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(54) **ACYLHYDRAZONE GRANULES FOR USE IN LAUNDRY DETERGENTS**

(57) The invention relates to granules of particular bleach catalysts i. e. acylhydrazone compounds, which comprise such compounds in a very high concentration. The granules are coated and are useful as bleach cata-

lysts in powder detergents. Further aspects of the invention are the use of the granules together with a peroxy compound, a granule-containing washing, cleaning or bleaching formulation, and the uncoated granules.

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## Description

**[0001]** The instant invention relates to granules of particular bleach catalysts, i. e. acylhydrazone compounds, which comprise such compounds in a very high concentration. The granules are coated and are useful as bleach catalysts in powder detergents. Further aspects of the invention are the use of the granules together with a peroxy compound, a granule-containing washing, cleaning or bleaching formulation, and the uncoated granules.

**[0002]** The search for efficient bleach catalysis has been the object of research since a long time. WO 2012/080088 discloses a new class of catalysts, namely specific acylhydrazone compounds. These acylhydrazone compounds provide excellent bleach performance, in particular as metal free bleach catalysts. The compounds are efficient without a central transition metal. This is a significant difference to prior art bleach catalysts, such as, for example, described in EP 630 946, US 5 965 506, US 5 733 341, WO 97 19162, US 6 486 110, US 6 562 775, EP 955 289, WO 00 53574, WO 00 53712, WO 01 05925 and EP 02 088 289.

**[0003]** However, the acylhydrazone compounds disclosed in WO 2012/080088 are not easily incorporated into powder detergents. The active is water-soluble and alkaline solutions are colored (yellow). Furthermore, the alkali may induce condensation reactions of the molecule which yields colored products. This will lead to a discoloration of the detergent powder when the active material (eg. as a powder) is mixed into the detergent and stored. Granulated acylhydrazone compounds incorporated in powder detergents will turn into a yellow or brown color with time, and the detergent material in close vicinity to the catalyst granules will be discolored, especially at humid conditions and open storage of the detergent. From a consumer perspective, this discoloration is not acceptable.

**[0004]** It is well known that coating the granules is a good method for solving such stability issues. As the active is water-soluble, the first approach is to apply a hydrophobic coating onto the granule surface. Wax-coatings are also an option.

**[0005]** For the performance of the coated granules, the properties of the coating material and the coating level must be adjusted in such a way that stability requirements in the detergents are met and at the same time the release of the active into the wash liquor is not delayed to a non-acceptable extent.

**[0006]** WO 2015/169851 discloses granules which comprise acylhydrazones in an amount of not more than 40% by weight, since the reference's process for the preparation of the granules requires a high level of formulation additives.

**[0007]** However, the need for cost-efficient use of the catalyst requires that the active level is as high as possible. With respect to the sustainability profile of the catalyst technology it is also preferable to load the detergent with the minimal amount of granules adjuvants, which also means maximising the acylhydrazone content.

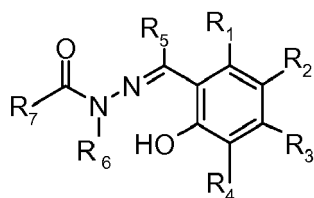
**[0008]** It has been the objective of the instant invention to find acylhydrazone granules with extremely high load of the acylhydrazone active. The coated granules of the instant invention are stable in the detergent at high humidity levels. At the same time, the acylhydrazone is released into the wash liquor as rapid and complete as from a low-concentrated granule, so the benefit of the active in the wash application is fully maintained.

**[0009]** In the context of this invention the terms granulate, granule and particulate composition are used as synonyms.

**[0010]** Accordingly, the present invention relates to a coated granule comprising a core pellet comprising

- a) 50% to 98% by weight based on the weight of the total granule of an acylhydrazone of formula (1),
- b) 1 % to 49% by weight based on the weight of the total granule of a water soluble binder,
- c) 0% to 15% by weight based on the weight of the total granule of water, and
- d) 0% to 10% by weight based on the weight of the total granule of further ingredients, and which core pellet is coated with
- e) 1 % to 40% by weight based on the weight of the total granule of at least one coating, the sum of components a) to e) adding to 100%, and

wherein the acylhydrazone of formula (1) is a compound of formula



(1)

wherein

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> independently from each other are hydrogen, halogen, hydroxy, nitro, N-mono- or N,N-di-

C<sub>1</sub>-C<sub>4</sub>alkylamino, or unsubstituted or substituted C<sub>1</sub>-C<sub>28</sub>alkyl, C<sub>1</sub>-C<sub>28</sub>alkoxy, C<sub>2</sub>-C<sub>28</sub>alkenyl, C<sub>2</sub>-C<sub>22</sub>alkinyl, C<sub>3</sub>-C<sub>12</sub>cycloalkyl, C<sub>3</sub>-C<sub>12</sub>cycloalkenyl, C<sub>7</sub>-C<sub>9</sub>aralkyl, C<sub>3</sub>-C<sub>2</sub>oheteroalkyl, C<sub>3</sub>-C<sub>12</sub>cycloheteroalkyl, C<sub>5</sub>-C<sub>16</sub>heteroaralkyl, phenyl or naphthyl, wherein the substituents for each of the radicals are selected from the group consisting of C<sub>1</sub>-C<sub>4</sub>alkyl; C<sub>1</sub>-C<sub>4</sub>alkoxy; hydroxy; sulfo; sulfato; halogen; cyano; nitro; carboxy; amino; N-mono-

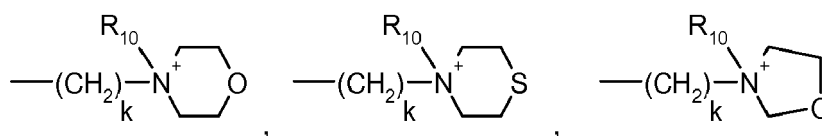
or N,N-di-C<sub>1</sub>-C<sub>4</sub>alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety; N-phenylamino; N-naphthylamino wherein the amino groups may be quaternised; phenyl; phenoxy and naphthylxy;

or R<sub>1</sub> and R<sub>2</sub>, R<sub>2</sub> and R<sub>3</sub> or R<sub>3</sub> and R<sub>4</sub> are linked together to form 1, 2 or 3 carbocyclic or heterocyclic rings, which may be uninterrupted or interrupted by one or more -O-, -S- or -NR<sub>11</sub>- and or which may be further fused with other aromatic rings and/or which may be substituted with one or more C<sub>1</sub>-C<sub>6</sub>alkyl groups;

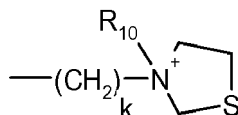
R<sub>5</sub> denotes hydrogen, unsubstituted or substituted C<sub>1</sub>-C<sub>28</sub>alkyl, C<sub>2</sub>-C<sub>28</sub>alkenyl, C<sub>2</sub>-C<sub>22</sub>alkinyl, C<sub>3</sub>-C<sub>12</sub>cycloalkyl, C<sub>3</sub>-C<sub>12</sub>cycloalkenyl, C<sub>7</sub>-C<sub>9</sub>aralkyl, C<sub>3</sub>-C<sub>2</sub>oheteroalkyl, C<sub>3</sub>-C<sub>12</sub>cycloheteroalkyl, C<sub>5</sub>-C<sub>16</sub>heteroaralkyl, phenyl or heteroaryl; wherein the substituents for each of the radicals are selected from the group consisting of C<sub>1</sub>-C<sub>4</sub>alkyl; C<sub>1</sub>-C<sub>4</sub>alkoxy; hydroxy; sulfo; sulfato; halogen; cyano; nitro; carboxy; amino; N-mono- or N,N-di-C<sub>1</sub>-C<sub>4</sub>alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety; N-phenylamino; N-naphthylamino wherein the amino groups may be quaternised; phenyl; phenoxy and naphthylxy;

R<sub>6</sub> denotes hydrogen, C<sub>1</sub>-C<sub>28</sub>alkyl, C<sub>2</sub>-C<sub>28</sub>alkenyl, C<sub>2</sub>-C<sub>22</sub>alkinyl, C<sub>3</sub>-C<sub>12</sub>cycloalkyl, C<sub>3</sub>-C<sub>12</sub>cycloalkenyl, C<sub>7</sub>-C<sub>9</sub>aralkyl, C<sub>3</sub>-C<sub>2</sub>oheteroalkyl, C<sub>3</sub>-C<sub>12</sub>cycloheteroalkyl, C<sub>5</sub>-C<sub>16</sub>heteroaralkyl, phenyl, naphthyl or heteroaryl; wherein the substituents for each of the radicals are selected from the group consisting of C<sub>1</sub>-C<sub>4</sub>alkyl; C<sub>1</sub>-C<sub>4</sub>alkoxy; hydroxy; sulfo; sulfato; halogen; cyano; nitro; carboxy; amino; N-mono- or N,N-di-C<sub>1</sub>-C<sub>4</sub>alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety; N-phenylamino; N-naphthylamino wherein the amino groups may be quaternised; phenyl; phenoxy and naphthylxy;

R<sub>7</sub> is a group



or



each group with an anion A<sup>-</sup>;

k is an integer from 1 to 4;

A<sup>-</sup> is the anion of an organic or inorganic acid;

R<sub>10</sub> denotes hydrogen, C<sub>1</sub>-C<sub>28</sub>alkyl, C<sub>2</sub>-C<sub>28</sub>alkenyl, C<sub>2</sub>-C<sub>22</sub>alkinyl, C<sub>3</sub>-C<sub>12</sub>cycloalkyl, C<sub>3</sub>-C<sub>12</sub>cycloalkenyl, C<sub>7</sub>-C<sub>9</sub>aralkyl, C<sub>3</sub>-C<sub>2</sub>oheteroalkyl, C<sub>3</sub>-C<sub>12</sub>cycloheteroalkyl or C<sub>5</sub>-C<sub>16</sub>heteroaralkyl; and

R<sub>11</sub> denotes hydrogen or C<sub>1</sub>-C<sub>18</sub>alkyl.

**[0011]** The core pellet is obtained by agglomeration of the active component with a water-soluble binder, water and optionally lower amounts of further ingredients, like fillers, processing aids, buffer salts, and pigment dyes or other dyes. For the binder, aqueous solutions of said water-soluble binders may be used. After granule formation, the material normally is dried eg. in a fluid bed dryer and then screened to remove the undersize / oversize material which is then recycled in the agglomeration process.

**[0012]** Particle agglomeration is a well-known mechanism to build larger aggregates out of fine particles. Among the many established technologies, wet granulation is often used in industry. Fine particles are brought into contact with each other, and stick together through the action of a liquid binder material. The binder may further strengthen the particle by formation of solid bridges that are obtained by thermal treatment of the wet granulate. Suitable equipment for wet granulation may be mixer granulators (eg. from Lödige or Eirich), drum granulators (eg. from Feeco), pan granulators (eg. from Eirich or Feeco) or fluid bed granulators (eg. from Glatt) The granules obtained from this process are usually spherical in shape which is advantageous for a subsequent coating step.

**[0013]** The prepared core pellets are, if necessary, made round in a rounder (spheronizer) in order to remove any sharp, friable edges, and then dried (when aqueous methods are used).

[0014] The final core pellets (uncoated granules) preferably have an average particle size ( $X_{50}$ ) of 300  $\mu\text{m}$  to 1500  $\mu\text{m}$ .

[0015] The water-soluble binder of the core pellet has preferably either a melting point (m.p.) of from 30 to 120°C, preferably from 35 to 100°C, and especially from 38 to 90°C, or has a glass transition temperature of from 30 to 220°C, preferably from 35 to 200°C, and especially from 38 to 190°C.

[0016] Preferably, the water-soluble binder is selected from the group consisting of polyvinylalcohols, polyvinylpyrrolidones, polyacrylates, cellulose derivatives, carbohydrates, polyethyleneglycols and mixtures thereof, and more preferably from the group consisting of polyvinylalcohols, polyvinylpyrrolidones, polyacrylates, polyethyleneglycols and mixtures thereof. Highly preferred are polyethyleneglycols.

[0017] Polyethylene glycols have for example a molecular weight of from 2000 to 1 000 000; especially from 2000 to 20000. There come also into consideration copolymers of glycol and propylene oxides having a molecular weight of > 3500.

[0018] Polyvinylpyrrolidones have for example a molecular weight of < 20000; copolymers of vinylpyrrolidone with vinyl acetate come also into consideration.

[0019] As polyacrylates there come also into consideration copolymers of ethyl acrylate and methacrylate and/or methacrylic acid (especially the ammonium salt).

[0020] As cellulose derivatives there comes also hydroxypropyl methylcellulose phthalate and also hydroxypropyl methylcellulose into consideration.

[0021] The water-soluble binder is preferably present in the granules in an amount of 1 to 40%, especially 1 to 30% and more preferably 1 to 20% by weight, based on the weight of the total granule. Preference is given to an amount of 1 to 15% and more preferably 1 to 10% by weight, based on the weight of the total granule. An amount of 1 to 6% by weight is of particular interest.

[0022] The core pellets may then be coated eg. to fulfill specific requirements for the use of the acylhydrazone in powder detergents. Hydrophilic or hydrophobic materials may be used as the coating materials. Many technologies are available to apply a coating in a batch-wise or continuous process. The particular technology also depends on the nature of the coating material. Hydrophobic coatings, eg. coating with fatty acids, is often applied via melt coating, where the molten coating is added to the core material and distributed on the surface of the particles. Examples are melt coating in a fluid bed or in a mixer, which may be batch or continuous wise. Hydrophilic coatings of water soluble, meltable material can also be applied with melt coating technologies.

[0023] Hydrophilic, water-soluble materials can be applied to the cores by applying an aqueous solution of the coating material to the cores. Suitable technologies are e.g. spray coating in a fluid bed, or in a mixer. The coating process can be batch or continuous wise. The water from the spray solution can be removed during or after the coating step, for example by drying, leaving the dried coating material on the core particles.

[0024] Water- insoluble materials, like dyes, pigments, fillers, can be added during the coating step, either as solids or as part of the coating fluid, and then constitute part of the coating.

[0025] The coating may be applied in such a way that the material forms a closed shell around the particle core. In another execution, the coating may cover only part of the surface of the cores. The expert skilled in the art will know how to direct the final material either in a fully or in a partially coated granule, eg. by adjusting the ratio between coating material and cores.

[0026] The granules preferably comprise two coatings.

[0027] In such a case, for example, the core granule particles are then coated with a first layer also called subcoating, preferably in a fluid bed or spouting bed coater, and then coated with a second layer, the so-called topcoating.

[0028] Preference is given to two layer coatings of a hydrophilic subcoat and a hydrophobic topcoat.

[0029] It is preferred that the granules comprise a subcoating in an amount of from 1 % to 20% by weight based on the weight of the total granule, and a topcoating in an amount of from 1 % to 20% by weight based on the weight of the total granule.

[0030] The amounts of the subcoating and the topcoating are preferably each from 3 to 15%, especially 5 to 15% by weight.

[0031] Preferably, the subcoating comprises hydroxypropylmethylcellulose (HPMC) and/or methylcellulose (MC).

[0032] HPMC and MC are nonionic cellulose ethers which are used in many different application fields. Chemically, part of the hydroxyl groups in the anhydroglucose units that build natural cellulose are substituted with methoxy groups in the case of MC, and both methoxy and hydroxypropoxy groups for the HPMC. A common way to designate the average level of substitution on the cellulose chain is to give the methoxyl content and the hydroxypropyl content in the product in wt-%. Both substitution levels and also the degree of polymerization have influence on the properties of the product.

[0033] A commercial MC may have about 15-40 wt-%, especially 28 - 30 wt-% of methoxy group content, and a commercial HPMC may have about 15-40 wt-%, especially 28-30 wt-% of methoxy group content and 7-12 wt-% of hydroxypropoxy group content. For coating purposes, low degree of polymerization is preferred in order to achieve low viscosity of the coating solution which is sprayed on the granules. Typically, the viscosity at 2.0 wt-%, in mPas is also displayed in the product description.

[0034] As an example, Tylose MOBS 3 P4 (Shin Etsu) is a product with methoxy group content of 28-30%, a hydroxypropoxy group content of 7-12%, and a viscosity within 2.4 - 3.6 mPas of a 2 wt-% solution in water at 20°C, measured with an Ubbelohde viscosimeter at 20°C.

[0035] Specifically, the HPMC and MC grades are of low molecular weight, and the HPMC is a mixture of HPMC 3 and HPMC 6, preferably a mixture of about 1:1 by weight.

[0036] The hydroxypropylmethylcellulose (HPMC) and methylcellulose (MC) preferably are dissolved in water and is then sprayed onto the granules.

[0037] Preferably, the water based coating when applied contains HPMC and MC in a weight ratio of from 1:1 to 10:1, especially 2:1 to 8:1.

[0038] When the subcoating process is complete, the topcoating is coated on the granules via melt coating technology, to give a second coating layer. Optionally, a small amount of silica is added into the fluid bed after the melt coating is completed, to improve the flowability of the product.

[0039] Preferably, the topcoating comprises a fatty acid, especially nonadecanoic acid, stearic acid, palmitic acid or myristic acid. More preferably, the topcoating comprises stearic acid. It is preferred that the topcoating comprises stearic acid and palmitic acid, especially in a weight ratio of 1:1 to 10:1.

[0040] The final coated granules according to the invention may be white / off-white, or colored. In case of a colored granule, the dye may be located in the granule core and/or in any of the coating layers.

[0041] The final two-layer coated granules preferably have an average particle size ( $X_{50}$ ) of 400  $\mu\text{m}$  to 1500  $\mu\text{m}$ .

[0042] The lower limit for the amount of acylhydrazones of formula (1) in the granules according to the present invention is preferably 55%, especially 60% and more preferably 65% by weight. The higher limit for the amount of acylhydrazones of formula (1) in the coated granules according to the present invention is preferably 95%, especially 90% and more preferably 85% by weight.

[0043] A preferred range for the amount of acylhydrazones of formula (1) in the granules according to the present invention is 55% to 95%, especially 60% to 95% and more preferably 60% to 90% by weight. Highly preferred is an amount of 60% to 85%, especially 65% to 85% by weight.

[0044] Other ingredients mean for example formulation aids, additives, fillers, processing aids, buffer salts, and pigment dyes or other dyes. Such ingredients may be part of the coating and preferably of the core pellet.

[0045] For example, such materials may be either useful for preparing the core pellet of the granule, and / or add an additional benefit in the laundry, and / or may serve as a filler, e.g. to enable a specific acylhydrazone content in the final product.

[0046] Among the preferred materials are those:

that are useful for pelletizing the core pellet, e.g. starch, modified starch, microcrystalline cellulose, calcium sulphate and so on, while it is understood in the context of the invention that these materials are not regarded as binders as specified above;

and / or those that are used as typical filler material in detergent compositions, eg. sodium sulphate, sodium chloride and the like;

and / or those that are used as a detergent ingredient and have some functionality in the laundry process beyond simply being a filler material, e.g. sodium silicates, zeolithes, phosphates, buffer materials like citrates, dispersing agents or suspending agents;

and / or inorganic material for increasing the whiteness of the granule core, e.g. titan dioxide.

[0047] Preferably, the granules according to the instant invention additionally comprise 0% to 1 % by weight based on the weight of the total granule of at least one dye or pigment or a mixture thereof. Such dye or pigment may be present in the core pellet or preferably in the coating.

[0048] Furthermore, the coated granules may comprise 0% to 2% by weight based on the weight of the total granule of a hydrophobic fine-particulate material. Such hydrophobic fine particulate material is, for example, silica as given hereinbefore.

[0049] The amount of further ingredients in the core pellet is preferably 0% to 8%, especially 0% to 6% and more preferably 0% to 4% by weight, based on the weight of the total granule.

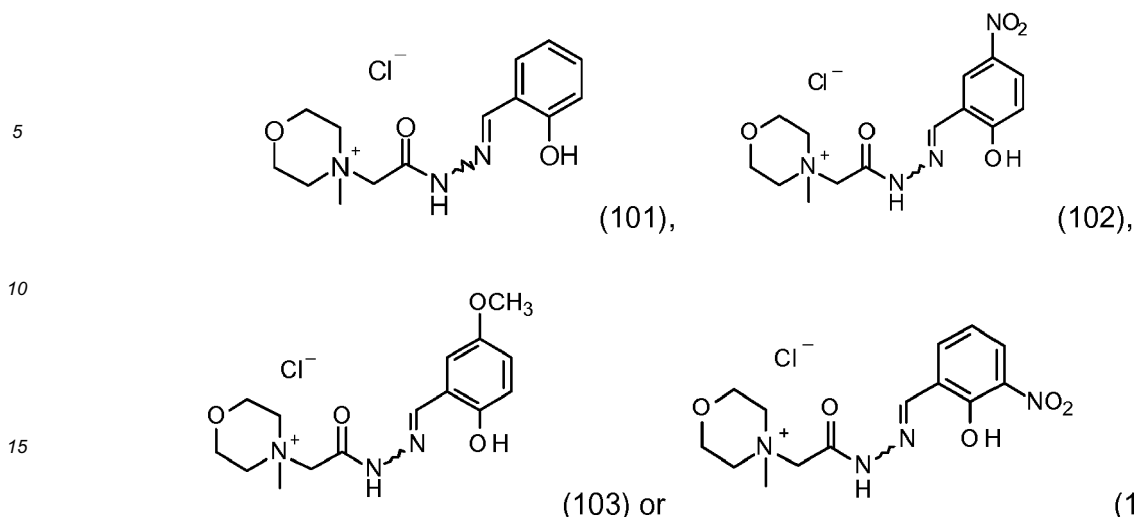
[0050] It is to be noted that further ingredients can be used for the preparation of the core pellets, but it is also possible to prepare these without the use of substantial amounts of further ingredients. There is especially no requirement to use other water-insoluble ingredients for such preparation.

[0051] Preferred are coated granules comprising a core pellet comprising

- a) 60% to 95% by weight based on the weight of the total granule of an acylhydrazone of formula (1), and
- b) 1 % to 20%, especially 1 to 15% by weight based on the weight of the total granule of a water soluble binder,
- c) 0% to 15% by weight based on the weight of the total granule of water, and







20 **[0061]** The acylhydrazones of formula (I) and their preparation are described in WO 2012/080088. These compounds are the active bleach catalysts in the final granules.

**[0062]** The present invention also relates to the use of a granule as described above together with a peroxy compound for bleaching stains or soiling on textile material in the context of a washing process.

**[0063]** The washing process may be at a temperature between 20° C and 95° C, preferably between 20° C and 60° C. The washing process is preferably carried out in an automatic washing machine.

25 **[0064]** Furthermore, the present invention relates to a washing, cleaning or bleaching composition comprising a granule as described above.

**[0065]** In such washing, cleaning or bleaching composition the granule is preferably used in an amount that gives a bleach catalyst concentration in the liquor of from 0.05 to 100 mg/l of liquor, preferably from 0.05 to 50 mg/l of liquor, more preferably from 0.05 to 30 mg/l of liquor when from 0.5 to 20 g/l of the washing, cleaning or bleaching composition are added to the liquor.

30 **[0066]** The compositions may for example comprise from 0 to 50% by weight, preferably from 0 to 30% by weight, A) of at least one anionic surfactant and/or B) of at least one non-ionic surfactant, from 0 to 70% by weight, preferably from 0 to 50% by weight, C) of at least one builder substance, from 1 to 99% by weight, preferably from 1 to 50% by weight, D) of at least one peroxide or at least one peroxide-forming substance.

**[0067]** The anionic surfactant A) can be, for example, a sulfate, sulfonate or carboxylate surfactant or a mixture thereof. Preferred sulfates are those having from 12 to 22 carbon atoms in the alkyl radical, optionally in combination with alkylethoxysulfates having from 10 to 20 carbon atoms in the alkyl radical.

40 **[0068]** Preferred sulfonates are, for example, alkybenzenesulfonates having from 9 to 15 carbon atoms in the alkyl radical. The cation in the anionic surfactants is preferably an alkali metal cation, especially sodium.

**[0069]** Preferred carboxylates are alkali metal sarcosinates of formula  $R_{50}-CO-N(R_{51})-CH_2COOM'_1$ , wherein  $R_{50}$  is alkyl or alkenyl having from 8 to 18 carbon atoms in the alkyl or alkenyl radical,  $R_{51}$  is  $C_1-C_4$ alkyl and  $M'_1$  is an alkali metal.

45 **[0070]** The non-ionic surfactant B) may be, for example, a primary or secondary alcohol ethoxylate, especially a  $C_8-C_{20}$  aliphatic alcohol ethoxylated with an average of from 1 to 20 mol of ethylene oxide per alcohol group.

**[0071]** Preference is given to primary and secondary  $C_{10}-C_{15}$  aliphatic alcohols ethoxylated with an average of from 1 to 10 mol of ethylene oxide per alcohol group.

**[0072]** Non-ethoxylated non-ionic surfactants, for example alkylpolyglycosides, glycerol monoethers and polyhydroxyamides (glucamide), may likewise be used.

50 **[0073]** When the compositions according to the invention contain a component C), the amount thereof is preferably from 1 to 70% by weight, and especially from 1 to 50% by weight, based on the total weight of the washing composition. Special preference is given to an amount of from 5 to 50% by weight and more especially an amount of from 10 to 50% by weight.

55 **[0074]** As builder substance C) there come into consideration, for example, alkali metal phosphates, especially tripolyphosphates, carbonates and hydrogen carbonates, especially their sodium salts, silicates, aluminum silicates, polycarboxylates, polycarboxylic acids, organic phosphonates, aminoalkylenepoly(alkylenephosphonate(s)) and mixtures of such compounds.

**[0075]** Silicates that are especially suitable are sodium salts of crystalline layered silicates of the formula



$\text{NaHSi}_t\text{O}_{2t+1}\cdot p\text{H}_2\text{O}$  or  $\text{Na}_2\text{Si}_t\text{O}_{2t+1}\cdot p\text{H}_2\text{O}$  wherein  $t$  is a number from 1.9 to 4 and  $p$  is a number from 0 to 20.

**[0076]** Among the aluminum silicates, preference is given to those commercially available under the names zeolite A, B, X and HS, and also to mixtures comprising two or more such components.

**[0077]** Among the polycarboxylates, preference is given to polyhydroxycarboxylates, especially citrates. Interesting polycarboxylic acids are nitrilotriacetic acid, ethylenediaminetetraacetic acid and ethylenediamine disuccinate either in racemic form or in the enantiomerically pure (S,S) form. There come also into consideration polyacrylates and copolymers of acrylic acid with maleic anhydride, both of which are preferred.

**[0078]** Phosphonates or aminoalkylenepoly(alkylenephosphonate(s)) that are especially suitable are alkali metal salts of 1-hydroxyethane-1,1-diphosphonic acid, nitrilotris(methylenephosphonic acid), ethylenediaminetetramethylenephosphonic acid and diethylenetriaminepentamethylenephosphonic acid.

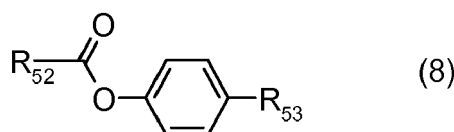
**[0079]** As peroxide component D) there come into consideration, for example, the organic and inorganic peroxides known in the literature and obtainable commercially that bleach textile materials at conventional washing temperatures, for example at from 10 to 95°C.

**[0080]** The organic peroxides are, for example, mono- or poly-peroxides, especially organic peracids or salts thereof, such as phthalimidoperoxyacaproic acid, peroxybenzoic acid, diperoxydodecanoic diacid, diperoxyonanoic diacid, diperoxydecanoic diacid, diperoxyphthalic acid or salts thereof.

**[0081]** Preferably, however, inorganic peroxides are used, for example persulfates, perborates, percarbonates and/or persilicates. It will be understood that mixtures of inorganic and/or organic peroxides can also be used. The peroxides may be in a variety of crystalline forms and have different water contents, and they may also be used together with other inorganic or organic compounds in order to improve their storage stability.

**[0082]** The peroxides are added to the composition preferably by mixing the components, for example using a screw metering system and/or a fluidised bed mixer.

**[0083]** In addition to the peroxides bleach activators may be present. Customary bleach activators are polyacylated alkylenediamines, especially tetraacetylenediamine (TAED), acylated glycolurils, especially tetraacetylglycoluril (TAGU), N,N-diacetyl-N,N-dimethylurea (DDU), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT) as well as compounds of the following formula (8)



wherein

$R_{52}$  is a sulfonate group, a carboxylic acid group or a carboxylate group and

$R_{53}$  is linear or branched  $C_7$ - $C_{15}$ alkyl.

**[0084]** Special activators are known under the names SNOBS, SLOBS and DOBA, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran and also acetylated sorbitol and mannitol and acylated sugar derivatives, especially pentaacetylglucose (PAG), sucrose polyacetate (SUPA), pentaacetylfructose, tetraacetylxylose and octaacetyllactose as well as acetylated, optionally N-alkylated glucamine and gluconolactone. Combinations of conventional bleach activators, known from German Patent Application DE-A-44 43 177 can also be used.

**[0085]** The compositions may comprise, in addition to the combination according to the invention, one or more optical brighteners, for example from the classes of bis-triazinyl-amino-stilbenedisulfonic acid, bis-triazolyl-stilbenedisulfonic acid, bis-styryl-biphenyl or bis-benzofuranyl biphenyl, a bis-benzoxalyl derivative, bis-benzimidazolyl derivative or coumarin derivative or a pyrazoline derivative.

**[0086]** The compositions may furthermore comprise dirt-suspending agents, for example sodium carboxymethylcellulose; pH regulators, for example alkali metal or alkaline earth metal silicates; foam regulators, for example soap; salts for adjusting the spray drying and the granulating properties, for example sodium sulfate; fragrances; antistatic agents; fabric conditioners; enzymes, such as amylase, protease, cellulase and lipase; further bleaching agents; pigments; and/or toning agents. These constituents should especially be stable to the bleaching agent employed.

**[0087]** In addition, the present invention relates to the core pellets, which are uncoated granules comprising

a) 50% to 99% by weight based on the weight of the total granule of an acylhydrazone of formula (1) according to claim 1,

b) 1 % to 50% by weight based on the weight of the total granule of a water soluble binder,

- c) 0% to 15% by weight based on the weight of the total granule of water, and  
 d) 0% to 10% by weight based on the weight of the total granule of further ingredients,

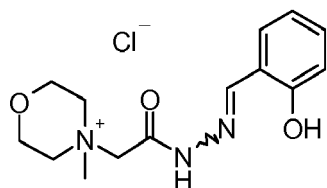
the sum of components a) to d) adding to 100%.

**[0088]** Definitions and preferences where applicable apply equally for all aspects of the invention.

**[0089]** The following Examples serve to illustrate the invention. Parts and percentages relate to weight, unless otherwise indicated.

Example 1: Mixer agglomeration of the catalyst:

**[0090]** In an Eirich lab mixer, 1300 g of the oxidation catalyst of formula (101)



(101)

are agglomerated with 195 g of a binder solution, containing 30 wt-% of Pluriol 8000 E (polyethylene glycol with a mean molecular weight of 8000; BASF), 1.2 wt-% of citric acid monohydrate and 2.8 wt-% of monosodium citrate dihydrate (Merck) in tap water. The speed of the mixing device is set at 3000 rpm, and the beaker rotates with 42 rpm. The binder solution is sprayed on the powder using a Schlick nozzle in 41 seconds. After addition of the binder solution is completed, the moist mixture is further granulated for 120 seconds. The granulator is discharged and 1410 g of granules are collected. After drying the sample in the oven at 70°C for 8 hours, 1351 g of dry granules are obtained. The sieve cut 400 - 1500 μm is taken for further coating experiments. The granule contains 90.9 wt-% of the compound of formula (101). These granules are the core pellets and coated as given in Examples 2 and 3.

Example 2: Coating of the catalyst granules of Example 1 with Hydroxypropyl Methylcellulose (HPMC) / Methyl Cellulose (MC) mixture:

**[0091]** 90 g of Tylose MOBS 3 P4 and 90 g of Tylose MOBS 6 P4 (Hydroxypropyl Methylcellulose, ShinEtsu) are blended with 45 g of Benecel A 15 (Methylcellulose, Ashland). The powder mixture is dispersed in 1500 g of hot water, and then 4 g of Puricolor Blue PBL 15-L is added. Cold tap water is added to the polymer solution until 2250 g of a clear coating solution is obtained. The solid content of the coating solution is 10 wt-%.

**[0092]** 1300 g of the core pellets of Example 1 are introduced into a STREA-1 laboratory fluid bed (Aeromatic-Fielder). After fluidisation of the pellets, coating solution with 139 g of solids is sprayed onto the pellets within 160 minutes. Inlet air temperature is 60°C, and product temperature is about 40°C. When spraying of the coating solution is finished, the heating of the inlet air is turned off, and the pellets are cooled down until the product temperature is about 30°C. 1365 g of subcoated granules are obtained.

Example 3: Coating of the subcoated granules of Example 2 with fatty acid mixture:

**[0093]** 1300 g of the subcoated granules of Example 2 are coated with a 3:1 mixture of stearic acid and palmitic acid in a GCPG-1 (Glatt) equipped with hot melt technology. A total mass of 170 g of the fatty acid mixture is sprayed on the subcoated granules within 25 minutes. Air inlet temperature is in the range of 41-47°C, product temperature is in the range of 35-44°C. After the hot melt coating is finished, the granules are cooled down to 35°C and then removed and screened over 400 - 2000 μm. 1470 g of two layer coated granules are obtained.

**[0094]** The compositions of the granules obtained in Examples 1 to 3 are summarized below:

Table 1: Granule compositions. All values refer to wt-%, based on the total weight of the corresponding granule.

	Example 1	Example 2	Example 3
Oxidation catalyst of formula (101)	90.9	82.0	72.6
Citric acid/ Citrate	0.5	0.5	0.4

## EP 3 382 004 A1

(continued)

	Example 1	Example 2	Example 3
Pluriol 8000 E	4.1	3.7	3.3
Subcoat Mix	--	9.7	8.5
Fatty acid mix	--	--	11.6
Water	4.5	4.1	3.6

### Application Example 1 - Stability of coated acylhydrazone granules in detergent:

**[0095]** 180 g of standard detergent ECE 98 (available at WFK Testgewebe GmbH, Christinenfeld 10, 41379 Brüggem-Bracht, Germany) are mixed with 20 g of sodium percarbonate granules (Fluka) in a turbula mixer.

**[0096]** As a reference a two layer coated granule comprising the compound of formula (101) is prepared according to the description given in Example E11 of WO 2015/169851.

**[0097]** 0.20 g of the two layer coated granule according to Example 3 (or 0.20 g of the reference two layer coated granule, respectively) is mixed with 19.8 g of ECE 98 containing 10 wt-% percarbonate. The mixture is homogenized using the turbula for 1 minute, and then transferred into a petridish. The petridish is stored open in a test chamber (KBF 115, Binder) at a constant climate of 35°C and 75% r.h (relative humidity).

**[0098]** After the indicated storage time, the petridishes are removed from the test chamber and the samples are visually evaluated on discolored (yellowish, brownish) particles.

Table 2: Results from storage tests.

Sample	Example 3 of the instant invention	Reference, Example E11 of WO 15/169851
Amount subcoat	8.5 wt-%	10 wt-%
Amount topcoat	11.6 wt-%	12 wt-%
after 11 days 35°C, 75%r.h.	no discolored particles	no discolored particles
after 21 days 35°C, 75%r.h.	no discolored particles	no discolored particles

**[0099]** The stability of the granule with very high active level is similar to that of the reference sample having a distinct lower amount of active. The Reference, Example E11 of WO 15/169851, comprises an amount of 26 weight-% of the compound of formula (101), based on the weight of the granule.

### Application Example 2 - Dispersion of coated granule in tap water:

**[0100]** In a glass beaker, the two layer coated granule according to Example 3 (or 0.20 g of the reference two layer coated granule given above, respectively) are introduced into 50 ml of cold tap water which contains 4 wt-% of buffer solution (pH = 10). The granule dispersions are stirred on a magnetic stirrer at about 400 rpm. After 10 minutes, the samples are removed from the magnetic stirrer and the dispersion is visually evaluated.

Table 3: Results from dispersion tests.

Sample	Example 3 of the instant invention	Reference, Example E11 of WO 15/169851
Amount subcoat	8.5 wt-%	10 wt-%
Amount topcoat	11.6 wt-%	12 wt-%
Remaining particles	few blue and white particles	more blue and white particles than for Example 3 of the instant invention

**[0101]** The two layer coated granule of the instant invention with very high active level shows less remaining particles than the reference granule, indicating an improved overall release of the active into the solution.

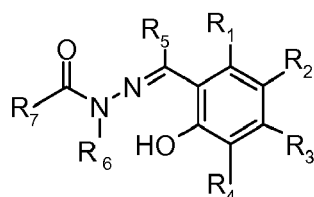
**[0102]** The Reference, Example E11 of WO 15/169851, comprises an amount of 26 weight-% of the compound of formula (101), based on the weight of the granule.

## Claims

1. A coated granule comprising a core pellet comprising

- 5 a) 50% to 98% by weight based on the weight of the total granule of an acylhydrazone of formula (1),  
 b) 1 % to 49% by weight based on the weight of the total granule of a water soluble binder,  
 c) 0% to 15% by weight based on the weight of the total granule of water, and  
 d) 0% to 10% by weight based on the weight of the total granule of further ingredients, and  
 10 which core pellet is coated with  
 e) 1 % to 40% by weight based on the weight of the total granule of at least one coating, the sum of components  
 a) to e) adding to 100%, and

wherein the acylhydrazone of formula (1) is a compound of formula



(1)

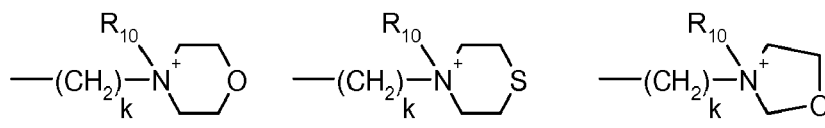
wherein

25  $R_1, R_2, R_3, R_4$  independently from each other are hydrogen, halogen, hydroxy, nitro, N-mono- or N,N-di- $C_1$ - $C_4$ alkylamino, or unsubstituted or substituted  $C_1$ - $C_{28}$ alkyl,  $C_1$ - $C_{28}$ alkoxy,  $C_2$ - $C_{28}$ alkenyl,  $C_2$ - $C_{22}$ alkinyl,  $C_3$ - $C_{12}$ cycloalkyl,  $C_3$ - $C_{12}$ cycloalkenyl,  $C_7$ - $C_9$ aralkyl,  $C_3$ - $C_2$ oheteroalkyl,  $C_3$ - $C_{12}$ cycloheteroalkyl,  $C_5$ - $C_{16}$ heteroaralkyl, phenyl or naphthyl, wherein the substituents for each of the radicals are selected from the group consisting of  $C_1$ - $C_4$ alkyl;  $C_1$ - $C_4$ alkoxy; hydroxy; sulfo; sulfato; halogen; cyano; nitro; carboxy; amino; N-mono- or N,N-di- $C_1$ - $C_4$ alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety; N-phenylamino; N-naphthylamino wherein the amino groups may be quaternised; phenyl; phenoxy and naphthyloxy; or  $R_1$  and  $R_2, R_2$  and  $R_3$  or  $R_3$  and  $R_4$  are linked together to form 1, 2 or 3 carbocyclic or heterocyclic rings, which may be uninterrupted or interrupted by one or more -O-, -S- or - $NR_{11}$ - and or which may be further fused with other aromatic rings and/or which may be substituted with one or more  $C_1$ - $C_6$ akyl groups;

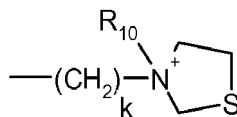
30  $R_5$  denotes hydrogen, unsubstituted or substituted  $C_1$ - $C_2$ alkyl,  $C_2$ - $C_{28}$ alkenyl,  $C_2$ - $C_{22}$ alkinyl,  $C_3$ - $C_{12}$ cycloalkyl,  $C_3$ - $C_{12}$ cycloalkenyl,  $C_7$ - $C_9$ aralkyl,  $C_3$ - $C_2$ oheteroalkyl,  $C_3$ - $C_{12}$ cycloheteroalkyl,  $C_5$ - $C_{16}$ heteroaralkyl, phenyl or heteroaryl; wherein the substituents for each of the radicals are selected from the group consisting of  $C_1$ - $C_4$ alkyl;  $C_1$ - $C_4$ alkoxy; hydroxy; sulfo; sulfato; halogen; cyano; nitro; carboxy; amino; N-mono- or N,N-di- $C_1$ - $C_4$ alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety; N-phenylamino; N-naphthylamino wherein the amino groups may be quaternised; phenyl; phenoxy and naphthyloxy;

35  $R_6$  denotes hydrogen,  $C_1$ - $C_{28}$ alkyl,  $C_2$ - $C_{28}$ alkenyl,  $C_2$ - $C_{22}$ alkinyl,  $C_3$ - $C_{12}$ cycloalkyl,  $C_3$ - $C_{12}$ cycloalkenyl,  $C_7$ - $C_9$ aralkyl,  $C_3$ - $C_2$ oheteroalkyl,  $C_3$ - $C_{12}$ cycloheteroalkyl,  $C_5$ - $C_{16}$ heteroaralkyl, phenyl, naphthyl or heteroaryl; wherein the substituents for each of the radicals are selected from the group consisting of  $C_1$ - $C_4$ alkyl;  $C_1$ - $C_4$ alkoxy; hydroxy; sulfo; sulfato; halogen; cyano; nitro; carboxy; amino; N-mono- or N,N-di- $C_1$ - $C_4$ alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety; N-phenylamino; N-naphthylamino wherein the amino groups may be quaternised; phenyl; phenoxy and naphthyloxy;

40  $R_7$  is a group



or



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each group with an anion A-;

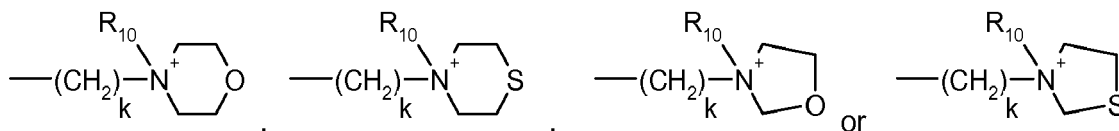
k is an integer from 1 to 4;

A- is the anion of an organic or inorganic acid;

10  $R_{10}$  denotes hydrogen, C<sub>1</sub>-C<sub>28</sub>alkyl, C<sub>2</sub>-C<sub>28</sub>alkenyl, C<sub>2</sub>-C<sub>22</sub>alkinyl, C<sub>3</sub>-C<sub>12</sub>cycloalkyl, C<sub>3</sub>-C<sub>12</sub>cycloalkenyl, C<sub>7</sub>-C<sub>9</sub>aralkyl, C<sub>3</sub>-C<sub>2</sub>oheteroalkyl, C<sub>3</sub>-C<sub>12</sub>cycloheteroalkyl or C<sub>5</sub>-C<sub>16</sub>heteroaralkyl; and  $R_{11}$  denotes hydrogen or C<sub>1</sub>-C<sub>18</sub>alkyl.

- 15 **2.** A granule according to claim 1, wherein the water-soluble binder is selected from the group consisting of polyvinylalcohols, polyvinylpyrrolidones, polyacrylates, cellulose derivatives, carbohydrates, polyethyleneglycols and mixtures thereof.
- 20 **3.** A granule according to claim 1 or 2, wherein the water-soluble binder is selected from the group consisting of polyvinylalcohols, polyvinylpyrrolidones, polyacrylates, polyethyleneglycols and mixtures thereof.
- 4.** A granule according to any of claims 1 to 3, wherein the water-soluble binder is present in an amount of 1 % to 20% by weight based on the weight of the total granule.
- 25 **5.** A granule according to any of claims 1 to 4, wherein the acylhydrazone of formula (1) is present in an amount of 55% to 95% by weight based on the weight of the total granule.
- 6.** A granule according to any of claims 1 to 5, wherein the acylhydrazone of formula (1) is present in an amount of 60% to 95% by weight based on the weight of the total granule.
- 30 **7.** A granule according to any of claims 1 to 6, comprising a subcoating in an amount of from 1 % to 20% by weight based on the weight of the total granule, and a topcoating in an amount of from 1 % to 20% by weight based on the weight of the total granule.
- 35 **8.** A granule according to claim 7, wherein the subcoating comprises hydroxypropylmethylcellulose (HPMC) and/or methylcellulose (MC).
- 9.** A granule according to claim 7 or 8, wherein the topcoating comprises a fatty acid, preferably nonadecanoic acid, stearic acid, palmitic acid or myristic acid.
- 40 **10.** A granule according to any of claims 1 to 9, wherein in the compound of formula (1)  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  independently from each other are hydrogen, hydroxy, halogen, nitro, methyl or methoxy;  $R_5$  denotes hydrogen or methyl;  $R_6$  denotes hydrogen or methyl;  $R_7$  is a group

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each group with an anion A-;

k is an integer from 1 to 2;

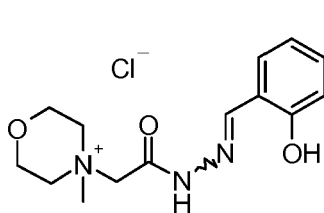
A- is the anion of an organic or inorganic acid; and

$R_{10}$  denotes hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl.

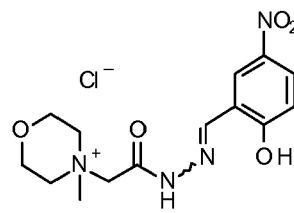
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- 11.** A granule according to any of claims 1 to 10, wherein the compound of formula (1) is a compound of formula

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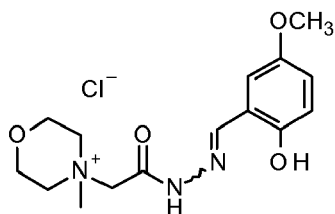


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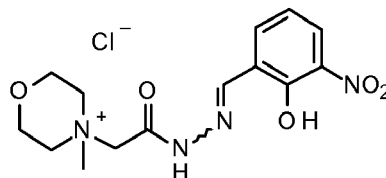


(102),

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(103) or



(104).

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12. Use of a granule according to any one of claims 1 to 11 together with a peroxy compound for bleaching stains or soiling on textile material in the context of a washing process.

13. A washing, cleaning or bleaching composition comprising a granule according to any one of claims 1 to 11.

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14. An uncoated granule comprising

- a) 50% to 99% by weight based on the weight of the total granule of an acylhydrazone of formula (1) according to claim 1,
- b) 1 % to 50% by weight based on the weight of the total granule of a water soluble binder,
- c) 0% to 15% by weight based on the weight of the total granule of water, and
- d) 0% to 10% by weight based on the weight of the total granule of further ingredients, the sum of components a) to d) adding to 100%.

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EUROPEAN SEARCH REPORT

Application Number  
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			TECHNICAL FIELDS SEARCHED (IPC)
			C11D
The present search report has been drawn up for all claims			
Place of search <b>Munich</b>		Date of completion of the search <b>20 June 2017</b>	Examiner <b>Saunders, Thomas</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	

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