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(54) **Multilayered detergent tablets**

(57) The present invention provides a detergent tablet comprising at least two layers whereby one of these layers comprises a larger quantity of a brightener component than the other layer. In a preferred embodiment,

the tablet comprises at least one coloured layer, whereby the colour is produced by a component having a function in cleaning.

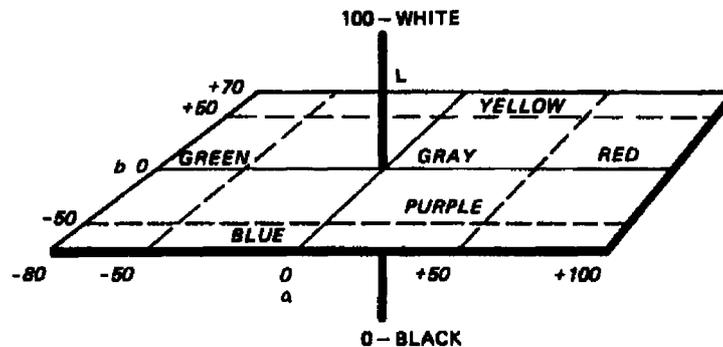


Fig. 1

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DescriptionTechnical Field

5 [0001] The invention relates to a detergent tablet.

Background of the Invention

10 [0002] Detergent products are widely used as consumer products and are widely produced by industry. Most consumers have come to expect detergent products having satisfactory aesthetics and being convenient to use. This lead for example to the development of a family of detergent products in a solid form usually called detergent tablets, some of these tablets having only one layer, and others being formed from several. In order to maintain the basic requirements of consumers, such detergent tablets may be coloured or may comprise layers exhibiting a tonal contrast. The tonal contrast between layers of a multilayer detergent tablet has the advantage to increase consumer acceptance, but
 15 has the disadvantage to introduce in the composition of such tablets elements such as a dye which has a function limited to an aesthetic improvement. Additionally, the introduction of a dye in a detergent product participates to the cost of the detergent product. It should also be noted that production and use of a dye is creating an extra burden to the environment.

20 [0003] The invention seeks to provide a detergent tablet comprising at least two layers, whereby the tonal contrast between these two layers is obtained, and whereby at least some of the above mentioned disadvantages are reduced.

Summary of the Invention

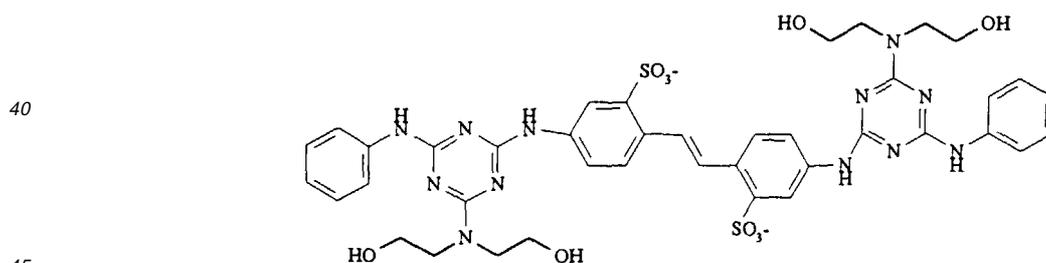
25 [0004] In accordance with the invention, this object is accomplished with a detergent tablet comprising at least two layer, whereby one of these layers comprises a larger quantity of a brightener component than the other layer.

Detailed Description of the Invention

30 [0005] The invention relates to a detergent tablet. By detergent tablet, it should be understood that the tablet comprises compounds such as surfactants which modify the surface tension of water.

[0006] The tablet according to the invention comprises at least two layers, whereby one of these layers comprises a larger quantity of a brightener component than the other layer. A brightener is typically a fluorescent whitening agent. Examples of brighteners include:

35 Disodium 4,4'-bis[[4-anilino-6-[bis(2-hydroxyethyl)amino-s-triazin-2-yl]-amino]-2,2'-stilbenedisulfonate. MW = 914:



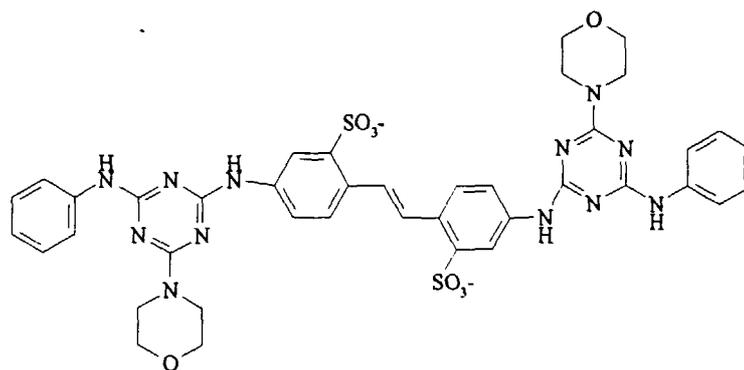
50 disodium 4,4'-bis[[4-anilino-6-morpholino-s-triazin-2-yl]-amino]-2,2'-stilbenedisulfonate MW = 924:

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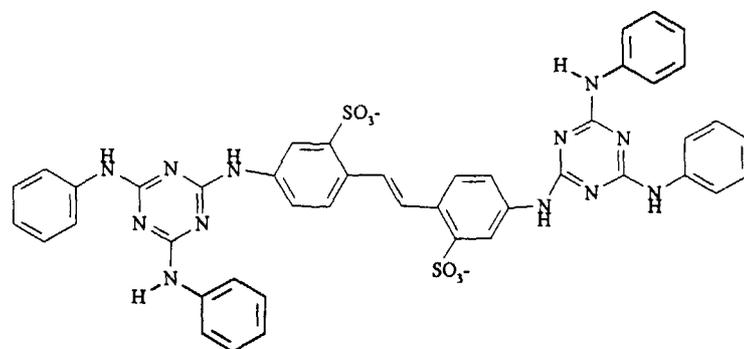


Disodium 4,4'-bis[(4,6-di-anilino-s-triazin-2-yl)-amino]-2,2'-stilbenedisulfonate:

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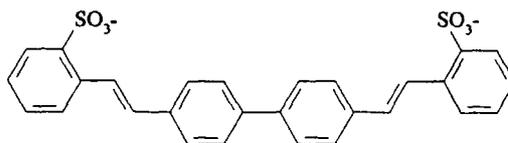
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disodium 4,4'-bis-(2-sulfostyryl)biphenyl MW = 562 (Na salt):

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[0007] Indeed, it was found that the higher concentration of a brightener component would lead to a higher L value, thus improving contrast between layers. Contrast is further improved in a more preferred embodiment of the invention, whereby the layer being comprising a larger quantity of brightener comprises a smaller quantity of coloured components, and even more preferably is free of any coloured components.

By larger quantity in one layer than in an other layer it should be understood that a larger quantity is a larger quantity by weight of a component, preferably more than 1 % more per weight of this component in one layer than in a other, more preferably more than 10%, even more preferably more than 50%, and most preferably when the other layer does not comprise at all of the component, whereas the one layer does. Smaller quantity is defined exactly in the opposite manner.

[0008] In a preferred embodiment, the invention relates to a coloured layer. It should be understood that the coloured layer is a layer which is not white.

Typically, according to the invention, colour is measured using a CHROMA METER. CR310 by MINOLTA having an illu-

mination / viewing angle fixed to 0°, using a standard illuminant C (Average daylight not including ultraviolet wavelength region), the measurement being on a 50 mm diameter area.

The measurement can be made on powder by depositing between 10 and 25 g, preferably 25 g, of powder in a beaker having a height of 10 cm and a 50 mm diameter, the temperature being of 20°C, the beaker being located on the light projection tube. The measurement can be directly made on a tablet, the tablet having a weight of 54 g for example, the light projection tube being placed on the tablet.

The measurement provides three values being the L, a and b values as illustrated on Figure 1.

The L value is a measurement of the black/white scale. Full white is L=100, and full black is L=0, the L values varying in between.

Similarly, the a value returns a measurement of the green/red scale. Full green is a=-80, full red being a=100, the a values varying in between.

Finally, the b value returns a measurement of the Blue/yellow scale. Full blue is b=-80, full yellow being b=70.

Such an L, a, b scale can be obtained from Hunter Lab 11491 Sunset Hills Road, Reston, VA 22090, USA.

When using the CHROMA METER. CR310 by MINOLTA the standard deviation of the measurement is of 0.07.

For the purpose of the invention, "white" should be understood as a measured colour whereby the a and b values are close to zero. It should be noted that a slight positive b value is acceptable in "white". The following range is typical: a measurement returning a between -6 and 6, b between -6 and 12, and L above 50 is considered white. A more preferred range would be a between -3 and 3, b between -3 and 10, and L above 70.

For example, a measurement returning a=-9, b=+3 and L=80 would be considered as green, with a slight shift to yellow.

It should also be understood that coloration of a layer is preferably a uniform coloration, whereby no differences of more than 50%, preferably 40%, more preferably 30% and most preferably 10% in the measured L, a and b values are existing between any different apparent portions of the coloured layer which are each representing at least 3% of the total apparent surface of the coloured layer.

According to the invention, tonal contrast is typically achieved by differences in the L value.

[0009] In a preferred embodiment of the invention, colour is produced by a component having a function in cleaning. By a component having a function in cleaning, it should be understood that the component is directly or indirectly active for removing soils or stains or for fabric care.

By directly active, it is meant that it is directly involved in removing soils or stains, this including for example surfactants, bleaching species, or enzymes, or for fabric care, including for example fabric softeners, dye transfer inhibition agents.

By indirectly active, it is meant that the component is for example favouring the activity of the directly active components, as is the case for example for builders, Highly soluble Compounds, hydrotrope compounds, compound having a Cohesive Effect, coating compounds, effervescent compounds, binders, non gelling binders, chelating agents, soil release agents, soil antiredeposition agents, dispersing agents.

[0010] Excluded here are compounds having no direct or indirect activity for cleaning such as perfumes or dyes.

Indeed, such elements have a purely aesthetic activity.

Indeed, an advantage of the invention is that the colour of the coloured layer is produced by a component having a function in cleaning, and not by a dye. It should be noted that small amounts of dye may be included to tune the aesthetic of the coloured layer. However, the main colour component is produced by the component having a function in cleaning.

By tuning, it should be understood that the a, b or L values can be modified of a few units, typically of about 3 to 5 units.

In a preferred embodiment, the colour of the coloured tablet is produced by a mixture of components having a function in cleaning.

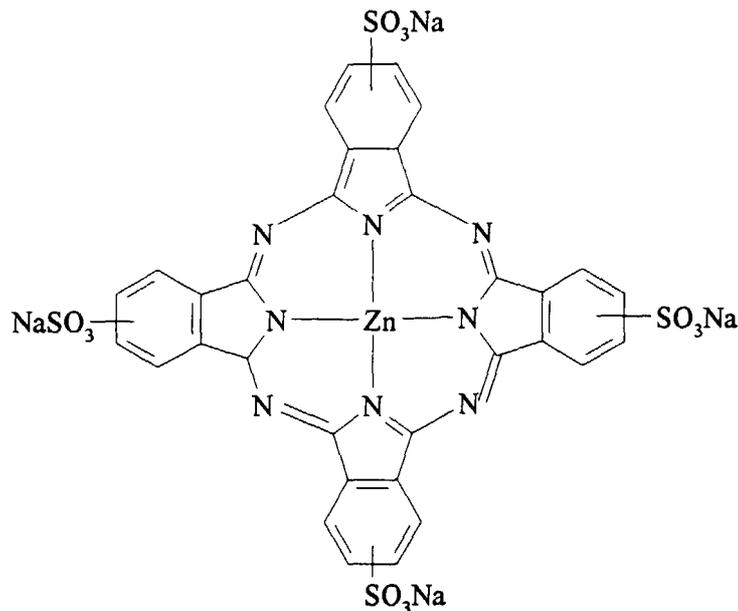
This allows to produce a preferred tablet according to a preferred embodiment of the invention which is free of dye.

[0011] In a more preferred embodiment according to the invention, the component having a function in cleaning, which produces the colour, is a coloured photobleach. A photobleach is typically a chemical compound which produces an oxidising compound which oxidises double bonds. It should be noted that the production of the oxidising compound is normally triggered by light (therefore the name photobleach). Normally, photobleaches have a colour. An intensive research effort has been produced by industry to develop a photobleach which would not produce a visible colour, as this visible colour has been considered as a disruption of the aesthetics of the detergents, this disruption being often avoided by encapsulating the photobleach. However, it has been found according to the invention that such a colour could be beneficially used to colour the layer, thereby avoiding use of dyes. This also has the advantage that a non-encapsulated photobleach can be used. Indeed, the photobleach of the preferred embodiment of the invention is not encapsulated but sprayed onto the detergent composition matrix, preferably together with a binder.

[0012] Photobleach compounds include the following:

Zinc Phthalocyanine Tetrasulfonate. Formula Weight = 986.

[0013] Other metal phthalocyanines can also be used.



25 **[0014]** The tablet according to the invention preferably comprises a binder. Such a binder may be useful for example to be sprayed onto the matrix together with the brightener component and optionally with the component having a function in cleaning and producing the colour, for example prior to compressing the matrix in tablet form.

The brightener component may also be added in the layer which comprises a larger quantity of a brightener component than the other layer as a dry ingredient prior to binder spray-on.

30 **[0015]** The invention also relates in an other aspect to a process for producing a detergent tablet, whereby a detergent composition matrix is formed in a first step, the matrix being sprayed with a brightener component, or by spraying binder on the matrix which already contains the Brightener as a dry ingredient, in the second step, the sprayed matrix being compressed to form a tablet in a third step. Indeed, spraying of the brightener allows to have an improved Brightener repartition allowing to obtain higher L values. In a preferred embodiment, the brightener component is sprayed in the

35 second step together with a non-ionic carrier, preferably a binder such as Poly Ethylene Glycol for example.

[0016] The invention in its various aspect also particularly applies to a detergent tablet, whereby the tablet is coated. Indeed, the coating of a tablet is producing a fading of the colours or tonal contrasts, as such colours or tonal contrasts have to pass through the screen produced by the coating. In such a case, an improved tonal contrast or colour level allows to maintain or improve the aesthetics, even through the coating.

40 **[0017]** In a further preferred embodiment according to the invention, the tablet has a tensile strength of less than 100kPa. Indeed, the tablet is preferred for use in laundry applications, whereby a low tensile strength is preferred to favour dissolution, when compared for example with auto-dish washing tablets. Indeed, high level of dyes in laundry tablets may result in stained garments, this being avoided with the tablet of the invention. Even more preferred are tablets having a coating. Indeed, tablets according to the invention and having a coating should have a colour and tonal contrast which is visible through the coating. With the usual dye technology, this implies use of high dye levels, thereby increasing the risk of staining garments. Therefore, the preferred embodiment of the invention is particularly advantageous in this case. This applies even more particularly to the case where a photobleach is used for producing colour, whereby the colour of the photobleach will fade when exposed to light, thereby further limiting staining garments. This also means that when using a photobleach, the detergent tablet should be stored in a package which does not allow

50 light to penetrate in the package, in order to avoid decomposition and loss of colour of the photobleach. This can be obtained by use of cartons or metallic foils for example. Most preferably, a tablet comprising a layer coloured by a photobleach is packed in a packaging system which prevents at least partially and preferably totally transmission of UV light.

[0018] 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

[0019] 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:

5 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.

10 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.

15 **[0020]** 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.

20 Example of highly soluble compounds include Sodium di isoalkylbenzene sulphonate or Sodium toluene sulphonate.

Cohesive Effect

25 **[0021]** 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.

30 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.

35 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.

40 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 solution is significantly increased. In a preferred embodiment, at least 1% per weight of a tablet or layer is formed from the highly soluble compound, more preferably at least 2%, even more preferably at least 3% and most preferably at least 5% per weight of the tablet or layer being formed from the highly soluble compound having a cohesive effect on the particulate material.

45 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.

50 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.

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Tablet Manufacture

[0022] The tablet may comprise several layers. For the purpose of manufacture of a single layer, the layer may be considered as a tablet itself.

10 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.

15 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.

20 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.

25 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.

35 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. 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 1.1 g/cc.

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

50 Hydrotrope compound

[0023] 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)):

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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.

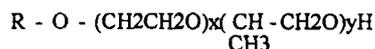
3. The specific compound is hydrotrope if the the Octanoic Acid is completely solubilised, i.e . if the solution comprises only one phase, the phase being a liquid phase.

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:

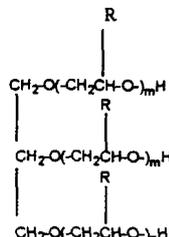
1. Nonionic hydrotrope with the following structure:



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

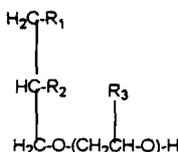
2. Anionic hydrotropes such as alkali metal aryl sulfonates. This includes alkali metal salts of benzoic acid, salicylic acid, benzenesulfonic acid and its many derivatives, naphthoic acid and various hydroaromatic acids. Examples of these are sodium, potassium and ammonium benzene sulfonate salts derived 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:



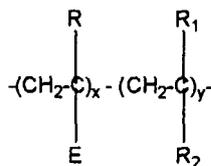
where l, m and n are each a number from 0 to about 20, with l+m+n = from about 2 to about 60 , preferably from about 10 to about 45 and R represents H, CH₃ or C₂H₅

Preferred alkoxyated glycerides have the following struture



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:



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 or 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.

Coating

[0024] Solidity of a tablet may be improved by making a coated tablet, the coating covering a non-coated tablet, thereby further improving the mechanical characteristics of the tablet while maintaining or further improving dissolution. 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.

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 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". Suitable coating materials are 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.

[0025] The coating material has a melting point preferably of from 40 °C to 200 °C. 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. Clearly substantially insoluble materials having a melting point below 40 °C are 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, the materials melt in the range from 60 °C to 160 °C, more preferably from 70 °C to 120 °C.

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.

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, alginic acid and its salts including sodium alginate, silicone dioxide, clay, polyvinylpyrrolidone, soy polysaccharides, ion exchange resins and mixtures thereof.

Tensile Strength

[0026] 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

[0027] 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

[0028] Detergent tablets may further comprise an effervescent.

[0029] 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).

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.

5 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.

Detergative surfactants

[0030] Surfactant are typically comprised in a detergent composition. The dissolution of surfactants is favoured by the addition of the highly soluble compound. 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.

35 Non gelling binders

[0031] 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, Alginate, 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.

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.

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 2% by weight of the tablet.

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

[0032] 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.

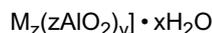
The level of builder can vary widely depending upon the end use of the composition.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, 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.

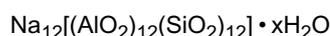
Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2\text{:Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is 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 detergency 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 carboxymethylloxysuccinic 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 dodeceny succinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodeceny succinate (preferred), 2-pentadeceny succinate, 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

[0033] 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 tetra-hydrate) 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-oxoperoxy caproic 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.

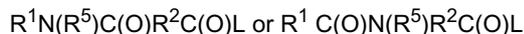
A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles 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,

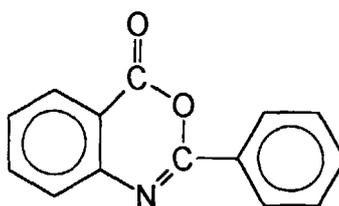
issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

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

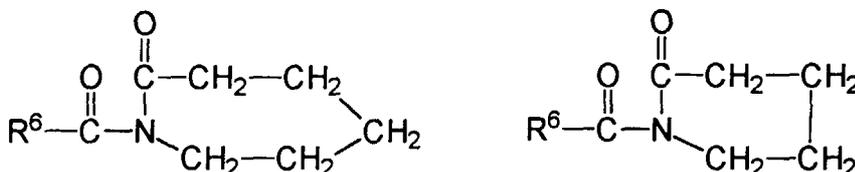


wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is 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)oxybenzene-sulfonate, (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. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $Mn^{IV}_2(u-O)_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(PF_6)_2$, $Mn^{III}_2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(ClO_4)_2$, $Mn^{IV}_4(u-O)_6(1,4,7\text{-triaza-cyclononane})_4(ClO_4)_4$, $Mn^{III}Mn^{IV}_4(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(ClO_4)_3$, $Mn^{IV}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})-(OCH_3)_3(PF_6)$, 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

[0034] Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the trade-names ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985).

[0035] Amylases include, for example, α -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME (Novo) is especially useful.

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. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. 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 commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. 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 bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various

techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

5 **[0036]** 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.

[0037] 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
10 include mono-layer, co-extruded or laminated films. Such films may comprise various components, such as polyethylene, poly-propylene, poly-styrene, poly-ethylene-terephthalate. Preferably, the packaging system is composed of a polyethylene and bi-oriented-poly-propylene co-extruded film with an MVTR of less than 1 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, even more preferably of less than 1 g/day/m² and most preferably of less than 0.5 g/day/m². The film (2) may have various thicknesses. The
15 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.
20 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
25 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
30 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
35 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.

EXAMPLES

40 Example 1

[0038]

i) A detergent base powder of composition C was prepared as follows: all the particulate material of base composition were mixed together in a mixing drum or spray drum to form a homogenous particulate mixture, apart from
45 the binder spray-on system, the fluorescer or brightener, and the photobleach Zinc Phthalocyanine sulphonate. The particulate mixture was thereafter divided in two equal parts, one part for making a white layer, another part for making a green layer. The white layer material is obtained by spraying the brightener or fluorescer together with half of the binder. The green layer material is obtained by spraying the photobleach Zinc Phthalocyanine sulphonate together with the rest of the binder. The layer were then processed independently in a Loedige KM 600®.

ii) Using a Bonals® rotary press both matrices were filled in two independent force feeding flasks. Both layers are compressed together in the precompression and compression stations to form a dual layer tablet.

iii) In this particular example, the tablets have a square cross section of 45 mm side, a height of 24 mm and a weight of 45 g. The height of the green bottom layer corresponded to 50% of the total height of the tablet.

iv) The tablet was thereafter coated with 2.5 g of coating formed from 80% by weight of sebacic acid and 20% by weight of Nymcel (=Carboxymethyl cellulose (degree of substitution 3) supplied by Metsa-Serla).

v) The colour of the white layer for the coated tablet was given by the following values: a=-2, b=10, L=85.

vi) The colour of the green layer for the coated tablet was given by the following values: a=-9, b=3, L=80.

It should be noted that the colour measurement on this square tablet was made by using 4 tablets put side by side to form a square having a 90 mm side, so that the colour measurement on a 50 mm diameter zone could be made.

[0039] Presented below are examples for base particulate material composition for making laundry detergent tablets according to the invention, whereby the fluorescer or brightener is preferably concentrated in a first layer, the Zinc Phthalocyanide sulphonate being preferably concentrated in the other layer. For example, any of these compositions could be used, whereby all of the brightener is located in one layer, the Zinc Phthalocyanide sulphonate being in the other. Other proportions between the layers may be used according to the invention.

	Composition A (% per weight)
Anionic Agglomerates 1	21.45
Anionic Agglomerates 2	13.00
Cationic Agglomerate	5.45
Layered Silicate	10.8
Sodium percarbonate	14.19
Bleach activator agglomerates	5.49
Sodium carbonate	13.82
EDDS/Sulphate particle	0.47
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.73
Soil Release Polymer	0.33
Fluorescer	0.18
Zinc Phthalocyanide sulphonate	0.025
Soap powder	1.40
Suds Suppressor	1.87
Citric acid	7.10
Protease	0.79
Lipase	0.28
Cellulase	0.22
Amylase	1.08
Binder Spray-on-system	1.325
TOTAL	100.00

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate.

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate.

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate.

Layered silicate comprises of 95% SKS 6 and 5% silicate.

Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

Binder spray-on system comprises of 50% Lutensit K-HD 96 and 50% PEG (polyethylene glycol).

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	Composition B (% per weight)
Anionic Agglomerates 1	21.45
Anionic Agglomerates 2	13.00
Cationic Agglomerate	5.45
Layered Silicate	10.8
Sodium percarbonate	14.19
Bleach activator agglomerates	5.49
Sodium carbonate	12.645
EDDS/Sulphate particle	0.47
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.73
Soil Release Polymer	0.33
Fluorescer	0.18
Zinc Phthalocyanide sulphonate	0.025
Soap powder	1.40
Suds Suppressor	1.87
Citric acid	7.10
Protease	0.79
Lipase	0.28
Cellulase	0.22
Amylase	1.08
Binder Spray-on-system	2.5
TOTAL	100.00

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate.

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate.

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate.

Layered silicate comprises of 95% SKS 6 and 5% silicate.

Bleach activator agglomerates comprise of 81 % TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

Binder spray-on system comprises of 50% Lutensit K-HD 96 and 50% PEG (polyethylene glycol).

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	Composition C (%)
Anionic agglomerates 1	9.1
Anionic agglomerates 2	22.5
Nonionic agglomerates	9.1

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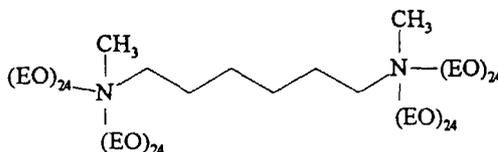
(continued)

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	Composition C
	(%)
Cationic agglomerates	4.6
Layered silicate	9.7
Sodium percarbonate	12.2
Bleach activator agglomerates	6.1
Sodium carbonate	7.67
EDDS/Sulphate particle	0.5
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.6
Soil Release Polymer	0.3
Fluorescer	0.2
Zinc Phthalocyanine sulphonate	0.03
Soap powder	1.2
Suds suppressor	2.8
Citric acid	5.5
Protease	1
Lipase	0.35
Cellulase	0.2
Amylase	1.1
Binder spray-on system	4.75
Perfume spray-on	0.5

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate
 Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate
 Nonionic agglomerate comprise 26% nonionic surfactant, 6% Lutensit K-HD 96, 40% Sodium acetate anhydrous, 20% carbonate and 8% zeolite.
 Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate
 Layered silicate comprises of 95% SKS 6 and 5% silicate
 Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.
 Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.
 Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.
 Binder spray-on system comprises 16% by weight of polymer of the following kind:

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68 % by weight of: PEG4000 and 16% by weight of DIBS (Sodium di isoalkylbenzene sulphonate or Sodium toluene sulphonate).

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	Composition D	
	(%)	
5	Anionic agglomerates 1	32
10	Cationic agglomerates	5
	Layered silicate	11.5
	Sodium percarbonate	16.2
15	Bleach activator agglomerates	4.7
	Sodium carbonate	3.76
	Sodium bicarbonate	2.0
20	Sodium sulphate	2.4
	EDDS/Sulphate particle	0.5
	Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.8
	Soil Release Polymer	0.3
25	Fluorescer	0.1
	Zinc Phthalocyanine sulphonate	0.02
30	Suds suppressor	2.1
	Citric acid	2
	Protease	0.7
	Lipase	0.2
35	Cellulase	0.2
	Amylase	0.6
	Perfume encapsulates	0.2
40	Polymer particle	3
	Perfume spray-on	0.35
	Nonionic spray-on system	5.17
45	Zeolite	6.2

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate

Layered silicate comprises of 95% SKS 6 and 5% silicate

50 Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

Perfume encapsulates comprise 50% perfume and 50% starch.

55 Polymer particle comprises 36%, 54% zeolite and 10% water

The Nonionic spray-on system comprises of 67% C12-C15 AE5 (alcohol with an average of 5 ethoxy groups per molecule), 24% N-methyl glucose amide and 9% water.

Claims

1. A detergent tablet comprising at least two layers whereby one of these layers comprises a larger quantity of a brightener component than the other layer.
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2. The detergent tablet according to claim 1, whereby it comprises one coloured layer, whereby the colour is produced by a component having a function in cleaning.
3. The detergent tablet according to claim 2, whereby the component having a function in cleaning is a coloured photo-bleach.
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4. The detergent tablet according to claim 2, whereby the coloured layer is free of dye.
5. The detergent tablet according to claim 1, whereby the layer comprising a larger quantity of a brightener component is free of any coloured component.
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6. The detergent tablet according to claim 1, whereby the tensile strength of the tablet is of less than 100 kPa.
7. The detergent tablet according to claim 1, whereby the tablet further comprises a binder.
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8. A process for producing a detergent tablet, whereby a detergent composition matrix is formed in a first step, the matrix being sprayed with a brightener component in the second step, the sprayed matrix being compressed to form a tablet in a third step.
- 25 9. A process according to claim 8, whereby the brightener component is sprayed in the second step together with a non-ionic carrier.
10. The detergent tablet according to any of the above claims, whereby the tablet is coated.

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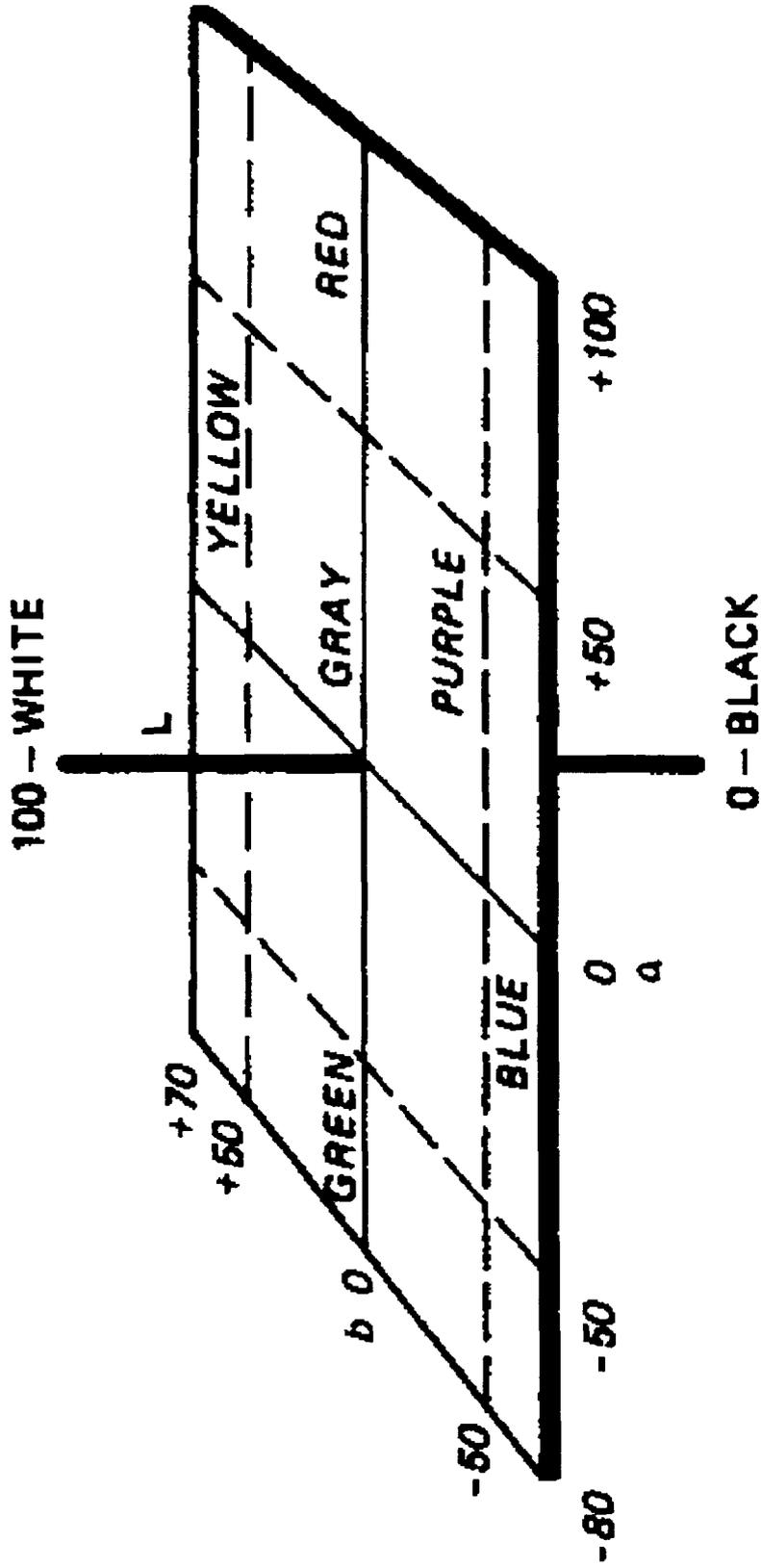


Fig. 1



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 87 0240

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