferably between 5% and 20%, most preferably between 5 and 10% by weight. Possible disintegrants are described in Handbook of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include starch: natural, modified or pregelatinized starch, sodium starch gluconate; gum: agar gum, guar gum, locust bean gum, karaya gum, pectin gum, tragacanth gum; croscarmylose Sodium, crospovidone, cellulose, carboxymethyl cellulose, algenic acid and its salts including sodium alginate, silicone dioxide, clay, polyvinylpyrrolidone, soy polysaccharides, ion exchange resins, polymers containing cationic (e.g. quaternary ammonium) groups, amine-substituted polyacrylates, polymerised cationic amino acids such as poly-L-lysine, polyallylamine hydrochloride) and mixtures thereof.

Preferably, the coating comprises an acid having a melting temperature of at least 145°C, such as adipic acid for example, as well as a clay, such as a bentonite clay for example, whereby the clay is used as a disintegrant and also to render the structure of adipic acid more favourable for water penetration, thus improving the dispersion of the adipic acid in a aqueous medium. Preferred are clays having a particle size of less than 75 µm, more preferably of less than 53 µm, in order to obtain the desired effect on the structure of the acid. Preferred are bentonite clays. Indeed the acid has a melting point such that traditional cellulosic disintegrants undergo a thermal degradation during the coating process, whereas such clays are found to be more heat stable. Further, traditional cellulosic disintegrant such as Nymcel™ for example are found to turn brown at these temperatures.

In another preferred embodiment, the coating further comprises reinforcing fibres. Such fibres have been found to improve further the resistance of the coating to mechanical stress and minimise the splitting defect occurrence. Such fibres are preferably having a length of at least 100 µm, more preferably of at least 200 µm and most preferably of at least 250 µm to allow structure reinforcement. Such fibres are preferably having a length of at less than 500 µm, more preferably of less than 400 µm and most preferably of less than 350 µm in order not to impact onto dispersion of the coating in an aqueous medium. Materials which may be used for these fibres include viscose rayon, natural nylon, synthetic nylon (polyamides types 6 and 6,6), acrylic, polyester, cotton and derivatives of cellulose such as CMCs. Most preferred is a cellulosic material available under the trade mark Solka-Floc™ from Fibers Sales & Development.

It should be noted that such fibres do not normally need pre-compression for reinforcing the coating structure. Such fibres are preferably added at a level of less than 5% by weight of the coating, more preferably less than 3% by weight. Such fibres are preferably added at a level of more than 0.5% by weight of the coating, more preferably more than 1% by weight.

5

Detergent surfactants

[0037] Surfactant are typically comprised in a detergent composition. The dissolution of surfactants is favoured by the addition of the highly soluble compound.

10 Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃-M⁺) CH₃ and CH₃ (CH₂)_y (CHOSO₃-M⁺) CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-C₁₈ glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts. In a preferred embodiment, the tablet comprises at least 5% per weight of surfactant, more preferably at least 15% per weight, even more preferably at least 25% per weight, and most preferably between 35% and 45% per weight of surfactant.

30 Non gelling binders

[0038] Non gelling binders can be integrated in detergent compositions to further facilitate dissolution.

If non gelling binders are used, suitable non-gelling binders include synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacrylates and water-soluble acrylate copolymers. The handbook of Pharmaceutical Excipients second edition, has the following binders classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferable binders also have an active cleaning function in the laundry wash such as cationic polymers, i.e. ethoxylated hexamethylene diamine quaternary compounds, bis-hexamethylene triamines, or others such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

40 Non-gelling binder materials are preferably sprayed on and hence have an appropriate melting point temperature below 90°C, preferably below 70°C and even more preferably below 50°C so as not to damage or degrade the other active ingredients in the matrix. Most preferred are non-aqueous liquid binders (i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry addition but which have binding properties within the tablet.

45 Non-gelling binder materials are preferably used in an amount within the range from 0.1 to 15% of the composition, more preferably below 5% and especially if it is a non laundry active material below 4% by weight of the tablet.

50 It is preferred that gelling binders, such as nonionic surfactants are avoided in their liquid or molten form. Nonionic surfactants and other gelling binders are not excluded from the compositions, but it is preferred that they be processed into the detergent tablets as components of particulate materials, and not as liquids.

Builders

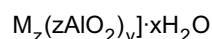
55 **[0039]** Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the triphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders. Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

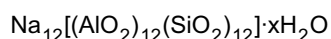
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergent builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator. In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Bleach

[0040] The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetrahydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

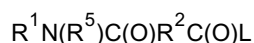
Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

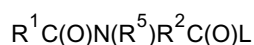
Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

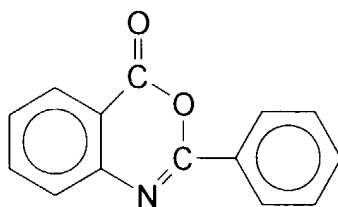
Highly preferred amido-derived bleach activators are those of the formulae:



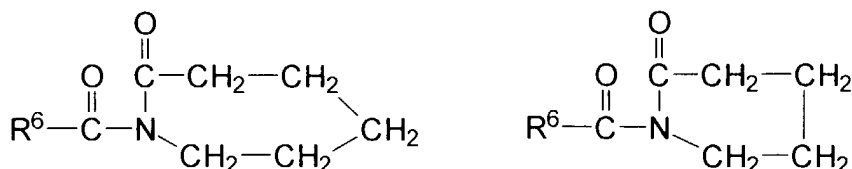
or



wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate. Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference. Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $Mn^{IV}_2(u-O)_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(PF_6)_2$, $Mn^{III}_2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_2$, $Mn^{IV}_4(u-O)_6(1,4,7\text{-triazacyclononane})_4(ClO_4)_4$, $Mn^{III}Mn^{IV}_4(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_3$, $Mn^{IV}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})-(OCH_3)_3(PF_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779;

5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Enzymes

[0041] Suitable enzymes for use in the compositions of the present invention include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, mannanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof. A preferred combination is a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and W096/02653 which discloses fungal cellulase produced respectively from *Humicola insolens*, *Trichoderma*, *Thielavia* and *Sporotrichum*. EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Preferred are these cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in W096/34092, W096/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Enzymatic system may be used as bleaching agents: The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromoperoxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases

include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when
 5 used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-
 10 A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout
 15 the pH range of 8-12, developed and sold as ESPERASE[®] by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE[®], DURAZYM[®] and SAVINASE[®] from Novo and MAXATASE[®], MAXACAL[®], PROPERASE[®] and MAXAPEM[®] (protein engineered Maxacal) from Gist-Brocades. Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP[®] described in WO91/02792 and their
 20 variants described in WO 95/23221. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516
 25 200 by Unilever.

Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers
 30 to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Suitable is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

[0042] A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid
 35 for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in W095/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of
 40 a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed June 04, 1997).

More preferred proteases are multiply-substituted protease variants. These protease variants comprise a substitution
 50 of an amino acid residue with another naturally occurring amino acid residue at an amino acid residue position corresponding to position 103 of *Bacillus amyloliquefaciens* subtilisin in combination with a substitution of an amino acid residue positions corresponding to positions 1, 3, 4, 8, 9, 10, 12, 13, 16, 17, 18, 19, 20, 21, 22, 24, 27, 33, 37, 38, 42, 43, 48, 55, 57, 58, 61, 62, 68, 72, 75, 76, 77, 78, 79, 86, 87, 89, 97, 98, 99, 101, 102, 104, 106, 107, 109, 111, 114, 116, 117, 119, 121, 123, 126, 128, 130, 131, 133, 134, 137, 140, 141, 142, 146, 147, 158, 159, 160, 166, 167, 170,
 55 173, 174, 177, 181, 182, 183, 184, 185, 188, 192, 194, 198, 203, 204, 205, 206, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 222, 224, 227, 228, 230, 232, 236, 237, 238, 240, 242, 243, 244, 245, 246, 247, 248, 249, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 265, 268, 269, 270, 271, 272, 274 and 275 of *Bacillus amyloliquefaciens* subtilisin; wherein when said protease variant includes a substitution of amino acid residues at positions

corresponding to positions 103 and 76, there is also a substitution of an amino acid residue at one or more amino acid residue positions other than amino acid residue positions corresponding to positions 27, 99, 101, 104, 107, 109, 123, 128, 166, 204, 206, 210, 216, 217, 218, 222, 260, 265 or 274 of *Bacillus amyloliquefaciens* subtilisin and/or multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 62, 212, 230, 232, 252 and 257 of *Bacillus amyloliquefaciens* subtilisin as described in PCT application Nos. PCT/US98/22588, PCT/US98/22482 and PCT/US98/22486 all filed on October 23, 1998 from The Procter & Gamble Company.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. W094/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and W096/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, W095/26397 and W096/23873 (all by Novo Nordisk). Examples of commercial α -amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban®, Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. W095/26397 describes other suitable amylases : α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α -amylase activity assay. Preferred are variants of the above enzymes, described in W096/23873 (Novo Nordisk). Preferably, the variants are those demonstrating improved thermal stability, more preferably those wherein at least one amino acid residue equivalent to F180, R181, G182, T183, G184, or K185 has been deleted from the parent α -amylase. Particularly preferred are those variants having improved thermal stability which comprise the amino acid deletions R181* + G182* or T183* + G184*. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermal stability and a higher activity level are described in W095/35382.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc. containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Co-pending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

[0043] Other components which are commonly used in detergent compositions and which may be incorporated into detergent tablets include chelating agents, soil release agents, soil antiredeposition agents, dispersing agents, suds suppressors, fabric softeners, dye transfer inhibition agents and perfumes.

[0044] The compounds disclosed above for a product are advantageously packed in a packaging system.

A packaging system may be formed from a sheet of flexible material. Materials suitable for use as a flexible sheet

include mono-layer, co-extruded or laminated films. Such films may comprise various components, such as poly-ethylene, poly-propylene, poly-styrene, poly-ethylene-terephthalate. Preferably, the packaging system is composed of a poly-ethylene and bi-oriented-polypropylene co-extruded film with an MVTR of less than 5 g/day/m². The MVTR of the packaging system is preferably of less than 10 g/day/m², more preferably of less than 5 g/day/m². The film (2) may have various thicknesses. The thickness should typically be between 10 and 150 μm, preferably between 15 and 120 μm, more preferably between 20 and 100 μm, even more preferably between 25 and 80 μm and most preferably between 30 and 40 μm.

A packaging material preferably comprises a barrier layer typically found with packaging materials having a low oxygen transmission rate, typically of less than 300 cm³/m²/day, preferably of less than 150 cm³/m²/day, more preferably of less than 100 cm³/m²/day, even more preferably of less than 50 cm³/m²/day and most preferably of less than 10 cm³/m²/day. Typical materials having such barrier properties include bi oriented polypropylene, poly ethylene terephthalate, Nylon, poly(ethylene vinyl alcohol) , or laminated materials comprising one of these, as well as SiOx (Silicium oxydes), or metallic foils such as aluminium foils for example. Such packaging material may have a beneficial influence on the stability of the product during storage for example.

Among the packing method used are typically the wrapping methods disclosed in WO92/20593, including flow wrapping or over wrapping. When using such processes, a longitudinal seal is provided, which may be a fin seal or an overlapping seal, after which a first end of the packaging system is closed with a first end seal, followed by closure of the second end with a second end seal. The packaging system may comprise re-closing means as described in WO92/20593. In particular, using a twist, a cold seal or an adhesive is particularly suited. Indeed, a band of cold seal or a band of adhesive may be applied to the surface of the packaging system at a position adjacent to the second end of the packaging system, so that this band may provide both the initial seal and re-closure of the packaging system. In such a case the adhesive or cold seal band may correspond to a region having a cohesive surface, i.e. a surface which will adhere only to another cohesive surface. Such re-closing means may also comprise spacers which will prevent unwanted adhesion. Such spacers are described in WO 95/13225, published on the 18th of May 1995. There may also be a plurality of spacers and a plurality of strips of adhesive material. The main requirement is that the communication between the exterior and the interior of the package should be minimal, even after first opening of the packaging system. A cold seal may be used, and in particular a grid of cold seal, whereby the cold seal is adapted so as to facilitate opening of the packaging system.

[0045] The invention will now be described by way of example and with reference to the accompanying drawings in which:

[0046] Figure 1 illustrates the second step of the process according to the invention, whereby a detergent tablet having two layers is being inserted in a first embodiment of a device according to the combination of the invention.

[0047] Figure 2 illustrates the third step of the process according to the invention of inserting the device containing the tablet of figure 1 into a washing machine.

[0048] Figure 3 illustrates the second step of the process according to the invention, whereby a detergent tablet having two layers is being inserted in a second embodiment of a device according to the combination of the invention.

[0049] Figure 4 illustrates the third step of the process according to the invention of inserting the device containing the tablet of figure 3 into a washing machine.

[0050] The device 2 of Figure 1 is partially formed from a flexible water permeable material 3. The flexible water permeable material 3 is a net material. The device 2 also comprises the impermeable flexible material 40, which is located in the part 6 opposed to the opening 5 of the device 2, and has substantially the shape of a cup. The opening 5 of the device 2 is provided with a string 7 linked to the net material 3, whereby such string 7 is used as closing means. The tablet 1 is also illustrated and is ready to be inserted in the device 2 according to the process of the invention to obtain the combination of the invention. Figure 2 illustrates how the device 2 containing the tablet 1 is thereafter inserted in a laundry washing machine. In this example, the "cup" shape of the portion of the device 2 made from a water impermeable material 40 allows to avoid particles from the tablet 1 to be deposited onto the supporting surface on which the device 2 is placed. Further, the cup shape comprises a rim or border which has substantially the shape of a band allowing a user to hold the device 2 without direct skin contact with the tablet 1.

[0051] The device 2 of Figure 3 is similar to the device of Figure 1. However, the impermeable flexible material 41 is only present in the form of a band, the band circumventing the device 2, so that the device 2 containing the tablet 1 as in Figure 4 may be held by a user avoiding direct contact with the tablet 1, while maximising the proportion of permeable flexible material 3 compared to impermeable flexible material 41 in order to accelerate tablet 1 dispersion. Figure 4 illustrates the insertion of the combination of the invention into a washing machine.

Claims

1. The combination of a detergent tablet (1) and of a device (2) to disperse the tablet (1) in an aqueous medium, the

device (2) containing the tablet (1), the device (2) being at least partially formed from a flexible water permeable material (3), and being characterised in that the device (2) is also partially formed from a flexible water impermeable material (40, 41).

- 5
2. The combination according to claim 1, the device (1) having an opening (5) and a part opposed to the opening (6), whereby the part (6) opposed to the opening is formed from the flexible water impermeable material (40).
- 10
3. The combination according to claim 1, the part of the device being formed from flexible water impermeable material being in the form of a band (41).
- 15
4. The combination according to any of the above claims, the flexible water permeable material (3) being a net material.
5. The combination according to any of the above claims, the device (2) comprising a sleeve, the sleeve having a length and a flexibility allowing to prevent that the tablet escapes from the sleeve during a normal wash operation.
- 20
6. The combination according to any of the above claims, whereby the tablet (1) has a tensile strength of at least 30 Kpa.
- 25
7. A process of dispersing a detergent tablet (1) in an aqueous medium in a washing machine comprising the first step of providing a detergent tablet (1) and a device (2) being at least partially formed from a flexible water permeable material (3), a second step of inserting the tablet (1) in the device (2), and a third step of inserting the device (2) containing the tablet (1) into the washing machine, the process being characterised in that the device (2) is also partially formed from a flexible water impermeable material (40, 41).
- 30
8. A process as in claim 7, whereby the detergent tablet (1) and the device (2) are according to any of the claims 2 to 6.
- 35
9. A process according to any of claims 7 or 8, whereby two or more tablets (1) are inserted into the device (2).
- 40
10. A kit comprising a device (2) and a plurality of detergent tablets (1) according to any of claims 1 to 6, the device (2) and the plurality of detergent tablets (1) being provided in a package.
- 45
- 50
- 55

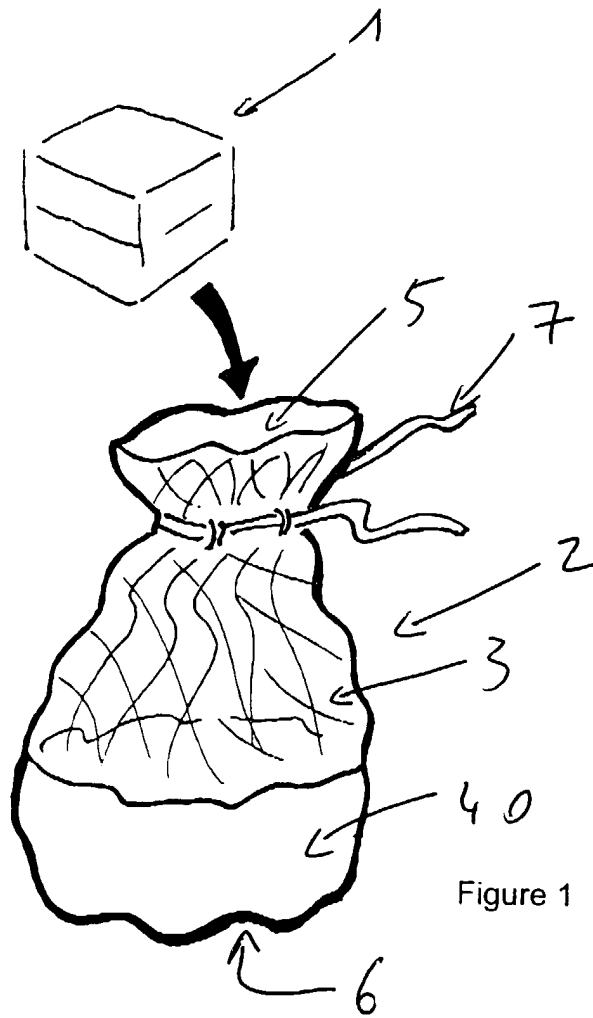


Figure 1

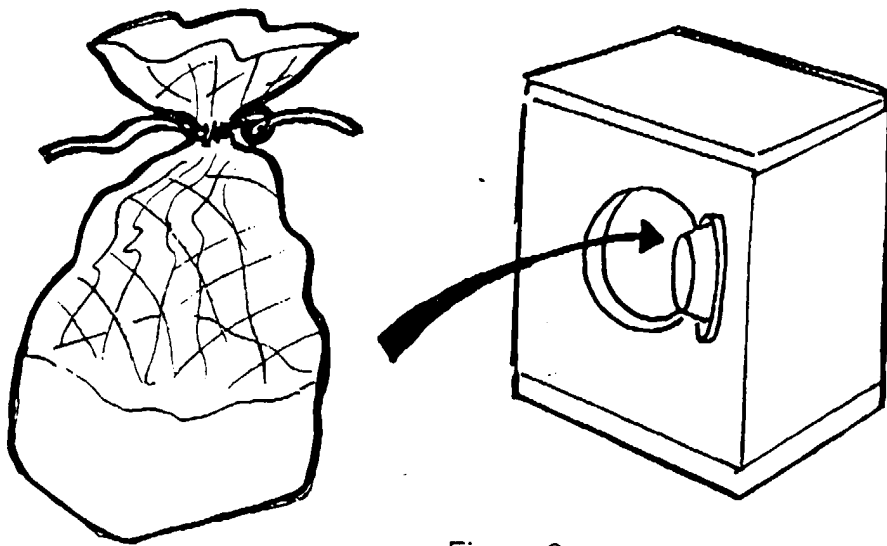
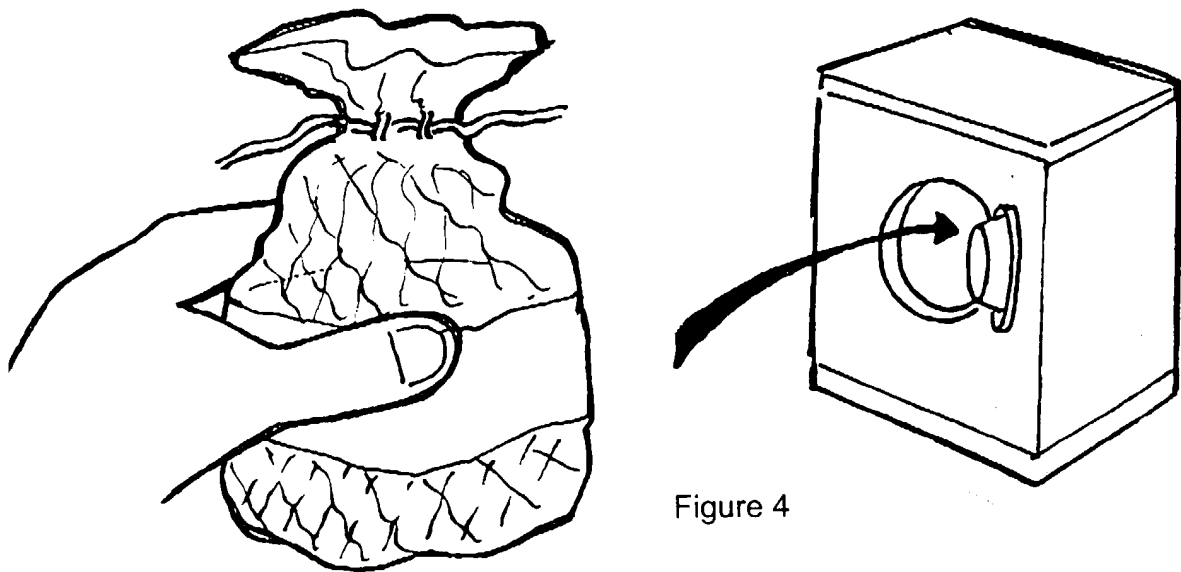
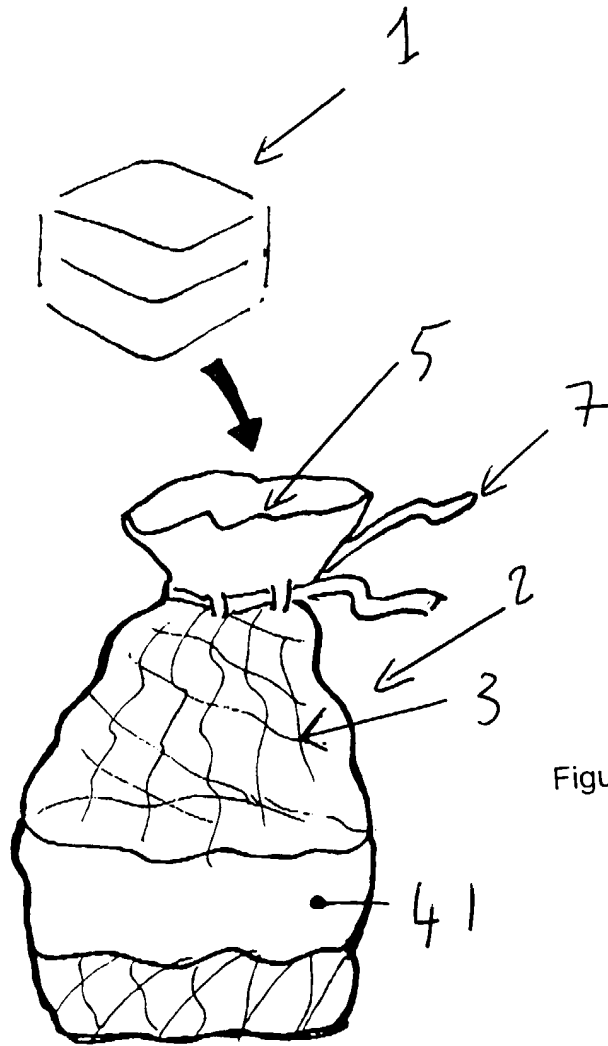


Figure 2





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 20 2367

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 345 409 A (HENKEL KGAA) 13 December 1989 (1989-12-13) * column 7, line 1 - column 8, line 15; figures 8,9 *	1,2,7,8	D06F39/02
A	EP 0 576 234 A (UNILEVER PLC ;UNILEVER NV (NL)) 29 December 1993 (1993-12-29) * the whole document *	1,5,7,9	
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A	WO 95 11330 A (CORNETTE HENRI ;AZZANI JEAN LUC (IT); PROCTER & GAMBLE (US)) 27 April 1995 (1995-04-27) * abstract *	1,7,10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			D06F A47L
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		17 November 1999	Norman, P
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ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 99 20 2367

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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