(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 885 953 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
12.12.2001 Bulletin 2001/50

(21) Application number: **97900465.2**

(22) Date of filing: **21.01.1997**

(51) Int Cl.[7]: **C11D 17/06**, C11D 3/33, C11D 3/37, C11D 10/02, C11D 3/12

(86) International application number:
PCT/JP97/00111

(87) International publication number:
WO 97/27282 (31.07.1997 Gazette 1997/33)

(54) HIGH-DENSITY GRANULATED DETERGENT COMPOSITION

GRANULIERTE WASCHMITTELZUSAMMENSETZUNG MIT HOHEM SCHÜTTGEWICHT

COMPOSITION DE DETERGENT GRANULEE HAUTE DENSITE

(84) Designated Contracting States:
DE FR GB

(30) Priority: **22.01.1996 JP 856096**
21.02.1996 JP 3378896

(43) Date of publication of application:
23.12.1998 Bulletin 1998/52

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(56) References cited:
EP-A- 0 509 382
DE-A- 3 739 610
JP-A- 7 089 913
WO-A-94/29421
JP-A- 3 160 100

- **DATABASE WPI Section Ch, Week 9316 Derwent Publications Ltd., London, GB; Class D25, AN 93-131475 XP002106828 & JP 05 070795 A (NIPPON SHOKUBAI CO LTD) , 23 March 1993 -& CHEMICAL ABSTRACTS, vol. 119, no. 18, 1 November 1993 Columbus, Ohio, US; abstract no. 183398, XP002106915**

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EP 0 885 953 B1

Printed by Jouve, 75001 PARIS (FR)

Description

Background of the Invention

Field of the Invention:

[0001] The present invention relates to a high-density detergent composition. In particular, it relates to a high-density powdered detergent composition being excellent in detergency and solubility at low temperature and exhibiting excellent biodegradability.

Description of Related Art:

[0002] A detergent composition for clothes is basically composed of a surfactant which solubilizes soil, separates it from fibers, and dissolves or disperses it in a washing solution, an alkaline substance which accelerates the decomposition or solubilization of soil, a high-molecular compound which suspends soil in a washing solution, a sequestering agent which removes substances lowering the power of surfactants, for example, calcium or magnesium ions from a washing solution, and so on.

[0003] Among these components, "builders for detergents" generally refer to substances which do not exhibit detergency per se but can enhance the detergency of a surfactant when used together with the surfactant. Among such builders for detergents, the above-mentioned sequestering agent serves to make a surfactant exhibit its performance more effectively, thus being one of the extremely important builders for detergents.

[0004] Phosphate salts such as sodium tripolyphosphate were formerly added to detergent compositions for clothes as the sequestering agent. However, such phosphate salts are believed to be one of the factors causing the eutrophication of lakes, marshes and so on. In the detergent industry, therefore, the use of the phosphate builders has been self-restrained, while the development of a detergent not containing any phosphate builder has been continued. The development of such a non-phosphorus detergent has been continued from about 1980. As a result, a crystalline sodium aluminosilicate having a specific structure (which is called "zeolite" in the detergent industry) is currently used as the main component of the sequestering agent, because it is free from the above problem unlike phosphate builders and has recently been stabilized in the cost.

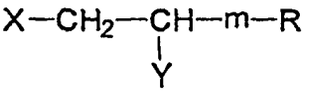
[0005] Further, a detergent composition for clothes has changed in the form from the late 1980s, so that a so-called compact detergent which has a high bulk density and is lowered in the volume of the composition used per washing run is now widely used. However, the particles constituting such a compact detergent are more highly compacted than those constituting the detergent of the prior art, thus being problematic in solubility. For example, washing with water having a temperature of as low as about 5 °C is not unusual in winter, and the standard time of ordinary home washing (exclusive of rinsing and dehydration) is as very short as about 10 minutes. When the use of a compact detergent under the conditions of such a low temperature and such a short washing time is taken into account, it is requisite that the solubility of a compact detergent is further improved to attain satisfactory detergency. However, the enhancement of the solubility to a certain level or higher is often accompanied with a lowering in the degree of freedom of the formulation of the detergent.

[0006] Meanwhile, zeolite which is currently used as the main builder is insoluble in water per se, and has the problem that when a powdered detergent containing zeolite comes into contact with water, it forms a difficultly soluble and highly viscous detergent paste through the interaction of the detergent with surfactants or inorganic salts.

[0007] Further, the mechanism how zeolite sequesters components enhancing the hardness of water (i.e., ions) lies essentially in ion exchange, and the rate of the ion exchange depends on the rate of diffusion of the ions in zeolite. When the temperature of water is low, accordingly, zeolite has another problem that it takes a remarkably long time to develop the ion exchange power.

[0008] Zeolite is most widely used as a representative non-phosphorus builder for detergents. As described above, however, zeolite often fails in exhibiting its performance under the conditions of low temperature and short washing time. Such insufficiency of the performance of zeolite as the builder for detergents is generally covered by a polymeric dispersant consisting of a polycarboxylic acid. Such polycarboxylic acids are also a kind of ion exchangers and are effective in sequestering polyvalent cations. However, the polycarboxylic acids are liable to thicken the above detergent paste, and therefor the use of the acids has a problem of lowering the solubility of a zeolite-containing detergent.

[0009] EP-A-0 509 382 teaches to stabilize bleaching agents in a detergent composition by means of the following nonphosphorus-containing biodegradable stabilizer.

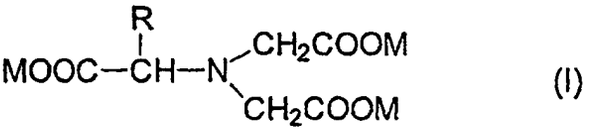


in which m is NR' or sulfur; X is SO_3H or COOH; Y is hydrogen, SO_3H or COOH; R and R' are, independently, hydrogen, $-CH(Z)CH_2(Z')$, $-CH(Z)CH(Z')(Z'')$ or $-CH_2COOH$; and Z, Z' and Z'' are, independently, hydrogen, OH, SO_3H or COOH; or a sodium, potassium or ammonium salt thereof.

[0010] JP-A-5070795 discloses a detergent composition containing

- 1 to 40 weight % of compounds which are obtained by reacting epoxy succinic acid with imino diacetic acid or glycine and
- 1 to 40 weight % of surfactants.

[0011] WO 94/29421 relates to the use of glycine-N,N-diacetic acid derivatives of the following formula (I)



(I)

wherein M represents H, optionally substituted ammonium, an alkaline metal or earth alkaline metal and R is inter alia optionally substituted C1-30 alkyl or C2-C30-alkenyl, as complexing agent for earth alkaline and heavy metal ions in powder washing agent formulations and as calcium sequestrating agent in oral hygiene products.

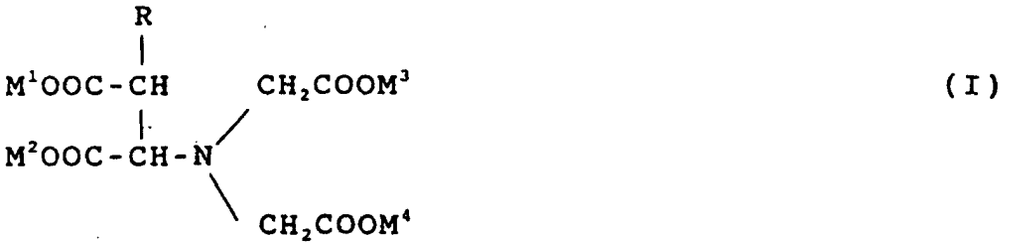
Disclosure of Invention

Summary of the Invention:

[0012] Under these circumstances, the present invention aims at providing a high-density powdered detergent composition exhibiting excellent solubility and detergency even under the condition of low water temperature.

[0013] The inventors of the present invention have made extensive studies for attaining the above aim. As a result of the studies, they have found that a high-density powdered detergent composition comprising an aluminosilicate and a specific aspartic acid diacetic acid salt serving as an organic builder is excellent in solubility and detergency even at low temperature. The present invention has been accomplished on the basis of this finding.

[0014] Namely, the present invention provides a high-density powdered detergent composition which has a bulk density of 0.6 to 1.2 g/ml and which comprises 0.5 to 30 % by weight of (a) an aspartic acid diacetic acid salt represented by the following formula (I), 20 to 50 % by weight of (b) an anionic surfactant, 1 to 30 % by weight of (d) an aluminosilicate and 0.5 to 25 parts by weight (per 100 parts of the component (b)) of (c) a nonionic surfactant having an HLB (Hydrophile Lypophile Balance) value of 10.5 to 15.0, each percentage being based on the total weight of the composition:

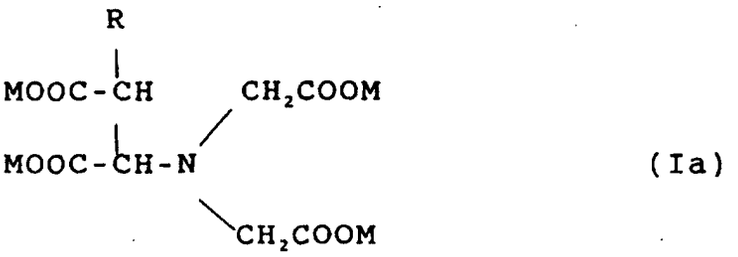


(I)

wherein R is H or OH; and M^1, M^2, M^3 and M^4 are each H, Na, K or NH_4.

[0015] In other words, the present invention relates to a high-density powdered detergent composition which comprises

0.5 to 30 % by weight of (a) an aspartic acid diacetic acid salt (ASDA) represented by the following formula (Ia):



(Ia)

(wherein M is selected from among H, Na, K and NH_4; and R is selected from between H and OH),
20 to 50 % by weight of (b) an anionic surfactant,
and 0.5 to 25 parts by weight (per 100 parts by weight of the component (b)) of (c) a nonionic surfactant having an HLB (Hydrophile Lypophile Balance) value of 10.5 to 15.0,
and which has a bulk density of 0.6 to 1.2 g/ml.

[0016] The high-density powdered detergent composition of the present invention will now be described in detail.

Detailed Description of the Invention:

(a) Organic builder

[0017] The organic builder to be used in the present invention is an aspartic acid diacetic acid salt represented by the formula (I).

[0018] In the formula (I), M^1, M^2, M^3 and M^4 (i.e., counter ions) are each generally hydrogen ion, sodium ion or potassium ion.

[0019] In the present invention, it is necessary from the standpoint of the detergency of the detergent composition that the organic builder (a) is contained in the composition in an amount of 0.5 to 30 % by weight, preferably 2 to 30 % by weight, still preferably 2 to 20 % by weight.

[0020] Specific examples of the compound (a) to be used in the present invention as the organic builder are disclosed in JP-A 7-89913 and US 5543566 corresponding to it.

(b) Anionic surfactant

[0021] Examples of the anionic surfactant include alkylbenzenesulfonic acid salts wherein the alkyl has 8 to 18 carbon atoms, salts of alkanesulfonic acids (SAS), salts of α-olefinsulfonic acids, salts of sulfates of primary and secondary higher alcohols, salts of sulfates of polyoxyethylene alkyl ethers, α-sulfofatty acid salts and C_{10}-C_{20} higher fatty acid salts. These anionic surfactants may be used each alone or as a mixture of two or more of them.

[0022] It is necessary that the component (b) is contained in the composition in an amount of 20 to 50 % by weight, preferably 20 to 40 % by weight. When the amount of the component (b) lies within this range, high detergency can be attained.

(c) Nonionic surfactant having an HLB value of 10.5 to 15.0

[0023] The HLB value used in this description refers to one calculated by Griffin's method. Examples of nonionic surfactants having HLB values falling within the above range include products of the adduction reaction of C_{10}-C_{18} linear and branched, primary and secondary alcohols with alkylene oxides such as ethylene oxide and propylene oxide in such ratios as to give HLB values falling within the above range (i.e., polyoxyalkylene alkyl ethers). The nonionic surfactant to be used in the present invention also includes polyoxyalkylene alkylphenyl ethers prepared in similar manners to that described above, fatty acid esters of polyoxyalkylene sorbitan, fatty acid esters of polyoxyalkylene glycol, fatty acid esters of polyoxyalkylene sorbitol, alkanolamides of polyoxyalkylene higher fatty acids, and esters of polyoxyalkylene higher fatty acids with polyhydric alcohols, whose HLB values fall within the above range.

[0024] The component (c) is used in an amount of 0.5 to 25 parts by weight, preferably 2.0 to 25 parts by weight, still preferably 2.0 to 15 parts by weight per 100 parts by weight of the component (b). When the components (b) and (c) are used at such a ratio, not only the ionic properties due to the component (b) are retained, i.e., excellent detergency

against inorganic particles and so on is exhibited, but also a contribution of the nonionic surfactant toward the detergency is found.

(d) Aluminosilicate

[0025] The aluminosilicate to be used in the present invention as the component (d) may be any of amorphous and crystalline ones.

[0026] It is preferable that the amorphous aluminosilicate be one containing silicon in an amount of 30 % by weight or above, still preferably 40 % by weight or above in terms of SiO_2. Further, the use of such an amorphous aluminosilicate as to give a 5 % dispersion (a dispersion of 5 g of a sample in 100 ml of water free from carbonic acid) having a pH of 9 or above brings about a detergent composition which exhibits excellent solubility even after the storage under high-humidity conditions. In other words, such an amorphous aluminosilicate is effective in protecting the detergent composition from the deterioration of solubility caused by storage under high-humidity conditions. The term "pH" used above with respect to a 5 % amorphous aluminosilicate dispersion refers to a value as determined according to JIS K6220.

[0027] Examples of the amorphous aluminosilicate to be used in the present invention include those represented by the following formula (i):

$$a(M_2O) \cdot Al_2O_3 \cdot b(SiO_2) \cdot c(H_2O) \quad \text{(i)}$$

wherein M is alkali metal; and a, b and c represent the molar proportions of the constituent components respectively. In general, a is a number of 0.7 to 2.0, b is a number of 0.8 or above but below 4,.and c is an arbitrary positive number.

[0028] These amorphous aluminosilicates exhibit high oil absorption and high cation exchange capacity.

[0029] Among the above amorphous aluminosilicates, those represented by the following formula (ii) are particularly preferable:

$$Na_2O \cdot Al_2O_3 \cdot b(SiO_2) \cdot c(H_2O) \quad \text{(ii)}$$

wherein b is a number of 1.8 to 3.2; and c is a number of 1 to 6.

[0030] Such amorphous aluminosilicates can be prepared by referring to, e.g., the process disclosed in JP-A 6-179899 and EP-A 593014 corresponding thereto.

[0031] On the other hand, crystalline aluminosilicate is generally called "zeolite", and is represented by the following formula (iii):

$$a'(M_2O) \cdot Al_2O_3 \cdot b'(SiO_2) \cdot w(H_2O) \quad \text{(iii)}$$

wherein M is alkali metal; and a', b' and w represent the molar proportions of the constituent components respectively, with a', b' and w being generally a number of 0.7 to 1.5, a number of 0.8 or above but below 6, and an arbitrary positive number, respectively.

[0032] Among the above crystalline aluminosilicates, those represented by the following formula (iv) are particularly preferable:

$$Na_2O \cdot Al_2O_3 \cdot n(SiO_2) \cdot w(H_2O) \quad \text{(iv)}$$

wherein n is a number of 1.8 to 3.0; and w is a number of 1 to 6.

[0033] The crystalline aluminosilicate (zeolite) to be used in the present invention is desirably a synthetic zeolite having a mean primary particle diameter of 0.1 to 10 μm, for example, zeolite A, X or P. The zeolite may be added in the form of a powder and/or a dry agglomerate prepared by drying a zeolite slurry.

[0034] In the present invention, it is necessary from the standpoint of the detergency of the resulting detergent composition that the aluminosilicate (d) is contained in the composition in an amount of 1 to 30 % by weight, preferably 5 to 25 % by weight.

[0035] Further, it is preferable in the present invention that the weight ratio of the component (a) to the component (d) [i.e., the (a)/(d) weight ratio] lie between 1 : 5 and 5 : 1.

[0036] Although the high-density powdered detergent composition of the present invention comprises the above components (a) to (d) as the essential components, it may further contain the following components.

<Crystalline silicate>

[0037] It is desirable from the standpoint of detergency that the high-density powdered detergent composition of the present invention contains a crystalline silicate. The crystalline silicate to be used in the present invention is preferably one essentially consisting of silicon dioxide (Si_2O) and an alkali metal oxide (i.e., an alkali metal silicate), still preferably an alkali metal silicate having an SiO_2 to M_2O ratio (wherein M is alkali metal) of 0.5 to 2.6. Although there have been known crystalline silicates having SiO_2 to M_2O ratios (wherein M is Na) of 1.9 to 4.0, crystalline silicates having silicone dioxide to alkali metal oxide ratios exceeding 2.6 are often unusable as the constituent of the high-density powdered detergent composition of the present invention.

[0038] Examples of the crystalline silicate to be favorably used in the present invention include those having the following compositions (II) and (III):

$$x(M_2O) \cdot y(SiO_2) \cdot z(Me_mO_n) \cdot w(H_2O) \quad (II)$$

wherein M is a Group Ia element of the periodic table; Me is at least one element selected from among Group IIa, IIb, IIIa, IVa and VIII elements of the periodic table; y/x is a number of 0.5 to 2.6, preferably 1.5 to 2.2; z/x is a number of 0.01 to 1.0, preferably 0.02 to 0.9, still preferably 0.02 to 0.5; w is a number of 0 to 20; and n/m is a number of 0.5 to 2.0, and

$$M_2O \cdot x'(SiO_2) \cdot y'(H_2O) \quad (III)$$

wherein M is alkali metal; x' is a number of 1.5 to 2.6; and y' is a number of 0 to 20.

[0039] Specific examples of the crystalline silicate represented by the above formula (II) are disclosed in JP-A 5-279013 and 7-89712 and US 5427711 corresponding to them. The crystalline silicates disclosed therein can be used in the present invention.

[0040] The crystalline silicate represented by the formula (II) exhibits a pH of 11 or above in the state of a 0.1 % by weight aqueous dispersion. That is, it exhibits a high alkalinizing power. Further, the crystalline silicate exhibits a particularly high buffer capacity in the alkaline (basic) region and its buffer capacity is higher than that of sodium carbonate or potassium carbonate.

[0041] The crystalline silicate represented by the formula (II) has an ion exchange capacity of at least 100 $CaCO_3$ mg/g, preferably 200 to 600 $CaCO_3$ mg/g, and therefore serves as one of the substances capable of capturing ions in the present invention.

[0042] As described above, the crystalline silicate represented by the formula (II) exhibits both a high alkalinizing power and a high buffer capacity in the alkaline (basic) range, and further has a high ion exchange capacity.

[0043] It is preferable that the crystalline silicate represented by the formula (II) have a mean particle diameter of 0.1 to 100 μm, still preferably 1 to 60 μm. When the mean particle diameter exceeds 100 μ m, the development of the ion exchange power of the silicate will be so slow as to bring about a lowering in the detergency, while when it is less than 0.1 μ m, the resulting silicate will exhibit high absorptivity for moisture and CO_2 owing to its enhanced specific surface area to result in remarkably deteriorated quality. The term "mean particle diameter" used in this description refers to a median diameter of particle size distribution.

[0044] The crystalline silicate having such a mean particle diameter can be produced by pulverizing crystalline silicate particles of somewhat large sizes by the use of a vibration mill, a hammer mill, a bowl mill, a roller mill or other pulverizer.

[0045] Next, the crystalline silicate represented by the formula (III) will be described.

[0046] Among the crystalline silicates represented by the formula (III), those wherein x' is 1.7 to 2.2 and y' is 0 are preferable. Further, those having a cation exchange capacity of 100 to 400 $CaCO_3$ mg/g are usable in the present invention. In the present invention, the crystalline silicate represented by the formula (III) serves as one of the substances capable of capturing ions.

[0047] As described above, the crystalline silicate represented by the formula (III) exhibits both a high alkalinizing power and a high buffer capacity in the alkaline (basic) range, and further has a high ion exchange capacity.

[0048] The crystalline silicate represented by the formula (III) can generally be prepared by firing amorphous glassy sodium silicate at 200 to 1000 °C to crystallize it, though the production processes therefor are disclosed in JP-A 60-227895 and US 4664839 corresponding thereto. Details of the production thereof are described also in, for example,

Phys. Chem. Glasses. *1*, 127-138 (1966), Z. Kristallogr., 129, p.p.396-404 (1969) and so on. Further, the crystalline silicate represented by the formula (III) is commercially available, e.g., under the trade name of "Na-SKS-6" (composition: δ -$Na_2Si_2O_5$) from Hoechst Ltd. as powder or granule.

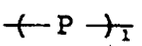
[0049] It is preferable that the crystalline silicate represented by the formula (III) as well as the one represented by the formula (II) have a mean particle diameter of 0.1 to 100 μm, still preferably 1 to 60 μm.

[0050] In the present invention, the crystalline silicates represented by the formula (II) and those represented by the formula (III) may be used each alone or as a mixture of two or more of them. Further, it is preferable that the silicate (s) account for 30 to 100 % by weight, still preferably 70 to 100 % by weight of the alkaline substances contained in the composition.

[0051] In the present invention, it is preferable that the crystalline silicate be contained in the composition in an amount of 1 to 40 % by weight, still preferably 5 to 35 % by weight. When the amount exceeds 40 % by weight, the resulting detergent composition will be poor in the physical properties as powder and often cause caking owing to its high hygroscopicity, resulting in difficult handling.

<Other builders>

[0052] A builder has both the effect of separating solid-particle dirt from clothes and dispersing it in a washing solution and the effect of preventing the solid-particle dirt thus dispersed from redepositing on clothes (resoiling clothes). In order to attain such effects of a builder sufficiently, it is preferable that the high-density powdered detergent composition contain a polycarboxylate having an average molecular weight of hundreds to a hundred thousand, for example, a random copolymer comprising at least one monomer selected from the group consisting of maleic acid, maleic anhydride and salts of maleic acid with sodium, potassium and ammonium and at least one monomer copolymerizable therewith (such as C_1-C_8 olefin, acrylic acid, methacrylic acid, itaconic acid or methallylsulfonic acid), or a homopolymer represented by the following formula (V):



(V)

wherein P is a constituent unit of a homopolymer resulting from a homopolymerizable monomer; and 1 is a value giving a homopolymer having an average molecular weight of hundreds to a hundred thousand. In this homopolymer, at least part of the constituent units (P's) are converted into at least one salt selected from the group consisting of sodium salt, potassium salt and ammonium salt.

[0053] In the above formula (V), the constituent unit of the homopolymer is one resulting from acrylic acid, methacrylic acid, maleic acid or the like.

[0054] In the present invention, it is preferable that one or more members selected from among the above random copolymers and the homopolymers of the formula (V) be used in a total amount (or in an amount, when only one of them is used) of 1 to 8 % by weight, still preferably 2 to 6 % by weight based on the total amount of the detergent composition containing the same. Among these polycarboxylates, salts of acrylic acid/maleic acid copolymers or polyacrylic acid with Na, K and/or NH_4 are particularly excellent. The average molecular weight thereof is preferably 1000 to 100000, still preferably 1000 to 80000.

[0055] In addition to the above builders, the high-density powdered detergent composition of the present invention can contain also the following inorganic or organic builders.

(I) Inorganic builders

1) alkaline salts such as sodium carbonate, potassium carbonate, sodium bicarbonate, sodium sulfite and sodium sesquicarbonate,
2) salts of phosphoric acids such as orthophosphoric acid, pyrophosphoric acid and tripolyphosphoric acid with alkali metals such as sodium and potassium,
3) neutral salts such as sodium sulfate

(II) Organic builders

1) alkali metal salts of phosphonic acids such as ethane-1,1-diphosphonic acid and ethane-1,1,2-triphosphonic acid,
2) polyelectrolytes such as polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone, carboxymethylcellulose and polyaspartic acid,

3) alkali metal salts of organic acids such as diglycolic acid and oxydisuccinic acid.

<Other components>

[0056] The high-density powdered detergent composition of the present invention may further contain other conventional components for detergents at need, and such components include bleaching agents, bleaching activators, enzymes, enzyme stabilizers, bluing agents, anticaking agents, antioxidants, fluorescent dyes and perfumes.

[0057] Examples of the bleaching agents include sodium percarbonate, sodium perborate (with its monohydrate being preferable) and sodium sulfate-hydrogen peroxide adduct, among which sodium percarbonate is particularly preferable.

[0058] Examples of the bleaching activators include tetraacetylethylenediamine, acetoxybenzenesulfonic acid salts, organic peroxy acid precursors described in JP-A 59-22999 and US 4412934 corresponding thereto, JP-A 63-258447 and US 4751015 corresponding thereto, and JP-A 6-316700, and metal catalysts wherein transition metals are stabilized with sequestering agents.

[0059] The enzyme to be optionally used in the present invention (which essentially exhibits enzymatic activity in the washing step) is preferably protease, esterase, lipase, carbohydrase, nuclease or pectinase.

[0060] Specific examples of the protease include pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, subtilisin, BPN, papain, bromelin, carboxypeptidases A and B, aminopeptidase and aspergillopeptidases A and B, which are commercially available under the trade names of "Sabinase" and "Alkarase" (from Novo Industri), "API21" (from Showa Denko, K.K.) and Maxacal (from Gist-Brocades); and proteases K-14 and K-16 described in JP-A 5-25492 and US 5312561 corresponding thereto.

[0061] Specific examples of the esterase include gastric lipase, pancreatic lipase, plant lipase, phospholipase, choline esterase and phosphatase.

[0062] The lipase may be a commercially available one such as "Lipolase" (a product of Novo Industri).

[0063] Specific examples of the carbohydrase include cellulase, maltase, saccharase, amylase, lysozyme, α-glycosidase and β-glycosidase.

[0064] The cellulase may be "Celluzyme" (a product of Novo Industri) or a cellulase described in claim 4 of JP-A 63-264699 and US 4822516 and 4978470 corresponding thereto, while the amylase may be "Termamyl" (a product of Novo Industri).

[0065] The enzyme stabilizers include reducing agents (such as sodium sulfite and sodium hydrogensulfite), calcium salts, magnesium salts, polyols, boron compounds.

[0066] Various bluing agents may also be added to the detergent composition at need. In particular, bluing agents whose chemical structures are described in JP-B 49-8005, 49-26286 and 53-45808 are preferably used.

[0067] Examples of the anticaking agents include p-toluenesulfonic acid salts, xylenesulfonic acid salts, acetic acid salts, sulfosuccinic acid salts, talc, finely powdered silica, clay and magnesium oxide. Among finely divided silica and so on, porous ones are usable also as carriers for nonionic surfactants. Further, clay (specifically, smectite clay) is effective also as softener.

[0068] Examples of the antioxidants include t-butylhydroxytoluene, 4,4'-butylidenebis(6-t-butyl-3-methylphenol), 2,2'-butylidenebis(6-t-butyl-4-methylphenol), monostyrenated cresol, distyrenated cresol, monostyrenated phenol, distyrenated phenol and 1,1'-bis(4-hydroxyphenyl)cyclohexane.

[0069] Further, the detergent composition may contain a fluorescent dye in an amount exceeding 0 % by weight but up to 1 % by weight, the fluorescent dye being at least one member selected from the group consisting of 4,4'-bis (2-sulfostyryl)biphenyl salts, 4,4'-bis(4-chloro-3-sulfostyryl)biphenyl salts, 2-(styrylphenyl)naphthothiazole derivatives, 4,4'-bis-(triazol-2-yl)stilbene derivatives and bis(triazinylamino)stilbenedisulfonic acid derivatives.

[0070] Examples of the perfumes include conventional ones for detergents as described in JP-A 63-101496.

[0071] The high-density powdered detergent composition of the present invention takes a powdery or granular form. The process for producing the composition is not particularly limited, but may be any known one. The bulk density of the composition can be enhanced by a process of spraying a nonionic surfactant on spraydried particles, a process of making a powdery component containing an oil-absorbing carrier occlude a nonionic surfactant, or by referring to the processes described in JP-A 61-69897, 61-69899 and 61-69900, JP-A 2-222498 and US 5052122 corresponding to it, JP-A 2-222499, JP-A 3-33199 and EP-A 339996 corresponding to it, JP-A 5-86400 and US 5282996 corresponding to it, and JP-A 5-209200 and US 5468516 corresponding to it.

[0072] When a crystalline aluminosilicate is used as the component (d), a small portion of the crystalline aluminosilicate may be added during the granulation or just before the completion of the granulation as the surface modifier for the granules. When a crystalline silicate is used, it is preferable that the silicate be added in the step of enhancing the bulk density or dry-blended with the granules. When an alkali metal carbonate is used, it may be added to the slurry or at any step during the granulation, or dry-blended with the granules.

[0073] It is desirable from the standpoint of the physical properties of the composition as powder that the high-density

powdered detergent composition of the present invention has a mean particle diameter of 200 to 1000 μm, particularly 200 to 600 μm. Further, the detergent composition of the present invention has a bulk density of 0.6 to 1.2 g/ml, preferably 0.6 to 1.0 g/ml.

[0074] The detergent composition of the present invention may be used in a suitable concentration, which depends on which of several washing methods (such as machine washing and immersion) is employed, quantity of clothes or water, extent of stains, operating conditions of the machine. In machine washing, for example, the composition may be used in a concentration of 0.03 to 0.3 % by weight.

[0075] As described above, the present invention provides a high-density powdered detergent composition which contains both an organic builder excellent in biodegradability and an inorganic builder and is enhanced in detergency.

Example:

[0076] The present invention will now be described in detail by referring to the following Example, though the present invention is not limited by it.

Example 1

<Preparation of high-density powdered detergent compositions>

[0077] · An aqueous slurry having a solid content of 60 % by weight was prepared by using 1.0 kg of ASDA, 0.5 kg of crystalline aluminosilicate, 4.0 kg of LAS, 0.4 kg of AA-MA copolymer, 0.4 kg of FA, and 0.73 kg of soda ash (sodium carbonate). The obtained slurry was subjected to spray drying. The particles thus obtained were put in a Lödige mixer (mfd. by Matsuzaka Giken K.K.), followed by the addition thereto of 0.25 kg of crystalline aluminosilicate, 2.0 kg of silicate (II), 0.1 kg of an enzyme, the balance of Glauber's salt and 0.05 kg of a fluorescent dye [i.e., 4,4'-bis(2-sulfostyryl) biphenyl salt]. The resulting mixture was agitated, while 0.07 kg of AE-1 and 0.1 kg of PEG which had been preheated to 70 °C were gradually dropped into the mixture. Thus, the mixture was granulated. Then, 0.25 kg of crystalline aluminosilicate was added to the granulated mixture, and the obtained mixture was further subjected to granulation. Thus, a high-density powdered detergent composition having a mean particle diameter of 450 μm and a bulk density of 0.805 g/ml was obtained.

[0078] The other high-density powdered detergent compositions were also prepared according to the same procedure as that described above except that components listed in Tables 1 and 2 were used in proportions specified in Tables 1 and 2. The obtained powdered detergent compositions had bulk densities of 0.800 ± 0.050 g/ml.

[0079] The high-density powdered detergent compositions were subjected to the following detergency test and solubility test. The results are given in Tables 1 and 2.

<Detergency test>

(Preparation of artificially stained cloths)

[0080] Artificially stained cloths were prepared by making an artificial dirt solution adhere to cloths, with the formulation of the artificial dirt solution being described below. This adhesion was conducted by printing cloths with the artificial dirt solution by the use of a gravure roll coater. The preparation of the artificially stained cloths was conducted under the conditions of a cell capacity of gravure roll of 58 cm^3/cm^2, a coating speed of 1.0 m/min, a drying temperature of 100 °C, and a drying time of one minute. Cotton shirting cloth #2003 (a product of Yato Shoten) was used in the above preparation of the artificially stained cloths.

[Formulation of artificial dirt solution]	
lauric acid	0.44 wt. %
myristic acid	3.09 wt. %
pentadecanoic acid	2.31 wt. %
palmitic acid	6.18 wt. %
heptadecanoic acid	0.44 wt. %
stearic acid	1.57 wt. %
oleic acid	7.75 wt. %
triolein	13.06 wt. %
n-hexadecyl palmitate	2.18 wt. %

(continued)

[Formulation of artificial dirt solution]	
squalene	6.53 wt. %
liquid-crystalline albumen lecithin	1.94 wt. %
Kanuma Aka-tsuchi (a kind of tephra)	8.11 wt. %
carbon black	0.01 wt. %
tap water	the balance

(Washing conditions and evaluation method)

[0081] Five artificially stained cloths (10 cm x 10 cm) prepared above and 1 l of an aqueous solution of a sample detergent composition were put in a Terg-O-Tometer to conduct the washing at 100 rpm. The washing conditions are as follows:

· Washing conditions	
washing time	10 min,
detergent concn.	0.067 w/v%,
hardness of water	4° DH,
temp. of water	20 °C, and
rinsing	with tap water (running water) for 5 min.

[0082] The detergency of each detergent composition was determined as follows. The reflectivities at 550 nm of the unstained cloth and the stained cloth before and after the washing were measured by the use of a self-colorimeter (mfd. by Shimadzu Corporation), and the rate (%) of cleansing was calculated according to the following formula. The rates of cleansing observed with respect to the five cloths simultaneously washed were averaged, and the average thus determined is given in Table 1 or 2 as the rate of cleansing of the composition.

$$\text{Rate of cleansing (\%)} = (\text{reflectivity after washing} - \text{that before washing})/(\text{that of unstained cloth} - \text{that before washing}) \times 100$$

<Solubility test>

[0083] A sample powdered detergent composition was classified by the use of sieves having opening sizes of 710 μm and 1000 μm respectively to obtain a fraction composed of particles having diameters falling within a predetermined range. Separately, one liter of tap water having a temperature of 5 °C was put in a beaker having a capacity of one liter, and a stirrer piece was thrown into the water and revolved at about 550 rpm to thereby agitate the water. A predetermined amount of the above fraction was thrown into the water. The conductivity of the contents of the beaker was determined with the lapse of time by the use of CM-60S mfd. by Toa Denki Kogyo K.K.

[0084] The conductivity value of the solution obtained by completely dissolving the fraction in the water being taken as the reference, the time elapsed (T90, unit: s) until the conductivity of the contents had reached 90 % of the reference was determined and employed as an indication of the solubility of the detergent composition.

Table 1

Formulation (wt. %)			Invention											
sample no.			1	2	3	4	5	6	7	8	9	10	11	12
component a	ASDA		10.0	10.0	10.0	10.0	5.0	15.0	20.0	10.0	10.0	10.0	10.0	10.0
component b	LAS		40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	30.0	40.0	40.0	40.0
	AS		0	0	0	0	0	0	0	0	10.0	0	0	0
	FA		4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
component c	AE-1		0.7	1.1	2.8	4.0	2.8	2.8	2.8	2.8	2.8	2.8	2.8	6.0
	AE-2		0	0	0	0	0	0	0	0	0	0	0	0
AE-3			0	0	0	0	0	0	0	0	0	0	0	0
component d	zeolite (cryst. alumino-silicate)		10.0	10.0	10.0	10.0	10.0	10.0	5.0	10.0	10.0	20.0	10.0	10.0
silicate (II)			20.0	20.0	20.0	20.0	20.0	20.0	20.0	0	20.0	10.0	20.0	20.0
silicate (III)			0	0	0	0	0	0	0	20.0	0	0	0	0
other components	AA-MA copolymer		4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	0	4.0
	PEG		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	sodium carbonate		7.3	6.9	5.2	4.0	10.2	0.2	0.2	5.2	5.2	5.2	9.2	1.0
	common component		balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance
sum total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Results														
rate of cleansing(%)			68.8	74.6	75.8	70.1	74.3	76.7	76.3	75.3	75.5	73.1	74.0	76.4
solubility, T90 (s)			117	116	115	121	126	109	110	117	118	130	106	130

Table 2

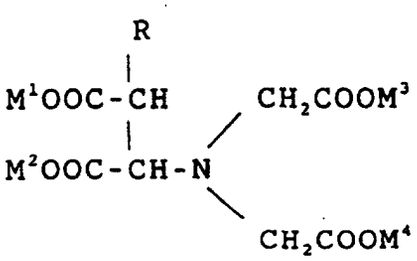
Formulation (wt. %)		sample no.	Invention						Comp.		
			13	14	15	16	17		1	2	3
component a	ASDA		10.0	10.0	10.0	10.0	0		10.0	0	0
	ASDA'		0	0	0	0	10.0		0	0	0
EDTA			0	0	0	0	0		0	0	10.0
component b	LAS		30.0	20.0	40.0	40.0	40.0		26.8	40.0	40.0
	AS		0	20	0	0	0		0	0	0
	FA		4.0	4.0	4.0	4.0	4.0		4.0	4.0	4.0
component c	AE-1		2.1	2.8	0	2.8	1.1		20	2.8	2.8
	AE-2		0	0	2.8	0	0		0	0	0
AE-3			0	0	0	0	0		0	0	0
component d	zeolite (cryst. aluminosilicate)		10.0	10.0	10.0	10.0	10.0		10.0	10.0	10.0
silicate (II)			20.0	20.0	20.0	0	20.0		20.0	20.0	20.0
silicate (III)			0	0	0	0	0		0	0	0
other components	AA-MA copolymer		4.0	4.0	4.0	4.0	4.0		4.0	4.0	4.0
	PEG		1.0	1.0	1.0	1.0	1.0		1.0	1.0	1.0
	sodium carbonate		15.9	5.2	5.2	25.2	6.9		1.2	15.2	5.2
	common component		balance	balance	balance	balance	balance		balance	balance	balance
sum total			100.0	100.0	100.0	100.0	100.0		100.0	100.0	100.0
Results	rate of cleansing(%)		71.5	71.0	74.8	72.8	70.4		56.5	61.5	66.0
	solubility, T90 (s)		126	121	123	132	127		117	224	189

notes)

- ASDA: tetrasodium salt of aspartic acid diacetic acid
- ASDA': tetrasodium salt of hydroxyaspartic acid diacetic acid (R in the formula (I) is OH)
- EDTA: tetrasodium ethylenediaminetetraacetate
- LAS: sodium salt of linear alkyl(C_{12})benzenesulfonic acid
- AS: sodium salt of dodecyl alcohol sulfate
- FA: sodium palmitate
- AE-1: polyoxyethylene dodecyl ether (HLB value: 13.1)
- AE-2: polyoxyethylene dodecyl ether (HLB value: 12.0)
- AE-3: polyoxyethylene dodecyl ether (HLB value: 16.0)
- ANE-1: polyoxyethylene nonylphenyl ether (HLB value: 13.0)
- cryst. aluminosilicate:
  (composition: $M_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, mean particle diam.: 2μm, ion exchange capacity: 290 $CaCO_3$ mg/g)
- silicate (II): crystalline silicate represented by the formula (II) (see "Detailed Description of the Invention")
  [composition: $M_2O{\cdot}1.8SiO_2{\cdot}0.02M'O$ (wherein M is Na and K, K/Na being 0.03; and M' is Ca and Mg, Mg/Ca being 0.01), mean particle diam: 30 μm, ion exchange capacity: 290 $CaCO_3$ mg/g]
- silicate (III): crystalline silicate represented by the formula (III) (see "Detailed Description of the invention")
  (composition: $M_2O{\cdot}2SiO_2$, mean particle diam: 30 μm, ion exchange capacity: 224 $CaCO_3$ mg/g)
- AA-MA copolymer: acrylic acid/maleic acid (7/3, by mole) copolymer having an average molecular weight of 70000
- PEG: polyethylene glycol having an average molecular weight of 7000
- common component: comprising 1 wt. % of an enzyme mixture [comprising Sabinase 12.0TW (a product of Novo Nordisk), Lipolase 100 T (a product of Novo Nordisk), Celluzyme 0.1T (a product of Novo Nordisk), and Termamyl 60T (a product of Novo Nordisk) at a weight ratio of 2 : 1 : 1 : 1], 0.5 wt. % of a fluorescent dye and the balance (such an amount as to make a total of 100 wt. %) of Glauber's salt, each content being based on the total weight of the detergent composition.

Claims

1. A high-density powdered detergent composition which has a bulk density of 0.6 to 1.2 g/ml and which comprises 0.5 to 30 % by weight of (a) an aspartic acid diacetic acid salt represented by the following formula (I), 20 to 50 % by weight of (b) an anionic surfactant, 1 to 30 % by weight of (d) an aluminosilicate and 0.5 to 25 parts by weight (per 100 parts of the component (b)) of (c) a nonionic surfactant having an HLB (Hydrophile Lypophile Balance) value of 10.5 to 15.0, each percentage being based on the total weight of the composition:



(I)

wherein R is H or OH; and M^1, M^2, M^3 and M^4 are each H, Na, K or NH_4.

2. The high-density powdered detergent composition according to claim 1, which further contains 1 to 40 % by weight (based on the total weight of the composition) of at least one member selected from the group consisting of crystalline silicates represented by the following formulae (II) and (III):

$$x(M_2O) \cdot y(SiO_2) \cdot z(Me_mO_n) \cdot w(H_2O) \quad (II)$$

wherein M is a Group Ia element of the periodic table; Me is at least one element selected from among Group IIa, IIb, IIIa, IVa and VIII elements of the periodic table; y/x is a number of 0.5 to 2.6; z/x is a number of 0.01 to 1.0; w

is a number of 0 to 20; and n/m is a number of 0.5 to 2.0, and

$$M_2O \cdot x'(SiO_2) \cdot y'(H_2O) \quad (III)$$

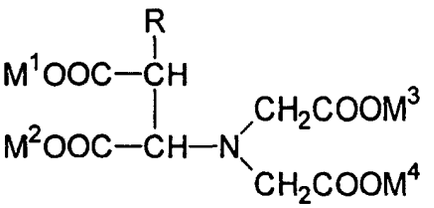
wherein M is alkali metal; x' is a number of 1.5 to 2.6; and y' is a number of 0 to 20.

3. The high-density powdered detergent composition according to claim 1, wherein the weight ratio of the component (a) to the component (d) lies between 1 : 5 and 5 : 1.

4. The high-density powdered detergent composition according to claim 1, which further contains a polycarboxylate having an average molecular weight of 1000 to 100000.

Patentansprüche

1. Hochdichte pulverige Detergenszusammensetzung, die eine Schüttdichte von 0,6 bis 1,2 g/ml aufweist und die 0,5 bis 30 Gew.% von (a) einem Asparaginsäure-Diessigsäuresalz, dargestellt durch die folgende Formel (I), 20 bis 50 Gew.% von (b) einem anionischen Tensid, 1 bis 30 Gew.% von (d) einem Aluminiumsilicat und 0,5 bis 25 Gew.-Teilen (pro 100 Teilen der Komponente (b)) von (c) einem nicht-ionischen Tensid mit einem HLB (Hydrophil/Lipophil-Gleichgewicht)-Wert von 10,5 bis 15,0 umfasst, wobei sich die Prozentsätze jeweils auf das Gesamtgewicht der Zusammensetzung beziehen:



(I)

wobei R H oder OH ist; und M^1, M^2, M^3 und M^4 jeweils H, Na, K oder NH_4 sind.

2. Hochdichte pulverige Detergenszusammensetzung nach Anspruch 1, die weiterhin 1 bis 40 Gew.% (in bezug auf das Gesamtgewicht der Zusammensetzung) mindestens eines Vertreters, ausgewählt aus der Gruppe bestehend aus kristallinen Silicaten, dargestellt durch die folgenden Formeln (II) und (III), enthält:

$$x(M_2O)\cdot y(SiO_2)\cdot z(Me_mO_n)\cdot w(H_2O) \quad (II)$$

wobei M ein Element der Gruppe Ia des Periodensystems ist; Me mindestens ein Element, ausgewählt aus Elementen der Gruppen IIa, IIb, IIIa, IVa und VIII des Periodensystems, ist; y/x eine Zahl von 0,5 bis 2,6 ist; z/x eine Zahl von 0,01 bis 1,0 ist; w eine Zahl von 0 bis 20 ist; und n/m eine Zahl von 0,5 bis 2 ist, und

$$M_2O\cdot x'(SiO_2)\cdot y'(H_2O) \quad (III)$$

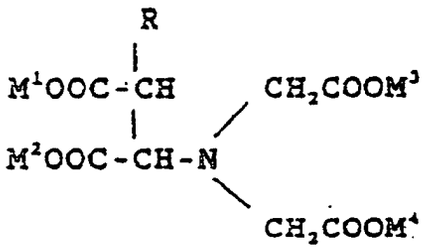
wobei M ein Alkalimetall ist; x' eine Zahl von 1,5 bis 2,6 ist; und y' eine Zahl von 0 bis 20 ist.

3. Hochdichte pulverige Detergenszusammensetzung gemäss Anspruch 1, wobei das Gewichtsverhältnis der Komponente (a) zur Komponente (d) zwischen 1:5 und 5:1 liegt.

4. Hochdichte pulverige Detergenszusammensetzung nach Anspruch 1, die weiterhin ein Polycarboxylat mit einem durchschnittlichen Molekulargewicht von 1.000 bis 100.000 enthält.

Revendications

1. Composition de détergent en poudre à densité élevée qui présente une masse volumique apparente de 0,6 à 1,2 g/ml et qui comprend de 0,5 à 30% en poids de .(a) un sel d'acide aspartique-acide diacétique représenté par la formule (I) suivante, 20 à 50% en poids de (b) un agent tensioactif anionique, 1 à 30% en poids de (d) un aluminosilicate et de 0,5 à 25 parties en poids (pour 100 parties du composant (b)) de (c) un agent tensioactif non ionique présentant une valeur HLB (équilibre hydrophile/lypophile) de 10,5 à 15,0, chaque pourcentage étant exprimé par rapport au poids total de la composition



(I)

où R représente H ou OH ; et M^1, M^2, M^3 et M^4 représentent chacun H, Na, K ou NH_4.

2. Composition de détergent en poudre à densité élevée selon la revendication 1, qui contient en outre de 1 à 40% en poids (exprimé par rapport au poids total de la composition) d'au moins un élément choisi dans le groupe constitué par des silicates cristallins représentés par les formules (II) et (III) suivantes :

$$x(M_2O)\cdot y(SiO_2)\cdot z(Me_mO_n)\cdot w(H_2O) \quad (II)$$

où M représente un élément du groupe la de la classification périodique ; Me représente au moins un élément choisi parmi les éléments des groupes IIa, IIb, IIIa, IVa et VIII de la classification périodique ; y/x représente un nombre de 0,5 à 2,6 ; z/x représente un nombre de 0,01 à 1,0 ; w représente un nombre de 0 à 20 ; et n/m représente un nombre de 0,5 à 2,0, et

$$M_2O \cdot x'(SiO_2) \cdot y'(H_2O) \quad (III)$$

où M représente un métal alcalin ; x' représente un nombre de 1,5 à 2,6 ; et y' représente un nombre de 0 à 20.

3. Composition de détergent en poudre à densité élevée selon la revendication 1, dans laquelle le rapport pondéral du composant (a) au composant (d) est compris entre 1 : 5 et 5 : 1.

4. Composition de détergent en poudre à masse volumique élevée selon la revendication 1, qui contient en outre un polycarboxylate présentant une masse moléculaire moyenne de 1000 à 100 000.