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(54) PARTICULATE DETERGENT

(57) The present invention relates to detergent particles comprising 5 to 50% by weight of a phosphate builder, 5 to 40% by weight of an anionic surfactant, and 1 to 30% by weight of a nonionic surfactant, the detergent particles having an average particle size of from 150 to 500 µm, a bulk density of 500 g/L or more, and a flow time of 10 seconds or less, wherein the detergent particles comprise a detergent particle being capable of releasing a bubble from an inner portion thereof in a process of dissolving the detergent particle in water, the bubble having a size of one-tenth or more of a particle size of the detergent particle, and wherein the detergent particles have a dissolution rate of 90% or more, as calculated by Equation 1:

Equation 1: Dissolution Rate (%) = $[1 - (T/S)] \times 100$,

wherein S is a weight (g) of the detergent particles supplied; and T is a dry weight of insoluble remnants of the detergent particles remaining on the sieve when an aqueous solution prepared under the above stirring conditions is filtered with the sieve.

According to the present invention, the dissolubility of the particles and the flowability are increased, so that easiness in washing with the detergent during hand-washing can be improved.

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Description

TECHNICAL FIELD

[0001] The present invention relates to detergent particles and a detergent composition comprising the detergent particles.

BACKGROUND ART

[0002] A powdery heavy duty detergent has been used for washing using a washing machine, and when there is a large amount of stains on fibers, it may be used for hand-washing. In the hand-washing, in order to allow a concentrated detergent solution to act on stains, it has been known from experience that the washing efficiency is excellent when the hand-washing is started by directly dispersing the powdery heavy duty detergent to a part of the washing items wetted with water. In this case, since the parts of the washing items themselves or the parts of the washing items with other fabric parts are rubbed together with hands, sufficient foaming is necessitated in order to have excellent sliding between the fibers. Especially, a powdery heavy duty detergent comprising a phosphate builder containing a large amount of an anionic surfactant has advantages of sufficient foaming and good sliding between the washing items during hand-washing. Further, in order to directly disperse a desired amount of the powder heavy duty detergent to a part of the washing items, it is necessary that the flowability of the powder is also high.

[0003] On the other hand, in order to impart great advantages in the improvement in the transportation efficiency and the convenience in the users upon transportation and measurement, the powdery heavy duty detergent has been highly densified. However, there has been an increasing concern on the dissolubility by compression of the detergent granules. Especially in the hand-washing, there are concerns that the detergent particle is not readily soluble during washing, and that the foaming rate which gives sliding between cloths is lowered.

[0004] Meanwhile, the washing machine has been developed to have a design in consideration of consumers' demands and water conservation and energy conservation. For instance, in the Japanese-made washing machines, since the mid 1990's, the washing machines have the tendency of having large volume capacity and water conservation, and short-period washing mode or gentle stirring mode meeting the demands of reduction in clothes damaging has been set. However, in either of the modes, the amount of work (i.e. mechanical power x time) of the washing machine tends to be lowered. As a result, there arise crucial problems that the dissolubility of the detergent granules is drastically lowered, so that the detergency becomes poor, and that the insoluble remnants remain on clothes. Also, in the European-made washing machines and the U.S.-made washing machines, it has been considered to be important to lower the washing temperature, from the viewpoint of energy conservation during washing. Therefore, there has been a demand for a detergent having excellent dissolubility.

[0005] In order to efficiently carry out not only washing using the washing machines but also washing by hand-washing in view of the above circumstances, there has been a demand for a detergent comprising a phosphate builder, the detergent having a high flowability, and also having fast foaming, easy washing, and quick disappearance of aggregates of the detergent particles by dissolving at a fast speed.

[0006] However, conventional high-density heavy duty detergents comprising a phosphate builder have had insufficient dissolubility. For instance, Japanese Patent Laid-Open No. Hei 2-49100 discloses a method for agitation-granulating spray-dried particles containing a large amount of an anionic surfactant, and Japanese Patent Laid-Open No. Hei 3-33199 discloses a method for granulation comprising dry-neutralizing an acid precursor of an anionic surfactant with a granular, solid alkalizing agent in a High-Speed Mixer, and thereafter adding a liquid binder. Since these compositions have a high mixing proportion of an anionic surfactant/nonionic surfactant, they have had high foamability but insufficient dissolubility. In order to improve the dissolubility, when the resulting detergent particles are simply made into fine powder, there arise such problems that the flowability of the powder is low, whereby the detergent powder cannot be easily acted on clothes during hand-washing, and that aggregates of the detergent particles are formed during washing at a low temperature in a washing machine. In addition, Japanese Patent Laid-Open No. Sho 52-110710 discloses a detergent comprising a phosphate builder and exhibiting high flowability, prepared by a process characterized by spraying about 12 to about 30% by weight of a nonionic surfactant to substrate beads each comprising a phosphate builder. However, this detergent is not only insufficient in the dissolubility but also insufficient in the foamability because the detergent contains a nonionic surfactant at a high content. Japanese Examined Publication No. Hei 6-49879 describes that as a surfactant composition suitable for a washing method, it is desirable that an anionic surfactant is contained in a relatively large amount for products for hand-washing. However, in order to efficiently wash by hand-washing, there has not yet been obtained a detergent comprising a phosphate builder, the detergent having a high flowability and also having fast foaming and easy washing due to a fast dissolving rate.

DISCLOSURE OF INVENTION

[0007] An object of the present invention is to provide detergent particles having increased dissolubility of the particles and flowability, in order to improve easiness in washing during hand-washing of the phosphate-containing, high-density powdery detergent comprising an anionic surfactant having high foamability, and a detergent composition comprising the detergent particles. Another object of the present invention is to provide phosphate-containing, high-density detergent particles having excellent detergency, owing to its excellent dissolubility of the particles and dispersibility even when the amount of work of the washing machine is low and the washing temperature is low, and a detergent composition comprising the detergent particles.

[0008] These objects and other objects of the present invention will be apparent from the following description.

[0009] Specifically, the present invention relates to:

[1] detergent particles comprising a phosphate builder, the detergent particles having an average particle size of from 150 to 500 μm, a bulk density of 500 g/L or more, and a flow time of 10 seconds or less, wherein the detergent particles comprise a detergent particle being capable of releasing a bubble from an inner portion thereof in a process of dissolving the detergent particle in water, the bubble having a size of one-tenth or more of a particle size of the detergent particle, and wherein the detergent particles have a dissolution rate of 90% or more, under conditions where the detergent particles are supplied in water at 5°C; stirred for 60 seconds under the stirring conditions that 1 g of the detergent particles are supplied to a 1-L beaker (inner diameter: 105 mm) which is charged with 1-L of hard water (71.2 mg $CaCO_3$/L, a molar ratio of Ca/Mg: 7/3), and stirred with a stirring bar (length: 35 mm, and diameter: 8 mm) at a rotational speed of 800 rpm; and filtered with a standard sieve having a sieve-opening of 74 μm as defined by JIS Z 8801, wherein the dissolution rate of the detergent particles is calculated by Equation (1):

$$\text{Dissolution Rate (\%)} = [1 - (T/S)] \times 100 \qquad (1)$$

wherein S is a weight (g) of the detergent particles supplied; and
T is a dry weight of insoluble remnants of the detergent particles remaining on the sieve when an aqueous solution prepared under the above stirring conditions is filtered with the sieve;

[2] detergent particles comprising a phosphate builder, the detergent particles having an average particle size of from 150 to 500 μm, a bulk density of 500 g/L or more, and a flow time of 10 seconds or less, wherein the detergent particles each comprises a base particle comprising a phosphate builder, a water-soluble polymer and a water-soluble salt excluding the phosphate builder, and a surfactant supported by the base particle, wherein the base particle has a localized structure in which a larger portion of the water-soluble polymer is present near the surface of the base particle rather than in the inner portion thereof, and wherein the detergent particles have a dissolution rate of 90% or more, as calculated by the above-mentioned equation (1), under conditions where the detergent particles are supplied in water at 5°C; stirred for 60 seconds under the stirring conditions;

[3] a process for preparing the detergent particles as defined in item [1] or [2] above, comprising the steps of:

Step (a): preparing a slurry containing a phosphate builder, a water-soluble polymer, and a water-soluble salt excluding the phosphate builder, wherein 60% by weight or more of water-soluble components including the water-soluble polymer and the water-soluble salt are dissolved in the slurry;
Step (b): spray-drying the slurry obtained in Step (a) to prepare base particles; and
Step (c): adding a surfactant to the base particles obtained in Step (b) to support the surfactant thereby; and

[4] a detergent composition comprising the detergent particles as defined in item [1] or [2] above in an amount of 50% by weight or more.

BRIEF DESCRIPTION OF THE DRAWING

[0010] Figure 1 is a graph showing comparative results of FT-IR/PAS measurements of Base Particles 1 retaining the original state and Base Particles 1 in a uniformly ground state, wherein the solid line indicates the data for the base particles retaining the original state, and the broken line indicates the data for the base particles in a uniformly ground state.

BEST MODE FOR CARRYING OUT THE INVENTION

[0011] The detergent particle as referred to in the present invention is a particle comprising a surfactant, a builder, and the like, and the detergent particles mean an aggregate thereof. In addition, the detergent composition means a composition comprising the detergent particles, and further comprising separately added detergent components other than the detergent particles (for instance, builder particles, fluorescent dyes, enzymes, perfumes, defoaming agents, bleaching agents, bleaching activators, and the like).

1. Mechanism of Fast Dissolubility

1.1 Fast Dissolubility by Releasing Bubble

[0012] Conventional compact detergent particle requires a relatively longer period of time for complete dissolution because it shows dissolution behavior in which the detergent particle gradually dissolves from a portion near the surface of the detergent particle.

[0013] On the other hand, the detergent particles of the present invention comprise a detergent particle capable of releasing a bubble of 1/10 or more of the particle size from the inner portion of the particle in a process in which the detergent particle is dissolved in water (hereinafter referred to as "bubble-releasing detergent particle"). In a process in which the bubble-releasing detergent particle is dissolved in water, the bubble-releasing particle firstly releases a bubble having a given size from the inner portion of the particle by allowing a small amount of water to enter into the inner portion thereof, and subsequently the particle itself undergoes disintegration (self-disintegration of the particle) by allowing a large amount of water to enter into the inner portion of the particle, so that not only the dissolution from a portion near the surface takes place but also the dissolution and disintegration from the inner portion of the particle take place.

[0014] The dissolution behavior described above can be confirmed by a digital microscope or optical microscope as a phenomenon in which a bubble of 1/10 or more, preferably 1/5 or more, more preferably 1/4 or more, still more preferably 1/3 or more, of the particle size of the particle (hereinafter referred to as "bubble having a given size") is released in the case where the bubble-releasing detergent particle is dissolved in water. On the other hand, in the conventional compact detergent particle, since the size of most of the bubbles generated is just less than 1/10 the size of the detergent particle, the particle itself does not undergo self-disintegration, so that sufficient fast dissolubility cannot be obtained. Incidentally, in the case where the bubble-releasing detergent particle is dissolved in water with a stand-still state, the bubble having a given size is generated preferably within 120 seconds, more preferably within 60 seconds, still more preferably within 45 seconds.

[0015] The bubble-releasing detergent particle may have a single or a plurality of pores capable of releasing a bubble having a given size, and the bubble-releasing detergent particle is not particularly limited in the form and structure of the particle. For example, the bubble-releasing detergent particle may be a uni-core detergent particle which is explained in the subsequent Section 4, or it may be a detergent particle other than the uni-core detergent particle, including, for example, a detergent particle in which the uni-core base particles are aggregated (hereinafter referred to as "multi-core detergent particle" as described in Sections 6 and 7). In addition, the bubble-releasing detergent particle constitutes preferably 40% by weight or more, more preferably 60% by weight or more, still more preferably 80% by weight or more, of the detergent particles.

[0016] The size of the bubble is measured as follows.

[0017] A double-sided adhesive tape is attached to a bottom center of a glass petri dish (inner diameter: 50 mm). The detergent particles are adhered to the double-sided adhesive tape. First, an equivalent diameter (α μm) for each of the particles is determined from an image obtained by a digital microscope. As a digital microscope, for example, "VH-6300" manufactured by KEYENCE CORPORATION can be used.

[0018] Subsequently, 5 mL of ion-exchanged water at 20°C is poured into the glass petri dish, and the dissolution behavior for the individual particles of the subject measurement is observed. When the bubble is released from the inner portion of the particle, the equivalent diameter (β μm) of the bubble is measured from an image of an instant at which the bubble leaves from the particle. Incidentally, in the case where a plurality of bubbles are released from the inner portion of the particle, "β μm" is referred to a maximum value of the equivalent diameter measured for each of the bubbles. The ratio of the bubble diameter to the particle size (β/α) for each of the particles is calculated.

[0019] In a preferable bubble-releasing detergent particle, it is preferable that a pore having a size of 1/10 to 4/5, preferably 1/5 to 4/5, the particle size is present in the inner portion of the particle.

[0020] The pore size can be determined as follows.

[0021] The selected particle is split at a cross section so as to include the maximum particle size without disintegrating the particle with a surgical knife, or the like. The split cross section is observed by a scanning electron microscope (SEM). An equivalent diameter (particle size) [γ μm] of a split cross section of the split particle and in the case where the presence of a pore in the inner portion of the particle is confirmed, an equivalent diameter of the pore (pore size) [δ μm] are measured. Incidentally, in the case where a plurality of pores are confirmed, the equivalent diameter δ μm is defined as the largest pore size among them. Thereafter, the ratio of the pore size to the particle size (δ/γ) is calculated.

[0022] It is preferable that the bubble-releasing detergent particle has uni-core property, from the viewpoint of dramatically enhancing the dissolution speed.

[0023] In addition, in the case where the bubble-releasing detergent particle is constituted by the base particle described in the subsequent Section 2, it is preferable that the base particle has a structure of having a pore in the inner portion of the base particle, the pore having a size of 1/10 to 4/5, preferably 1/5 to 4/5, the particle size of the base particle. The pore size can be determined by the method described above.

1.2 Fast Dissolubility by Localized Structure of Base Particle

[0024] In the detergent particles of the present invention, apart from the dissolution mechanism by releasing bubble mentioned above, or in combination with the dissolution mechanism, the fast dissolubility from the particle surface can be observed. The features thereof reside in that the detergent particles comprise base particles and a surfactant supported to the base particles, the base particles comprising a phosphate builder, a water-soluble polymer, and a water-soluble salt excluding the phosphate builder, wherein the base particle has a localized structure such that a larger amount of the water-soluble polymer is present near the surface of the base particle rather than in the inner portion thereof (hereinafter simply referred to as "localized structure of the base particle"). The base particle in which a larger amount of the water-soluble polymer is localized near the surface can exhibit fast dissolubility because the water-soluble components near the surface are more quickly dissolved in water, thereby showing a dissolution behavior in which the disintegration of the detergent particle from the particle surface is accelerated. Incidentally, the most preferable embodiment for exhibiting fast dissolubility is a detergent particle having the localized structure described above and further being the bubble-releasing detergent particle. In this case, the detergent particle may be not only the uni-core detergent particle but also the multi-core detergent particle.

2. Composition of Base Particles

[0025] The base particles constituting the detergent particles of the present invention each comprises as main components a phosphate builder (A), a water-soluble polymer (B), and a water-soluble salt (C) excluding the phosphate builder, and the particle is used to support a surfactant. An aggregate thereof is referred to as "base particles."

[0026] As Component (A), tripolyphosphates, orthophosphates and pyrophosphates are preferable. It is favorable that the content of the tripolyphosphate is 60% by weight or more, more preferably 70% by weight or more, still more preferably 80% by weight or more of the entire phosphate builder, in which case the content of the orthophosphate is from 1 to 10% by weight, or that the content of the pyrophosphate is from 2 to 10% by weight (the weight ratio being calculated as an anhydride). In addition, as the counter ions, the alkali metals are preferable, especially, sodium and/or potassium is preferable. Incidentally, it is preferable that the amount of the phosphate builder formulated is from 3 to 60% by weight of the detergent composition.

[0027] As Component (B), there can be included carboxylic acid-based polymers, carboxymethyl cellulose, water-soluble starches, sugars, and the like, among which the carboxylic acid-based polymers are preferable.

[0028] Especially, the salts of acrylic acid-maleic acid copolymers and the salts of polyacrylic acids are excellent. It is preferable that the molecular weight is 1000 to 80000.

[0029] In addition, polymers such as polyglyoxylates; cellulose derivatives such as carboxymethyl cellulose; and aminocarboxylic acid-based polymers such as polyaspartates can be used.

[0030] As Component (C), which is a water-soluble salt excluding Component (A), there can be included, for example, inorganic salts such as carbonates, hydrogencarbonates, sulfates, sulfites, hydrogensulfates and halides; and water-soluble organic acid salts having low-molecular weights such as citrates and fumarates. Among them, carbonates, sulfates, and sulfites are preferable. Especially preferable are sodium carbonate, potassium carbonate and sodium sulfate. The inorganic salts are preferable because the bubble in the detergent particle is further thermally expanded by causing hydration heat and dissolution heat by the reaction with water after the preparation of the base particles, thereby accelerating the self-disintegration of the particle.

[0031] Here, sodium carbonate is preferable as an alkalizing agent showing a suitable pH buffer region in the washing liquid. Other alkalizing agents include amorphous or crystalline silicates. The amorphous silicate (water glass) has been widely used as an alkalizing agent as detergent starting materials, and also has an effect of enhancing the particle strength of a base particle. As to this matter, Japanese Examined Patent Publication No. Hei 6-49879 describes that a spray-dried carrier comprising sodium sulfate, sodium carbonate, a nonionic surfactant, and sodium polyacrylate enhances the particle strength by the inclusion of sodium silicate. Also, in Japanese Patent Laid-Open No. Sho 52-110710, an amorphous silicate is used in order to enhance the particle strength of a base particle. However, when a large amount of the silicate is contained in the base particle, the dissolubility is impaired. The amount of the amorphous silicate formulated is preferably less than 8% by weight, more preferably less than 5% by weight, still more preferably less than 3% by weight, most preferably substantially not included, of the base particle.

[0032] In addition, the salts having a high degree of dissociation, such as sulfates and sulfites, enhance ionic strength of the washing liquid, thereby favorably acting against sebum stain deterging, and the like. In addition, the sulfite has an effect of reducing hypochlorite ions contained in tap water, thereby preventing oxidation degradation of the detergent components such as enzymes and perfumes. As the organic salts, those base materials having a large $pKCa^{2+}$ and/or having a large cationic exchange capacity are preferable in expectation of imparting the metal ion capturing ability. Besides the citrates and fumarates, there can be also included methyliminodiacetates, iminodisuccinates, ethylenediaminedisuccinates, taurine diacetates, hydroxyethyliminodiacetates, β-alanine diacetate, hydroxyiminodisuccinates, methylglycine diacetate, glutamic acid diacetate, asparagine diacetate, serine diacetate, and the like.

[0033] In addition, when anions different from the carbonates, such as sulfates and sulfites, and cations different from sodium, such as potassium and ammonium, are mixed in the base particle, there is an effect for the anti-caking property.

[0034] The composition of the base particles is as follows. The amount of Component (A) is preferably from 5 to 90% by weight, more preferably from 10 to 70% by weight, most preferably from 15 to 60% by weight. The amount of Component (B) is preferably from 2 to 30% by weight, more preferably from 3 to 20% by weight, most preferably from 5 to 20% by weight, and especially, in order to exhibit a higher particle strength, it is preferable that the amount is 5% by weight or more, more preferably 7% by weight or more. The amount of Component (C) is preferably from 5 to 78% by weight, more preferably from 10 to 70% by weight, still more preferably from 10 to 67% by weight, especially preferably from 20 to 60% by weight, most preferably from 20 to 55% by weight. In addition, when an amorphous silicate is used as an alkalizing agent, the amount of the amorphous silicate formulated is preferably less than 3% by weight, more preferably less than 1% by weight, most preferably substantially not included, of the base particle, from the viewpoint of the dissolubility. In addition, it is desirable that the amount of the water-soluble polymer formulated is 2% by weight or more, preferably 4% by weight or more, more preferably 6% by weight or more, and that the amount formulated is 30% by weight or less, preferably 25% by weight or less, more preferably 20% by weight or less. Within the above ranges, the base particle is favorable in the aspects of having a structure in which near the surface of the base particle is coated with a water-soluble polymer, so that the coating layer is sufficiently formed on the particle surface, whereby its particle strength can be made sufficient. Also, it is preferable from the viewpoint of the dissolubility of the resulting detergent composition.

[0035] In addition, besides these three components, the base particles may also comprise auxiliary components such as fluorescent dyes, pigments and dyes. Among them, it is favorable to use a water-insoluble inorganic compound such as zeolite, from the viewpoint of enhancing the localized structure of the base particle.

[0036] Incidentally, when a large amount of a surfactant, especially an anionic surfactant, is contained in the base particle, the particle strength is lowered. The content of the anionic surfactant is preferably less than 10% by weight, more preferably less than 7% by weight, still more preferably less than 5% by weight, of the base particle. It is preferable that the anionic surfactant is supported to the base particle by including the anionic surfactant in a liquid mixture of surfactants described below.

[0037] The water-insoluble inorganic compound is preferably those having a primary average particle size of from 0.1 to 20 μm. The water-insoluble inorganic compound includes, for example, crystalline or amorphous aluminosilicates, silicon dioxide, hydrated silicate compounds, clay compounds such as perlite and bentonite, and the like.

[0038] In order to obtain the desired particle strength and bulk density, although the surfactant is substantially not an essential component of the base particle, the surfactant may be added to a slurry prepared in Step (a) in order to improve the drying efficiency in Step (b). The amount of the surfactant is preferably 10% by weight or less, more preferably from 0.1 to 10% by weight, most preferably from 0.1 to 5% by weight, of the slurry. Incidentally, the formulation amounts are on the basis of the solid ingredients of the slurry.

[0039] Higher the supporting ability of the base particle, more likely the fast dissolubility is exhibited even when a large amount of the surfactant is added.

[0040] The factors for improving the supporting ability of the base particle include the use of both carbonates and sulfates as the water-soluble salts excluding the phosphate builder. It is preferable to be used for the base particle 10% by weight or more of sodium carbonate and/or potassium carbonate as carbonates, and 3% by weight or more of sodium sulfate as a sulfate. Especially, in the case where the content of the phosphate builder is lower than 20% by weight, it is more preferable to use sodium sulfate and the carbonate so that the ratio of sodium sulfate/carbonate is from 2/1 to 1/4. Other factors for improving the supporting ability of the base particle include use of base materials having a large supporting ability (oil-absorbing ability) to the water-insoluble inorganic compound. For example, A-type zeolite is preferable from the viewpoints of the metal ion capturing ability and the economic advantages. Here, the value of oil-absorbing ability of A-type zeolite measured by a method according to JIS K 5101 is 40 mL/100 g or more (examples include trade name:

"TOYOBUILDER," manufactured by Tosoh Corporation). Besides the above, P-type (examples include trade names: "Doucil A24" and "ZSE064"; manufactured by Crosfield B.V.; oil-absorbing ability: 60 to 150 mL/100 g); X-type zeolite (examples include trade name: "Wessalith XD"; manufactured by Degussa-AG; oil-absorbing ability: 80 to 100 mL/100 g), and hybrid zeolite described in WO 98/42622. In addition, amorphous silica, amorphous aluminosilicates and the like, which have a low metal ion capturing ability but a high oil-absorbing ability, can be used as the water-insoluble inorganic compound. Examples include amorphous aluminosilicates including those described in Japanese Patent Laid-Open No. Sho 62-191417, page 2, lower right column, line 19 to page 5, upper left column, line 17 (especially, the initial temperature being preferably within the range from 15° to 60°C); and those described in Japanese Patent Laid-Open No. Sho 62-191419, page 2, lower right column, line 20 to page 5, lower left column, line 11 (especially, the oil-absorbing amount being 170 mL/100 g); amorphous aluminosilicates (oil-absorbing ability: 285 mL/100 g) including those described in Japanese Patent Laid-Open No. Hei 9-132794, column 17, line 46 to column 18, line 38; Japanese Patent Laid-Open No. Hei 7-10526, column 3, line 3 to column 5, line 9; Japanese Patent Laid-Open No. Hei 6-227811, column 2, line 15 to column 5, line 2; Japanese Patent Laid-Open No. Hei 8-119622, column 2, line 18 to column 3, line 47, and the like.

[0041] For example, there can be used as an oil-absorbing carrier, "TOKSIL NR" (manufactured by Tokuyama Soda Co., Ltd.; oil-absorbing ability: 210 to 270 mL/100 g); "FLOWRITE" (the same as above; oil-absorbing ability: 400 to 600 mL/100 g); "TIXOLEX 25" (manufactured by Kofran Chemical; oil-absorbing ability: 220 to 270 mL/100 g); "SILOPURE" (manufactured by Fuji Devison Co., Ltd.; oil-absorbing ability: 240 to 280 mL/100 g), and the like. Especially, as the oil-absorbing carriers, favorable are those having properties described in Japanese Patent Laid-Open No. Hei 5-5100, column 4, line 34 to column 6, line 16 (especially, the oil-absorbing carriers described in column 4, lines 43 to 49); and Japanese Patent Laid-Open No. Hei 6-179899, column 12, line 12 to column 13, line 17, and column 17, line 34 to column 19, line 17.

[0042] In the present invention, from the viewpoint of maintaining high dissolubility even after stored for a long period of time (without undergoing property changes), it is desirable that the aluminosilicates have SiO_2/Al_2O_3 (molar ratio) of 4.0 or less, preferably 3.3 or less.

3. Localized Structure of Base Particle

[0043] As a method for confirming the localized structure of the base particle, there can be employed, for instance, a combined method of Fourier transform infrared spectroscopy (FT-IR) and photoacoustic spectroscopy (PAS) (simply abbreviated as "FT-IR/PAS"). As described in *"APPLIED SPECTROSCOPY;"* **47**, 1311-1316 (1993), the distribution state of the substances in the direction of depth from the surface of the samples can be confirmed by FT-IR/PAS. The measurement method will be exemplified below.

[0044] Each cell is charged with each base particle of two different states to conduct FT-IR/PAS measurement, and the structure of the base particle can be determined by comparing the measurement values. In other words, one FT-IR/PAS measurement is taken for the base particle in a state where the desired structure is retained, and another FT-IR/PAS measurement is taken for the comparative sample in which the base particle is in a uniform state by sufficiently grinding the base particle with an agate mortar, or the like. The measurement is carried out, for instance, by using an infrared spectrometer "FTS-60A/896" manufactured by Bio-Rad Laboratories, and the PAS cell includes an acoustic detector "Model 300" manufactured by MTEC Corporation. The measurement conditions are resolution of 8 cm^{-1}, scanning speed of 0.63 cm/s, and 128 scans. In the above measurement conditions, the information up to a depth of about 10 μm from the surface of the base particle is contained. In the PAS spectra of the base particle, for instance, each of the characteristic peaks of sodium tripolyphosphate and sodium polyacrylate can be read off at near 900 cm^{-1} (P-O-P anti-symmetric stretching vibration; broad peak ranging from 850 to 950 cm^{-1}), and 1576 cm^{-1} (CO^{2-} anti-symmetric stretching vibration), respectively, and the areal intensity of each peak is measured. The relative areal intensity of the characteristic peaks of the water-soluble polymer to the characteristic peaks of the phosphate builder, when measured for each of the state in which the structure of the base particle is retained, and the state in which the base particle is uniformly ground, is obtained. The resulting areal relative intensity is then compared with the relative areal intensity of the characteristic peaks of the water-soluble polymer to the characteristic peaks of the phosphate builder, when measured for each of the above states, and thereby the structural features of the base particle can be determined. In addition, in the case where zeolite is contained in the base particle, there can be deduced the structural features of the base particle by the use of the comparison of the relative areal intensity of the characteristic peaks of the water-soluble polymer to the characteristic peaks of the zeolite (1009 cm^{-1}; Si-O-Si anti-symmetric stretching vibration). Concretely, it can be proven that the base particle has a localized structure such that a larger portion of the water-soluble polymer is included near the surface of the base particle than the inner portion thereof, and that a larger portion of the water-insoluble inorganic compound is included in the inner portion of the base particle than near the surface thereof, in the case where a phosphate builder is included near the surface rather than the inner portion thereof, or where a water-insoluble inorganic compound is included in the composition of the base particle.

[0045] With respect to the base particle, ratios of the relative areal intensity based on the characteristic peaks of the phosphate builder such as a tripolyphosphate, when measured in the state in which the localized structure of the components is retained, to the relative areal intensity based on the characteristic peaks of the phosphate builder, when measured in the state in which the base particle is ground to give a uniform state are calculated. As to the water-soluble polymer, the ratio is 1.1 or more, preferably 1.3 or more, more preferably 1.5 or more. When the base particle has these ratios of relative areal intensities, the base particle can be said to have a localized structure.

[0046] Furthermore, as to the water-soluble salt excluding the phosphate builder, such as carbonates, the base particle has a localized structure such that the ratios of relative areal intensity based on the characteristic peaks of the phosphate builder are 1.1 or more, preferably 1.3 or more, as a preferred embodiment of the present invention.

[0047] The base particle retaining the original state or in a uniformly ground state is measured by FT-IR/PAS, and the results standardized with the peak intensity of the sodium tripolyphosphate are illustrated in Figure 1. It is clear from Figure 1 that the relative areal intensity of sodium polyacrylate to the sodium tripolyphosphate, when measured in the state in which the base particle retains the original state, is higher than the relative areal intensity when measured in the state in which the base particle is ground to give a uniform state. In addition, in Figure 1, it is clear that the relative areal intensity of sodium carbonate (characteristic peaks: 1434 cm^{-1}; CO_3^{2-} stretching vibration) to the sodium tripolyphosphate is higher. Incidentally, as the base particle illustrated in Figure 1, Base Particles 1 of the inventive product described in Examples set forth below are used.

[0048] As other examples of the method of structural analysis of the base particle, there can be employed energy dispersion-type X-ray spectroscopy (EDS) and electron probe microanalysis (EPMA). By these analysis methods, two-dimensional distribution of elements can be analyzed by scanning the sample surface with an electron beam. For instance, as the energy dispersion-type X-ray diffractometer, there can be employed "EMAX 3770" manufactured by Horiba, LTD. which is attached to SEM such as a field emission scanning electron microscope "Model S-4000," manufactured by Hitachi, Ltd.

[0049] In the cases where the base particle is embedded in a resin, the distribution state of elements measured with respect to C, Na, P and S of the split cross section of the base particle split with a microtome, further Al, Si and the like where zeolite is used is such that Na, S and C are present in larger amounts in the outer side of the particle cross section, and that P, Al and Si are present in larger amounts in the central portion. Therefore, there can be confirmed the structure of the base particle in which a larger amount of the phosphate builders is included near the surface thereof, and a larger amount of the water-insoluble inorganic compound is included in the central portion.

4. Detergent Particles Comprising Uni-Core Detergent Particle, and Base Particle

[0050] It is preferable that the detergent particles of the present invention comprise a uni-core detergent particle from the viewpoints of the flowability and the fast dissolubility of the detergent particles. "Uni-core detergent particle" refers to a detergent particle comprising a base particle and a surfactant supported thereby, which is a detergent particle comprising a single detergent particle having one base particle as a core.

[0051] As an index for expressing the uni-core property, the degree of particle growth as defined by the following equation:

$$\text{Degree of Particle growth} = \frac{\text{Average Particle Size of Final Detergent Particles}}{\text{Average Particle Size of Base Particles}}$$

can be employed. The degree of particle growth is preferably 1.5 or less, more preferably 1.3 or less, especially preferably 1.2 or less.

[0052] "Final detergent particles" refer to either of the detergent particles obtained after supporting a surfactant to base particles, or the detergent particles in which the resulting particles are subjected to surface modification treatment.

[0053] In the present invention, the surfactant to be supported by the base particle includes one or more kinds of anionic surfactants and nonionic surfactants, and, if necessary, amphoteric surfactants and cationic surfactants.

[0054] The anionic surfactant is preferably salts of esters obtained from an alcohol or an alkoxylated product thereof and sulfuric acid; alkylbenzenesulfonates; paraffinsulfonates; α-olefinsulfonates; salts of α-sulfonated fatty acids or salts of esters thereof; and salts of fatty acids. Especially, the linear alkylbenzenesulfonates of which an alkyl moiety has 10 to 14 carbon atoms, more preferably 12 to 14 carbon atoms, are preferable. As the counter ions, a preference is given to the alkali metals and amines, and especially sodium, potassium, monoethanolamine, and diethanolamine are preferable.

[0055] The nonionic surfactant includes polyoxyalkylene alkyl ethers, alkyl polyglycosides, polyoxyalkylene alkylphenyl ethers, polyoxyalkylene sorbitan fatty acid esters, polyoxyalkylene glycol fatty acid esters, polyoxyethylene polyoxypropylene block polymers, polyoxyalkylene alkylolamides, and the like.

[0056] Especially preferable are the polyoxyalkylene alkyl ether prepared by adding an alkylene oxide such as ethylene oxide or propylene oxide to an alcohol having 10 to 18 carbon atoms in an amount of 4 to 20 moles [HLB value (calculated by Griffin method) being from 10.5 to 15.0, preferably from 11.0 to 14.5]; and the polyoxyalkylene alkylolamide.

[0057] The amount of the surfactant is preferably from 5 to 80 parts by weight, more preferably from 5 to 60 parts by weight, still more preferably from 10 to 60 parts by weight, especially preferably from 20 to 60 parts by weight, based on 100 parts by weight of the base particles, from the viewpoint of the detergency. Here, the supporting amount of the anionic surfactant is preferably from 1 to 60 parts by weight, more preferably from 1 to 50 parts by weight, especially preferably from 3 to 40 parts by weight. The supporting amount of the nonionic surfactant is preferably from 1 to 45 parts by weight, more preferably from 1 to 35 parts by weight, and preferably from 4 to 25 parts by weight. The anionic surfactant and the nonionic surfactant may preferably be used as a mixture from the viewpoints of the foaming property, the detergency, and the properties of a liquid mixture of surfactants to be supported during hand-washing. In this case, the mixing ratio (weight ratio) of the anionic surfactant/the nonionic surfactant is from 4/1 to 1/3, preferably from 3/1 to 1/2, more preferably from 2/1 to 1/1.5. In addition, an amphoteric surfactant or a cationic surfactant may be also used together therewith. The term "supporting amount of the surfactant" referred to herein does not include the amount of the surfactant added when a surfactant is added in the preparation of slurry in the subsequent Step (a) of Section 5.1.

[0058] The favorable properties for the base particles used in the present invention are as follows.

4.1 Properties of Base Particles

4.1.1 Bulk density:

[0059] From 400 to 1000 g/L, preferably from 500 to 800 g/L. The bulk density is measured by a method according to JIS K 3362. In the above range, when the detergent particles having a bulk density of 500 g/L or more, those having an excellent fast dissolubility can be obtained.

4.1.2 Average particle size:

[0060] From 150 to 500 µm, preferably from 180 to 300 µm. The average particle size is measured using standard sieves according to JIS Z 8801. For example, nine-step sieves each having a sieve-opening of 2000 µm, 1400 µm, 1000 µm, 710 µm, 500 µm, 355 µm, 250 µm, 180 µm, or 125 µm, and a receiving tray are used, and the sieves and the receiving tray are attached to a rotating and tapping shaker machine (manufactured by HEIKO SEISAKUSHO, tapping: 156 times/min, rolling: 290 times/min). A 100 g sample is vibrated for 10 minutes to be classified. Thereafter, the mass base frequency is sequentially cumulated for each of sieve-on granules in the order of the receiving tray, and sieves having a sieve-opening of 125 µm, 180 µm, 250 µm, 355 µm, 500 µm, 710 µm, 1000 µm, 1400 µm, and 2000 µm. When a sieve-opening of a first sieve of which cumulative mass base frequency is 50% or more is defined as **a** µm, and a sieve-opening of one sieve-opening larger than **a** µm is defined as **b** µm, in the case where the cumulative mass base frequency from the receiving tray to the **a** µm-sieve is defined as **c**%, and the mass base frequency of granules on the **a** µm-sieve is defined as **d**%, the average particle size can be calculated according to the following equation:

$$(\text{Average particle size}) = 10^{A}:$$

wherein

$$A = \frac{50-(c-\frac{d}{\log b - \log a} \times \log b)}{\frac{d}{\log b - \log a}}$$

[0061] Incidentally, the sieves used are appropriately adjusted so that the particle size distribution of powder to be measured can be accurately estimated.

4.1.3 Particle strength:

[0062] Ranging from 50 to 2000 kg/cm^2. The preferable particle strength in the step of making into the preparation using a liquid mixture of surfactants comprising an anionic surfactant, is from 100 to 1500 kg/cm^2, especially preferably from 150 to 1000 kg/cm^2. In the case where the weight ratio of the anionic surfactant/the nonionic surfactant in the liquid mixture of surfactants is from 4/1 to 1/3, it is preferable that the particle strength is from 150 to 1000 kg/cm^2. In the above range, the base particles show an excellent disintegration property, so that the detergent particles having an excellent fast dissolubility can be obtained. The particle strength is measured by the following method.

[0063] A cylindrical vessel of an inner diameter of 3 cm and a height of 8 cm is charged with 20 g of a sample, and the sample-containing vessel (manufactured by Tsutsui Rikagaku Kikai K.K., "Model TVP1" tapping-type close-packed bulk density measurement device; tapping conditions: period 36 times/minute, free flow from a height of 60 mm) is tapped for 30 times. The sample height (an initial sample height) at that time is measured. Thereafter, an entire upper surface of the sample kept in the vessel is pressed at a rate of 10 mm/min with a pressing machine to take measurements for a load-displacement curve. The slope of the linear portion at a displacement rate of 5% or less is multiplied by an initial sample height, and the resulting product is divided by a pressed area, to give a quotient which is defined as particle strength.

4.1.4 Supporting ability:

[0064] 20 mL/100 g or more, preferably 40 mL/100 g or more. In the above range, the aggregation of the base particles with each other can be suppressed in the step of making into the preparation using a liquid mixture of surfactants comprising an anionic surfactant, so that the uni-core property of the particle in the detergent particles can be favorably maintained. The supporting ability is measured by the following method.

[0065] A cylindrical mixing vessel of an inner diameter of about 5 cm and a height of about 15 cm which is equipped with agitation impellers in the inner portion thereof is charged with 100 g of a sample. With stirring the contents at 350 rpm, linseed oil is supplied at a rate of about 10 mL/min at 25°C. The amount of linseed oil supplied when the agitation torque reaches the highest level is defined as the supporting ability.

4.1.5 Water content:

[0066] The water content is 20% by weight or less, preferably 10% by weight or less, especially preferably 5% by weight or less. In the above range, the base particles having excellent properties can be obtained. The water content is measured by the following method.

[0067] A three-gram sample is placed on a weighing dish, and the sample is dried with an electric dryer at 105°C for 2 hours. The sample after drying is weighed. The water content is calculated from the weights of the sample before and after drying, which the water content is expressed in percentage.

4.2 Properties of Detergent Particles

4.2.1 Uni-Core Property

[0068] The uni-core property of the detergent particle can be confirmed by at least one method of Method (a), Method (b), and Method (c) described below.

Method (a): a method comprising splitting some of the detergent particles arbitrarily sampled from the detergent particles of a size near their average particle size, and confirming the uni-core property by observing presence or absence of the base particle and the number of the base particle in the detergent particle by a scanning electron microscope (SEM).

Method (b): a method comprising extracting an organic solvent-soluble component in the detergent particle with an organic solvent which does not dissolve the water-soluble polymer in the base particle in the detergent particle [for instance, in the case where a polyacrylate is present as a water-soluble polymer, and an anionic surfactant (LAS) or a nonionic surfactant is present as a surfactant in the base particle, ethanol can be favorably used.]; and thereafter observing the organic solvent-insoluble component by SEM observation. In other words, in the case where one base particle is present in the organic solvent-insoluble component obtained by treating a single detergent particle with the above organic solvent, the detergent particle is found to be a uni-core detergent particle.

Method (c): a method of confirming the uni-core property comprising detecting a two-dimensional elemental distribution of the split cross section of the detergent particle embedded in the resin by means of EDS or EPMA.

4.2.2 Fast Dissolubility

4.2.2.1 60-Seconds Dissolution Rate

[0069] The detergent particles comprising the uni-core detergent particle of the present invention have a fast dissolubility. The fast dissolubility of the uni-core detergent particle can be evaluated by 60-seconds dissolution rate. Here, the fast dissolubility for 60-seconds dissolution rate of the detergent particles refers to the fact that the dissolution rate of the detergent particles is 90% or more, preferably 94% or more, more preferably 97% or more, as calculated by the following method as a measurement method which is closely related to the disappearance speed of the detergent particle during hand-washing.

[0070] The test conditions described above are concretely detailed below. A 1-L beaker (a cylindrical form having an inner diameter of 105 mm and a height of 150 mm, for instance, a 1-L glass beaker manufactured by Iwaki Glass Co., Ltd.) is charged with 1 L of hard water cooled to 5°C and having a water hardness corresponding to 71.2 mg $CaCO_3$/L (a molar ratio of Ca/Mg: 7/3). With keeping the water temperature constant at 5°C with a water bath, water is stirred with a stirring bar [length: 35 mm and diameter: 8 mm, for instance, Model "TEFLON SA" (MARUGATA-HOSOGATA), manufactured by ADVANTEC] at a rotational speed (800 rpm), such that a depth of swirling to the water depth is about 1/3. The detergent particles which are accurately sample-reduced and weighed so as to be 1.0000 g ± 0.0010 g are supplied and dispersed in water with stirring, and stirring is continued. After 60 seconds from supplying the particles, a liquid dispersion of the detergent particles in the beaker is filtered with a standard sieve (diameter: 100 mm) having a sieve-opening of 74 µm as defined by JIS Z 8801 of a known weight. Thereafter, water-containing detergent particles remaining on the sieve are collected in an open vessel of a known weight together with the sieve. Incidentally, the operation time from the start of filtration to collection of the sieve is set at 10 sec ± 2 sec. The insoluble remnants of the collected detergent particles are dried for one hour in an electric dryer heated to 105°C. Thereafter, the dried insoluble remnants are cooled by keeping in a desiccator with a silica gel (25°C) for 30 minutes. After cooling the insoluble remnants, a total weight of the dried insoluble remnants of the detergent, the sieve and the collected vessel is measured, and the dissolution rate (%) of the detergent particles is calculated by Equation (1) described above.

[0071] Even in the above evaluation method using low-temperature water, the detergent particles of the present invention have the high dissolution rate. Especially, since the detergent particles and/or the aggregates of the detergent particles are highly rapidly dissolved during hand-washing, there is an advantage that hand-washing can be easily carried out. The excellent dissolubility of the present invention not only has the effect of improving the detergency by eluting the deterging components into a washtub more quickly, but also has a great merit in terms of the quality that the insoluble remnants of the detergent are not present even washing with low mechanical power or for a short time period, such as hand-washing mode, gentle stirring mode, and speed washing mode employed in fully automatic washing machines.

[0072] The favorable properties of the detergent particles which preferably comprise a uni-core detergent particle, obtained in the present invention, are as follows. Incidentally, the bulk-density and the average particle size are measured in the same manner as in the base particle.

4.2.2.2 Hand-Washing Dissolubility of Detergent Composition

[0073] The detergent composition of the present invention also exhibits a remarkably excellent hand-washing dissolubility as compared to that of conventional detergent compositions. The hand-washing dissolubility refers to a measure of the dissolubility when a detergent composition is previously dissolved in a vessel such as a washbowl in advance in the case where stained garments are hand-washed, and expressed as dissolution time period. Hand-washing is customarily widely employed for washing not only as a matter of course for users whose main washing method is hand-washing but also as pre-washing of stained garments for users whose main washing method is machine washing. Therefore, the hand-washing dissolubility is important as a measure for reflecting a more excellent easy-to-use property.

[0074] A concrete method for measurement is as follows. In a washbowl (for example, Model "KW-30" washtub manufactured by YAZAKI, inner volume: 8.2 L) made of polypropylene having a largest opening diameter of 31 cm, a bottom diameter of 24 cm and a height of 13 cm is placed 5.0 L of tap water at 25°C. Next, 15 g of a detergent composition to be tested is dispersed on entire water surface uniformly and quickly (within 3 seconds or so as a standard) so as not to aggregate in one site. From this point of time, a panelist initiates stirring with one hand (the dominant hand), with widely stretched five fingers sensing the detergent granules existing at the bottom of the washbowl with finger tips (inner side of the fingers), in such a manner of gently touching the bottom of washbowl with finger tips. Here, stirring is carried out by repeating each clockwise rotations and counterclockwise rotations alternating with a period of 5 rotations. The stirring is carried out so as not to spill the sample solution from the side wall of the washbowl (the stirring is carried out at about 1.0 second per one rotation, and when reversely rotated, a stand-still is held for about 1.0 second as a standard.). In the manner described above, the stirring is continued until the detergent granules are no longer sensed, and the period of time is measured. A panelist repeats a test for a test sample until the standard deviation of the determined period of time for three runs is within ± 5%, and the average period of time of the three runs is referred to as the period of time for the hand-washing dissolubility of the panelist.

[0075] The evaluation is carried out by panelists of 10 or more, and an average value of the period of time for the hand-washing dissolubility for the middle 60% of the panelists, excluding the top 20% and the bottom 20% of the panelists, is referred to as the period of time of the hand-washing dissolubility of the tested detergent composition.

[0076] The hand-washing dissolubility of the detergent composition of the present invention is preferably 80 seconds or less, more preferably 60 seconds or less, still more preferably 40 seconds or less.

4.2.3 Bulk density:

[0077] 500 g/L or more, preferably from 500 to 1000 g/L, more preferably from 600 to 1000 g/L, especially preferably from 650 to 850 g/L.

4.2.4 Average particle size:

[0078] From 150 to 500 μm, preferably from 180 to 400 μm, more preferably from 200 to 350 μm, especially preferably from 220 to 300 μm.

4.2.5 Flowability:

[0079] In hand-washing, an operation that detergent particles are dispersed on parts of washing items may be carried out. In order to facilitate this operation, it is important that the flowability of the detergent particles is high. The flowability, as evaluated by the flow time, is 10 seconds or shorter, preferably 8 seconds or shorter, more preferably 7 seconds or shorter. The flow time refers to a time period required for cascading 100 mL of powder from a hopper used in a measurement of bulk density as defined in JIS K 3362. In order to increase the flowability, the mass base frequency of the classified particles having a size of less than 125 μm is preferably 0.2 or less, more preferably 0.12 or less, still more preferably 0.07 or less.

4.2.6 Caking property:

[0080] Evaluated as sieve permeability of preferably 90% or more, more preferably 95% or more. The testing method is as follows. An open-top box having dimensions of 10.2 cm in length, 6.2 cm in width, and 4 cm in height is made out of a filter paper (No. 2, manufactured by ADVANTEC) by stapling the filter paper at four corners. A 50 g sample is placed in this box, and an acrylic resin plate and a lead plate (or an iron plate) with a total weight of 15 g + 250 g are placed on the sample. The above box is maintained in a thermostat kept at a temperature of 30°C and at a constant humidity, the caking conditions after 7 days or after one month are evaluated by calculating the permeability as explained below.

<Permeability>

[0081] A sample obtained after the above test is gently placed on a sieve (sieve opening: 4760 μm, as defined by JIS Z 8801), and the weight of the powder passing through the sieve is measured. The permeability (%) based on the whole sample is calculated.

4.2.7 Bleeding-out property:

[0082] A container with dimensions of 10 cm long x 6 cm broad x 4 cm high, with an open top surface, is made using a Model No. 2 filter paper according to JIS P 3801 (for example, manufactured by Toyo Roshi K.K., "Qualitative No. 2 Filter Paper"). A line with a width of 0.5 to 1.0 mm is diagonally drawn on the bottom surface of the container, which is the surface of the packed sample, using a Magic Marker (manufactured by K.K. UCHIDA YOKO, "Magic Ink M700-T1"). A 100 g sample is packed in this container, and an acrylic resin plate and a lead plate (or an iron plate) with a total weight of 15 g + 250 g are placed on the sample. The container is placed in a moisture-proof container, and allowed to stand in a thermostat kept at a temperature of 30°C. After 7 days, the bleeding-out property was evaluated by visually examining the degree of blur of the Magic Marker. The evaluation criteria are as follows.

Rank 5: Blurred width of the Magic Marker being 2 cm or more.
Rank 4: Blurred width of the Magic Marker being 1 cm or more.
Rank 3: Blurred width of the Magic Marker being 0.5 cm or more.
Rank 2: Slight blur of the Magic Marker being found.
Rank 1: No blur of the Magic Marker being found.

5. Process for Preparing Detergent Particles

[0083] The detergent particles of the present invention can be prepared by a process comprising the following Step (a) to Step (c):

Step (a):	preparing a slurry comprising a phosphate builder, a water-soluble polymer, and a water-soluble salt excluding the phosphate builder, wherein 60% by weight or more of water-soluble components comprising the water-soluble polymer and the water-soluble salt are dissolved in the slurry;
Step (b):	spray-drying the slurry obtained in Step (a) to prepare base particles; and
Step (c):	adding a surfactant to the base particles obtained in Step (b) to support the surfactant thereby.

[0084] Moreover, in order to further improve the properties and quality of the resulting detergent particles, it is preferable to further add a surface-modifying step (d) subsequent to Step (c). Preferred embodiments for each of Steps (a) to (c) and a surface-modifying step (d) will be described below.

5.1 Step (a) (Step for Preparation of Slurry)

[0085] The slurry used in the present invention may be a non-harding slurry which can be conveyed with a pump. Also, the addition process of the components and their order can be appropriately varied depending upon the preparation conditions. It is preferable that the amount of the phosphate builder (A) in the slurry is from 3 to 45% by weight, and the amounts of the water-soluble components (B and C), i.e., the water-soluble polymer and the water-soluble salt excluding the phosphate, in the slurry are from 1 to 15% by weight, and from 3 to 40% by weight, respectively.

[0086] Also, it is preferable that the temperature of the slurry is usually from 30° to 80°C. When the temperature of the slurry is in the above range, it is preferable from the aspects of the dissolubility of the water-soluble polymer (B) and the liquid conveyability thereof with a pump.

[0087] A process for forming a slurry includes, for instance, a process comprising adding an entire amount or almost the entire amount of water to a mixing vessel at first, and sequentially or simultaneously adding other components, preferably after a stage where a water temperature almost reaches an operable temperature. The usual order of addition comprises firstly adding liquid components such as a surfactant and a polyacrylate, and subsequently adding a water-soluble, powdery starting material such as soda ash. In addition, small amounts of the auxiliary components such as a fluorescent dye are added. Finally, a phosphate builder such as a tripolyphosphate is added. At this time, for the purpose of improving blending efficiency, the water-insoluble component may be added in two or more separate portions. Also, the powdery starting materials may be previously blended, and the blended powder starting materials may then be added to an aqueous medium. Further, after the addition of the entire components, water may be added to adjust its viscosity or the water content of the slurry. After the addition of the entire components to the slurry, the components are blended for preferably 10 minutes or more, more preferably 30 minutes or more, to prepare a uniform slurry.

5.2 Step (b) (Step for Preparation of Base Particles)

[0088] As the drying process of the slurry, in order to allow the base particle to have desired pores capable of releasing a bubble which is the feature of the present invention, and to also allow the base particle to have the localized structure of the components, it is preferable that the slurry is instantaneously dried, and it especially preferably is spray-dried to have a particle shape which is substantially spherical. A spray-drying tower may be either of a countercurrent tower or a cocurrent tower. The spray-drying tower is more preferably a countercurrent tower, from the viewpoints of the improvement in the particle strength of the base particles, and the like. An atomization device for the slurry may be any of a pressure spray nozzle, a two-fluid-spray nozzle, and a rotary disc form. The atomization device for the slurry is especially preferably a pressure spray nozzle because the base particles have an average particle size of from 150 to 500 µm, preferably from 180 to 300 µm. Usually, the temperature of the high-temperature gas supplied to the drying tower is preferably from 150° to 300°C, more preferably from 170° to 250°C. In addition, usually, the temperature of the gas exhausted from the drying tower is preferably from 70° to 125°C, more preferably from 80° to 115°C.

5.3 Step (c) (Step of Supporting Surfactant)

[0089] The process of supporting a surfactant to base particles can be carried out, for instance, by using a batch type mixer or a continuous mixer. In addition, in the case where the process is carried out in a batch process, the process for supplying the base particles and a surfactant to a mixer, includes various processes, for example, ones described below. Incidentally, Processes (1) to (3) are carried out with operating the mixer.

(1) Base particles are first supplied in the mixer, and a surfactant is then added thereto. (2) Base particles and a surfactant are supplied in a mixer in small amounts. (3) A portion of base particles are supplied in the mixer, and the remaining base particles and a surfactant are then supplied thereto in small amounts.

[0090] Among these processes, item (1) above is especially preferable. In addition, it is preferable that the surfactant is added in a liquid state, and it is more preferable that the surfactant in a liquid state is supplied by spraying.

[0091] Among the surfactants, those which are present in a solid or paste-like form even when heated to a temperature within a practical temperature range can be added to the base particles in the form of a liquid mixture or aqueous solution by previously dispersing or dissolving the solid or paste-like surfactant in a low-viscosity surfactant, for example, a nonionic surfactant, an aqueous solution thereof or water, to prepare a liquid mixture or aqueous solution of surfactants. By this process, the surfactants which are present in the solid or paste-like form can be easily added to the base particles, thereby making it further advantageous in the preparation of the detergent particles comprising a uni-core detergent particle. The mixing ratio of the low-viscosity surfactant or water to the solid or paste-like surfactant is preferably such that the resulting liquid mixture or aqueous solution has a viscosity in a sprayable range. Generally, since an anionic surfactant (excluding an acid precursor) is most likely to be in a solid state or a highly viscous, paste-like state, it is preferable that the anionic surfactant is mixed with a nonionic surfactant in a liquid state to adjust the viscosity such that the surfactants can be supported to the base particles. From this viewpoint, the weight ratio of the anionic surfactant/the nonionic surfactant is preferably 4/1 to 1/3. More preferably, the weight ratio of the anionic surfactant/the nonionic surfactant is from 3/1 to 1/2, still more preferably from 2/1 to 1/1.5. For instance, in the case of mixing a polyoxyethylene dodecyl ether and sodium dodecylbenzenesulfonate, the liquid mixture of surfactants which is easily sprayable can be obtained by adjusting the ratio of the polyoxyethylene dodecyl ether to sodium dodecylbenzenesulfonate to 1:1.4 or less. In addition, in the case where the content of the anionic surfactant is high, it is preferable that a component other than the surfactant is added as a viscosity-reducing agent. The viscosity-reducing agent includes polyhydric alcohols such as polyethylene glycols, polypropylene glycols, co-adducts of polyethylene glycols with polypropylene glycols, ethylene glycol, and glycerol, each having a molecular weight of from 300 to 100000.

[0092] The process for preparing the above liquid mixture includes, for example, a process of supplying a solid or paste-like surfactant to a low-viscosity surfactant or water, and mixing the surfactants; and a process of neutralizing an acid precursor of a surfactant in a low-viscosity surfactant or water with an alkalizing agent (for instance, an aqueous sodium hydroxide or an aqueous potassium hydroxide), to prepare a liquid mixture of surfactants.

[0093] In addition, in this step, an acid precursor of an anionic surfactant can be added before adding a surfactant, simultaneously with adding a surfactant, in the course of adding a surfactant, or after adding a surfactant. By adding the acid precursor of an anionic surfactant, there can be achieved high concentration of the surfactants, control for an oil-absorbing ability of the base particles, and improvements in properties and quality, such as suppression of bleeding-out of the nonionic surfactant and the flowability, of the resulting detergent particles.

[0094] The acid precursor of an anionic surfactant which can be used in the present invention includes, for example, alkylbenzenesulfonic acids, alkylether or alkenylether sulfuric acids, alkylsulfuric or alkyenylsulfuric acids, α-olefinsulfonic acids, α-sulfonated fatty acids, alkylether or alkenylether carboxylic acids, fatty acids, and the like. Especially, it is preferable that the fatty acid is added after adding the surfactant, from the viewpoint of improvement in the flowability of the detergent particles.

[0095] The amount of the acid precursor used is preferably from 0.5 to 30 parts by weight, more preferably from 1 to 20 parts by weight, based on 100 parts by weight of the base particles. In the above range, the uni-core property of the particle in the detergent particles tends to be maintained; therefore, the detergent particles show good fast dissolubility. In addition, as the process for adding the acid precursor of an anionic surfactant, it is preferable that those in a liquid state at an ordinary temperature are supplied by spraying. Those in a solid state at an ordinary temperature may be added as a powder, or they may be supplied by spraying after melting the solid. Here, in a case of adding the acid precursor as a powder, it is preferable that the temperature of the detergent particles in the mixer is raised to a temperature at which the powder melts.

[0096] Mixers preferably usable for Step (c) are, for instance, Henschel Mixer (manufactured by Mitsui Miike Machinery Co., Ltd.); High-Speed Mixer (Fukae Powtec Corp.); Vertical Granulator (manufactured by Powrex Corp.); Lödige Mixer (manufactured by Matsuzaka Giken Co., Ltd.); PLOUGH SHARE Mixer (manufactured by PACIFIC MACHINERY & ENGINEERING Co., LTD.); Nauta Mixer (manufactured by Hosokawa Micron Corp.); and the like. From the viewpoint of preparing detergent particles comprising a uni-core detergent particle in a large amount, preferable mixers are those devices less likely to apply strong shearing force to the base particle (i.e. those mixers less likely to cause disintegration of the base particle), and from the viewpoint of the dispersion efficiency of the surfactants, those devices with good mixing efficiency are preferable. Among them, a particular preference is given to a mixer comprising an agitating shaft arranged along the center line of a horizontal, cylindrical blending vessel and agitating impellers arranged on the agitating shaft, to carry out blending of the powders (horizontal mixers), including Lödige Mixer, PLOUGH SHARE Mixer, and the like. In addition, those mixers listed above in a continuous process can be also used to support the surfactant by the base particles. Also, as the mixers for a continuous process other than those listed above, there can be used, for instance, Flexo Mix (manufactured by Powrex Corp.); TURBULIZER (manufactured by Hosokawa Micron Corp.), and the like.

[0097] As preferable mixing conditions, from the viewpoints of the suppression of the disintegration of the base particle and the mixing efficiency, the Froude number of a main shaft is preferably from 0.5 to 8, more preferably from 0.5 to 4. Further, in the case where the mixer is equipped with disintegration impellers, the Froude number of the disintegration impellers is preferably 200 or less, and it is more preferable that disintegration impellers substantially are not rotated.

[0098] In addition, in this Step, when a nonionic surfactant is used, a melting point-elevating agent of the nonionic surfactant, which is a water-soluble, nonionic organic compound (hereinafter referred to as "melting point-elevating agent") having a melting point of from 45° to 100°C and a molecular weight of from 1000 to 30000, or an aqueous solution thereof can be added before adding a surfactant, simultaneously with adding a surfactant, in the course of adding a surfactant, or after adding a surfactant, or previously mixed with a surfactant and the mixture can be added. By adding the melting point-elevating agent, the caking property and the bleeding-out property of the surfactants in the detergent particles can be suppressed. The melting point-elevating agent includes polyethylene glycols, polypropylene glycols, polyoxyethylene alkyl ethers, pluronic type nonionic surfactants, and the like.

[0099] The amount of the melting point-elevating agent used is preferably from 0.5 to 5 parts by weight, preferably from 0.5 to 3 parts by weight, based on 100 parts by weight of the base particles. The above range is preferable from the viewpoints of the maintenance of the uni-core property, the fast dissolubility, and the suppression of the bleeding-out property and the caking property, each property of which is owned by the detergent particle contained in the detergent particles. A process for adding the melting point-elevating agent, comprising adding by previously mixing the melting point-elevating agent with a surfactant by an arbitrary process, or comprising adding a surfactant, and thereafter adding the melting point-elevating agent, is advantageous for the suppression of the bleeding-out property and the caking property of the detergent particles.

[0100] As to the temperature within the mixer, it is more preferable that mixing is carried out by heating to a temperature equal to or higher than the melting point of the surfactant. Here, the temperature to be heated is preferably a temperature higher than the pour point of the surfactant added in order to promote the support of the surfactant, and the practical temperature range is preferably from a temperature exceeding a pour point to a temperature higher than the pour point by 50°C, more preferably a temperature higher than the pour point by 10° to 30°C. Incidentally, the melting point of the surfactant is measured according to the method of JIS K 2269. In addition, in the case where an acid precursor of an anionic surfactant is added in this Step, it is more preferable to mix the components after heating to a temperature at which the acid precursor of an anionic surfactant can react.

[0101] The mixing time in a batch process and the average residence time in the mixing in a continuous process for obtaining the suitable detergent particles are preferably from 1 to 20 minutes, more preferably from 2 to 10 minutes.

[0102] In addition, in the case where an aqueous solution of a surfactant or an aqueous solution of a water-soluble, nonionic organic compound is added, a step of drying excess water contents during mixing and/or after mixing may be included.

[0103] A powdery surfactant and/or a powdery builder can be added before adding a surfactant, simultaneously with adding a surfactant, in the course of adding a surfactant, or after adding a surfactant. By adding the powdery builder, the particle size of the detergent particles can be controlled, and an improvement in detergency can be achieved. Especially in the case where the acid precursor of an anionic surfactant is added, it is effective to add a powdery builder showing alkaline property prior to adding the acid precursor from the viewpoint of accelerating the neutralization reaction. Incidentally, the term "powdery builder" mentioned herein refers to an agent for enhancing detergency other than surfactants which is in a powdery form, concretely, including base materials showing metal ion capturing ability, such as zeolite, citrates and tripolyphosphates; base materials showing alkalizing ability, such as sodium carbonate and potassium carbonate; base materials having both metal ion capturing ability and alkalizing ability, such as crystalline silicates; other base materials enhancing ionic strength, such as sodium sulfate; and the like. A fine powder employed in this step is used, if desired, after the particle size is adjusted by pulverization.

[0104] In addition, crystalline silicates described in Japanese Patent Laid-Open No. Hei 5-279013, column 3, line 17 to column 6, line 24 (especially, those prepared by a process comprising calcinating and crystallizing at a temperature of from 500° to 1000°C being preferable); Japanese Patent Laid-Open No. Hei 7-89712, column 2, line 45 to column 9, line 34; and Japanese Patent Laid-Open No. Sho 60-227895, page 2, lower right column, line 18 to page 4, upper right column, line 3 (especially the silicates in Table 2 being preferable) can be used as powdery builders. Here, the alkali metal silicates having an SiO_2/M_2O ratio, wherein M is an alkali metal, of from 0.5 to 3.2, preferably from 1.5 to 2.6, are favorably used.

[0105] The amount of the powdery builder used is preferably from 0.5 to 12 parts by weight, more preferably from 1 to 6 parts by weight, based on 100 parts by weight of the base particles. In the above range, the uni-core property of the detergent particle contained in the detergent particles is maintained, an excellent fast dissolubility is obtained, and the control for the particle size is favorable.

5.4 Step (d) (Surface-Modifying Step)

[0106] In the present invention, there may be carried out a surface-modifying step comprising adding a surface coating agent such as (1) a fine powder, or (2) liquid materials in one step, or repeated in two steps.

[0107] From the viewpoints of improvements in the flowability and the non-caking properties of the detergent particles, it is preferable to include the surface-modifying step. The devices used in the surface-modifying step are not limited to specified ones, and preferably are the mixers exemplified in Step (c) above. Each of the surface coating agents will be explained below.

(1) Fine Powder

[0108] It is preferable that the average particle size of the primary particle is 10 μm or less, more preferably from 0.1 to 10 μm. The above range is favorable from the viewpoints of the improvements in the coating ratio of the particle surface of the detergent particles, the flowability and the anti-caking property of the detergent particles. The average particle size can be measured by a method utilizing light scattering by, for instance, a particle analyzer (manufactured by Horiba, LTD.), or it may be measured by a microscopic observation or the like. In addition, it is preferable that the fine powder has a high ion exchange capacity or a high alkalizing ability from the aspect of detergency.

[0109] The fine powder is desirably crystalline or amorphous aluminosilicates. Besides them, a fine powder such as sodium tripolyphosphate, sodium sulfate, calcium silicate, silicon dioxide, bentonite, talc, clay, amorphous silica derivatives, silicate compounds such as crystalline silicate compounds, is preferable. The fine powder employed in the surface-modifying step is used, if desired, after the particle size is adjusted by pulverization or the like. In the case where a tripolyphosphate and sodium sulfate are used as a fine powder in the surface-modifying step, and where a water-insoluble builder is not used in the base particle, the detergent particles are dissolved in a state of transparent to semitransparent during washing. Such a state is favorable in a hand-washing because the degree of stain removal is easily recognized. In the detergent particles, there can be also similarly used a metal soap of which primary particles have a size of 0.1 to 10 μm, a powdery surfactant (for instance, alkylsulfates, and the like), or a water-soluble organic salt. In addition, when the crystalline silicate compound is used, it is preferably used in admixture with fine powder other than the crystalline silicate compound for the purpose of preventing deterioration owing to aggregation of the crystalline silicates by moisture absorption and carbon dioxide absorption, and the like.

[0110] The amount of the fine powder used is preferably from 0.5 to 40 parts by weight, more preferably from 1 to 30 parts by weight, especially preferably from 2 to 20 parts by weight, based on 100 parts by weight of the detergent particles. In the above range, the flowability is improved, thereby giving a good texture to consumers.

(2) Liquid Materials

[0111] The liquid materials include aqueous solutions or molten products of water-soluble polymers, fatty acids, and the like.

(2-1) Water-Soluble Polymer

[0112] The water-soluble polymer includes carboxymethyl cellulose, polyethylene glycols, polycarboxylates such as sodium polyacrylates and copolymers of acryl acid and maleic acid and salts thereof, and the like. The amount of the water-soluble polymer used is preferably from 0.5 to 10 parts by weight, more preferably from 1 to 8 parts by weight, especially preferably from 2 to 6 parts by weight, based on 100 parts by weight of the detergent particles. In the above range, a powder exhibiting excellent flowability and anti-caking properties can be obtained, while the uni-core property of the detergent particle contained in the detergent particles is maintained and an excellent fast dissolubility is obtained.

(2-2) Fatty Acid

[0113] The fatty acid includes, for example, fatty acids having 10 to 22 carbon atoms, and the like. The amount of the fatty acid used is preferably from 0.5 to 5 parts by weight, especially preferably from 0.5 to 3 parts by weight, based on 100 parts by weight of the detergent particles. In a case of a fatty acid in a solid state at ordinary temperature, it is preferable that the fatty acid is heated to a temperature showing flowability, and then supplied to the detergent particles by spraying.

[0114] Incidentally, each content of the phosphate builder, the anionic surfactant, and the nonionic surfactant in the detergent particles is as follows.

[0115] The phosphate builder has a content of preferably from 5 to 50% by weight, more preferably from 7 to 40% by weight, still more preferably from 9 to 35% by weight. Also, the anionic surfactant has a content of preferably from 5 to 40% by weight, more preferably from 6 to 35% by weight, still more preferably from 7 to 35% by weight. The nonionic surfactant has a content of preferably from 1 to 30% by weight, more preferably from 1 to 25% by weight, still more preferably from 1 to 20% by weight.

[0116] Here, the above content of each of the components is the total amount used in one or more steps of Step (a) to Step (d).

6. Detergent Particles Comprising Multi-Core Detergent Particle

[0117] The detergent particles of the present invention can be constituted by a multi-core detergent particle. The multi-core detergent particle may be those in which the base particles constituting the uni-core detergent particle described above are aggregated, or those in which a water-soluble salt, for example, sodium carbonate, and the like used as a core are aggregated, and it is preferable that the detergent particle is capable of releasing a bubble having a given size. Especially, the use of the above base particle contributes to the localized structure of the base particle, so that the fast dissolubility can be further improved. Therefore, as the base particle, the base particle described in the uni-core detergent particle above can be used, and as the surfactant which can be supported by the base particle, the surfactant described in the uni-core detergent particle above can be used. In addition, the multi-core detergent particle can be easily formed by increasing the amount of the surfactant. Incidentally, the dissolution acceleration between the base particles can be enhanced by using a foaming agent such as sodium bicarbonate or a percarbonate.

7. Properties of the Detergent Particles Comprising Multi-Core Detergent Particle

[0118] The multi-core detergent particles of the present invention show similarly high dissolution rate as the detergent particles comprising the uni-core detergent particle, and have a higher fast dissolubility than the dissolubility of conventional detergents. The fast dissolubility of the detergent particles can be confirmed by the method of Section 4.2.2 described above.

[0119] In addition, as to the bulk density, the average particle size, the flowability, the caking property, and the bleeding-out property, it is preferable that the multi-core detergent particles have similar properties to those of the detergent particles comprising the uni-core detergent particle described in Sections 4.2.3 through 4.2.7 above.

8. Detergent Composition

[0120] The detergent composition of the present invention comprises (a) detergent particles comprising a uni-core detergent particle and/or a multi-core detergent particle; and (b) detergent components separately added, other than Component (a).

[0121] In this case, the detergent composition comprises 50% by weight or more, preferably 60% by weight or more, more preferably 80% by weight or more of the above detergent particles in the detergent composition.

[0122] In the above detergent composition, in the process of dissolving the detergent composition in water, the particle constituting the detergent composition which is allowed to dissolve by releasing from the inner portion of the particle a bubble of the size of preferably 1/10 or more of the particle size of the particle constituting the detergent composition, and the particle constituting the detergent composition occupies preferably 40% by weight or more, more preferably 60% by weight or more, still more preferably 80% by weight or more, of the entire particle constituting the detergent composition.

[0123] The detergent composition of the present invention has a fast dissolubility, and its fast dissolubility can be confirmed by the method as described in Section 4.2.2 (in this case, the "detergent particles" should read 'detergent composition').

EXAMPLES

Preparation of Base Particle

[0124] Base Particles 1 were prepared by the following procedures.

[0125] Six-hundred and sixty four kilograms of water was added to a 1 m^3-mixing vessel having agitation impellers. After the water temperature reached 55°C, 57 kg of sodium carbonate, 28 kg of sodium sulfate, 6.2 kg of sodium sulfite, 2.1 kg of a dye, and the like were added thereto. After stirring the mixture for 15 minutes, 70 kg of a 40% by weight-aqueous sodium polyacrylate solution was added thereto. After stirring the resulting mixture for 15 minutes, the mixture was stirred for additional 15 minutes. Thereafter, 277 kg of sodium tripolyphosphate was added thereto, and the obtained mixture was stirred for 30 minutes to give a uniform slurry. The final temperature of this slurry was 58°C. In addition, the water content in this slurry was 64% by weight.

[0126] This slurry was sprayed with a pressure spray nozzle arranged near the top of a spray-drying tower at a spraying pressure of 25 kg/cm^2, to give Base Particles 1. A high-temperature gas fed to the spray-drying tower was supplied from the lower portion of the tower at a temperature of 225°C and exhausted from the top of the tower at 105°C. Base Particles 2 to 4 were prepared in the same manner. The composition and the properties of each group of Base Particles are shown in Table 1. With regard to Base Particles 4, as a result of SEM observation, it was observed that pores having a pore size of from 1/10 to 4/5 or more of the particle size were found in 80% or more of the particles. Further, as a result of analyses by FT-IR/PAS, SEM observation and EDS, it was confirmed that higher proportions of the tripolyphosphate were found in the inner portion of the particle, and that the water-soluble polymer and the water-soluble salt had a coating-type particle structure in which larger amounts of them were present near the particle surface.

Table 1

Base Particles	1	2	3	4
Composition of Base Particle (% by weight)				
Component A				
Sodium Tripolyphosphate ∗1	67.4	43.5	34	18
Component B				
Sodium Polyacrylate ∗2	6.9	7	6.7	8
Acrylic Acid/Maleic Acid Copolymer ∗3		2	2	
Component C				
Sodium Carbonate ∗4	13.9	15	14	17
Sodium Sulfate	6.9	7	6.7	5
Sodium Sulfite	1.5	1.5	1.5	1.5
Others				
Sodium Dodecylbenzenesulfonate ∗5		4		2
Auxiliary Components (Dye, etc.) ∗6	0.5	0.5	0.5	0.5
Zeolite*7		15	31	44
Water	2.9	4.5	3.6	4
	100	100	100	100
Slurry Formation				
Water Content of Aqueous Slurry (% by weight)	64	57	42	38
Spray Drying				
Supplied Gas Temperature (°C)	225	226	232	230
Exhausted Gas Temperature (°C)	105	104	110	107
Spraying Pressure (kg/cm^2)	25	25	25	25
Properties of Base Particles				
Bulk Density (g/L)	630	615	650	670
Average Particle Size (μm)	250	270	235	220
Particle Strength (kg/cm^2)	280	260	240	290
Supporting Ability (mL/100g)	48	43	54	65
Water Content (% by weight)	5	3.1	6	3.3

∗1): Manufactured by Central Glass Co., Ltd.
∗2): Average molecular weight: 10000
∗3): Manufactured by BASF, Sokalan CP5
∗4): DENSE ASH (manufactured by Central Glass Co., Ltd.)
∗5): NEOPELEX F65 (manufactured by Kao Corporation)
∗6): Fluorescent dye "Tinopal CBS-X", manufactured by Ciba Specialty Chemicals K.K.
∗7): Zeolite 4A-type, average particle size: 3.5 μm (manufactured by Tosoh Corporation)

Example 1

[0127] The detergent particles of the present invention were obtained by adding a surfactant to Base Particles 1 in a ratio shown in Table 2 to support it on them.

[0128] Twelve parts by weight of the anionic surfactant, 10 parts by weight of the nonionic surfactant, 1 part by weight of the polyethylene glycol and 0.5 parts by weight of palmitic acid, as listed in Table 2, were heated to 80°C. Next, 100 parts by weight of the above Base Particles were supplied into Lödige Mixer (manufactured by Matsuzaka Giken Co., Ltd.; capacity: 20 L; equipped with a jacket), and the stirring was started under the conditions of a main shaft: 60 rpm and a chopper: stop. Incidentally, hot water at 80°C was allowed to flow into the jacket at 10 L/minute. The above nonionic surfactant was supplied into the above mixer over a period of 2 minutes, and thereafter the components were stirred for 4 minutes and discharged. The properties of the obtained detergent particles are shown in Table 2.

Table 2

	Examples					
	1	2	3	4	5	6
<u>Composition (Parts by Weight)</u>						
Base Particles No. (Used Amount: 100 Parts by Weight *8)	1	2	3	3	4	3
Nonionic Surfactant						
Polyoxyethylene Alkyl Ether *1	10	22	10	20	10	16
Anionic Surfactant						
LAS-Na *2	12		12		12	21.5
Acid Precursor of Anionic Surfactant						
LAS-Acid Type *3				10		
Palmitic Acid *4	0.5	0.5	0.5	0.5	0.5	1.3
Melting Point -Elevating Agent for Nonionic Surfactant						
Polyethylene Glycol *5	1	2	1	1	1	1.6
Surface Coating Agent (Fine Powder)						
Crystalline Aluminosilicate *6	10	12		3	4	
Amorphous Aluminosilicate *7				8		
Sodium Tripolyphosphate *9			16		13	25.6
Crystalline Layered Silicate *10		6				
<u>Properties</u>						
Average Particle Size [μm]	255	265	270	245	260	283
Degree of Particle Growth	1.02	1.06	1.08	1.61	1.04	1.08
Bulk Density [g/L]	680	690	660	610	690	685
Flowability [s]	6.9	7.2	7.8	6.5	6.8	7.7
60-Seconds Dissolution Rate [%]	98.4	99.1	98.1	97.8	99.1	98.4
Split Cross Section by SEM Observation		Uni-Core		Multi-Core	Uni-Core	Uni-Core
Hand-Washing Dissolubility [s]	47	37	48	51	41	44

*1: EMULGEN 108KM, average moles of ethylene oxides: 8.5 (manufactured by Kao Corporation)

*2: NEOPELEX F65 (sodium linear alkyl(10-13 carbon atoms)benzenesulfonate) (manufactured by Kao Corporation)

*3: NEOPELEX FS (linear alkyl(10-13 carbon atoms)benzenesulfonic acid) (manufactured by Kao Corporation)

*4: LUNAC P-95 (manufactured by Kao Corporation)

*5: K-PEG6000, average molecular weight: 8500 (manufactured by Kao Corporation)

*6: Zeolite 4A-type, average particle size: 3.5 μm (manufactured by Tosoh Corporation)

*7: Product described in Preparation Example 2 of Japanese Patent Laid-Open No. Hei 9-132794, average particle size: 8 μm

*8: Particles classified on sieves with sizes between 125 μm and 180 μm

*9: Product prepared by pulverizing the sodium tripolyphosphate shown in Table 1 to an average particle size of 6 μm

*10: Product prepared by pulverizing SKS-6 manufactured by Clariant Tokuyama K.K. to an average particle size of 12 μm

[0129] Further, the surface of the detergent particles was surface-coated with 10 parts by weight of a crystalline aluminosilicate under the conditions of a main shaft: 150 rpm and a chopper: 5000 rpm. As to the properties of the obtained detergent particles, the dissolubility was retained, and the flowability was improved.

Example 2

[0130] The detergent particles of the present invention were obtained by adding a surfactant solution previously mixed with the polyethylene glycol shown in Table 2 to Base Particles 2.

[0131] Twenty two parts by weight of the nonionic surfactant and 2 parts by weight of the polyethylene glycol, as listed in Table 2, were mixed with heating to 70°C, to prepare a liquid mixture. Next, 100 parts by weight of the above Base Particles were supplied into the same mixer as in Example 1, and the stirring was started under the conditions of a main shaft: 60 rpm and a chopper: stop. Incidentally, hot water at 75°C was allowed to flow into the jacket at 10 L/minute. The above liquid mixture was supplied into the above mixer over a period of 2 minutes, and thereafter the components were stirred for 4 minutes. Further, the stirring conditions were changed to a main shaft: 150 rpm and a chopper: 5000 rpm, and the particle surface of the detergent particles was surface-coated with 12 parts by weight of a crystalline aluminosilicate and 6 parts by weight of a crystalline silicate. The properties of the obtained detergent particles are shown in Table 2.

[0132] By formulating the polyethylene glycol, the anti-caking property of the detergent particles was further improved, and bleeding out of the nonionic surfactant was further suppressed.

Example 3

[0133] The detergent particles of the present invention were obtained in the same manner as in Example 1 by adding a surfactant and the like to Base Particles 3 in a ratio shown in Table 2. In Example 3, the particle surface of the detergent particles was surface-coated with 16% by weight of pulverized sodium tripolyphosphate. The properties of the obtained detergent particles are shown in Table 2.

[0134] The hollowness of the detergent particles was measured. As a result, it was found that there were pores having a pore size of from 1/10 to 4/5 the particle size in 65% of the particles.

[0135] Further, the dissolution behavior of the detergent particles was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 63% of the particles (Incidentally, an average value of size of released bubbles/particle size in 63% of the particles was 1.7/5.).

Example 4

[0136] Base Particles 3 were classified, and the base particles classified on sieves with sizes between 125 μm and 180 μm were used as base particles. Further, as a method for adding an anionic surfactant, an acid precursor of an anionic surfactant was used, and a nonionic surfactant was supplied into a mixer without mixing with the acid precursor. Thereafter, the acid precursor of the anionic surfactant (dodecylbenzenesulfonic acid) was supplied into the mixer, to give the detergent particles of the present invention.

[0137] Next, 100 parts by weight of the above Base Particles were supplied into the same mixer as in Example 1, and the stirring was started under the conditions of a main shaft: 150 rpm and a chopper: 4000 rpm. Incidentally, hot water at 60°C was allowed to flow into the jacket at 10 L/minute. The above liquid mixture was supplied into the above mixer over a period of 2 minutes, and thereafter the components were stirred for 3 minutes. Next, 10.5 parts by weight of an acid precursor of an anionic surfactant heated to 45°C was supplied into the above mixer over a period of 2 minutes, and thereafter the components were stirred for 4 minutes. Further, the particle surface of the detergent particles was surface-coated with 8 parts by weight of an amorphous aluminosilicate and 3 parts of a crystalline sodium aluminosilicate. The properties of the obtained detergent particles are shown in Table 2.

Example 5

[0138] The detergent particles of the present invention were obtained by adding a surfactant and the like to Base Particles 4 in a ratio shown in Table 2. The detergent particles were obtained in the same manner as in Example 1 except that 13 parts of pulverized sodium tripolyphosphate, and a crystalline sodium aluminosilicate were used for the surface of the detergent particles.

[0139] The hollowness of the detergent particles was measured. As a result, it was found that there were pores having a pore size of from 1/10 to 4/5 the particle size in 85% of the particles.

[0140] Further, the dissolution behavior of the detergent particles was observed. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 83% of the particles (Incidentally, an average value of size of released bubbles/particle size in 83% of the particles was 2.8/5.).

Example 6

[0141] The detergent particles of the present invention were obtained in the same manner as in Example 1 by adding a surfactant and the like to Base Particles 3 in a ratio shown in Table 2. In Example 6, the particle surface of the detergent particles was surface-coated with 25.6 parts by weight of pulverized sodium tripolyphosphate. The properties of the obtained detergent particles are shown in Table 2.

[0142] In addition, the hollowness of the detergent particles was measured. As a result, it was found that there were pores having a pore size of from 1/10 to 4/5 the particle size in 60% of the particles.

[0143] Further, the dissolution behavior of the detergent particles was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 61% of the particles (Incidentally, an average value of size of released bubbles/particle size in 61% of the particles was 1.7/5.).

Examples 7 and 8

[0144] The detergent compositions of the present invention were obtained by adding the enzyme granule to detergent particles of Example 4 in a ratio shown in Table 3. The properties of the obtained detergent compositions are shown in Table 3. Incidentally, the enzyme of the enzyme granule shown in Table 3 was "Savinase 18T Type W," manufactured by NOVO Nordisk.

Table 3

	Example 7	Example 8
Composition		
Detergent Particles	100 Parts (Example 4)	100 Parts (Example 5)
Enzyme Granule	2 Parts	4 Parts
Properties		
Average Particle Size [µm]	250	265
Bulk Density [g/L]	620	700
60-Seconds Dissolution Rate [%]	97	98
30-Seconds Dissolution Rate [%]	86	92

[0145] It is clear from the results shown in Table 3 that the detergent compositions obtained in Examples 7 and 8 are both excellent in the dissolubility.

Test Example 1

[0146] The results of the dissolubility of the particles and the hand-washing dissolubility for 8 kinds of representative detergent compositions which have been sold or were sold in the past in Asia, Europe and the U.S.A. are shown in Table 4. It is clear from the results shown in Table 4 that these marketed detergents are low in the level of the dissolubility of the particles, and also poor in the hand-washing dissolubility. In addition, among Marketed Detergents A to H, Detergent A which was the most excellent in the dissolubility of the particles and the hand-washing dissolubility, was notably poor in the flowability.

Table 4

		60-Seconds Dissolution Rate [%]	Time Period of Hand-Washing Dissolubility [s]
Asia	Marketed Detergent A 1)	84.1	111
	Marketed Detergent B	77.6	135
	Marketed Detergent C	67.2	152
	Marketed Detergent D	70.9	130
Europe	Marketed Detergent E	72.1	121
	Marketed Detergent F	74.4	141
U.S.A.	Marketed Detergent G	57.6	164
	Marketed Detergent H	58.0	156

1) Bulk density: 560 g/L

[0147] In the determination of the flowability, the flowability was so low that 100 mL of the powder was hardly cascaded from the hopper used in the measurement of bulk density.

INDUSTRIAL APPLICABILITY

[0148] The detergent composition of the present invention is excellent in the detergency even when the amount of work of the washing machine is low, and excellent in the flowability, the dissolubility of the particles and the dispersibility so as to facilitate hand-washing.

EQUIVALENT

[0149] The present invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

Claims

1. Detergent particles comprising a phosphate builder, the detergent particles having an average particle size of from 150 to 500 µm, a bulk density of 500 g/L or more, and a flow time of 10 seconds or less, wherein the detergent particles comprise a detergent particle being capable of releasing a bubble from an inner portion thereof in a process of dissolving the detergent particle in water, the bubble having a size of one-tenth or more of a particle size of the detergent particle, and wherein the detergent particles have a dissolution rate of 90% or more, under conditions where the detergent particles are supplied in water at 5°C; stirred for 60 seconds under the stirring conditions that 1 g of the detergent particles are supplied to a 1-L beaker (inner diameter: 105 mm) which is charged with 1-L of hard water (71.2 mg $CaC0_3$/L, a molar ratio of Ca/Mg: 7/3), and stirred with a stirring bar (length: 35 mm, and diameter: 8 mm) at a rotational speed of 800 rpm; and filtered with a standard sieve having a sieve-opening of 74 µm as defined by JIS Z 8801, wherein the dissolution rate of the detergent particles is calculated by Equation (1):

$$\text{Dissolution Rate (\%)} = [1 - (T/S)] \times 100 \qquad (1)$$

wherein S is a weight (g) of the detergent particles supplied; and
T is a dry weight of insoluble remnants of the detergent particles remaining on the sieve when an aqueous solution prepared under the above stirring conditions is filtered with the sieve.

2. The detergent particles according to claim 1, wherein the detergent particles each comprises a base particle comprising a phosphate builder, a water-soluble polymer and a water-soluble salt excluding the phosphate builder, and a surfactant supported by the base particle, wherein the base particle has a localized structure in which a larger portion of the water-soluble polymer is present near the surface of the base particle rather than in the inner portion thereof.

3. Detergent particles comprising a phosphate builder, the detergent particles having an average particle size of from 150 to 500 µm, a bulk density of 500 g/L or more, and a flow time of 10 seconds or less, wherein the detergent particles each comprises a base particle comprising a phosphate builder, a water-soluble polymer and a water-soluble salt excluding the phosphate builder, and a surfactant supported by the base particle, wherein the base particle has a localized structure in which a larger portion of the water-soluble polymer is present near the surface of the base particle rather than in the inner portion thereof, and wherein the detergent particles have a dissolution rate of 90% or more, under conditions where the detergent particles are supplied in water at 5°C; stirred for 60 seconds under the stirring conditions that 1 g of the detergent particles are supplied to a 1-L beaker (inner diameter: 105 mm) which is charged with 1-L of hard water (71.2 mg $CaC0_3$/L, a molar ratio of Ca/Mg: 7/3), and stirred with a stirring bar (length: 35 mm, and diameter: 8 mm) at a rotational speed of 800 rpm; and filtered with a standard sieve having a sieve-opening of 74 µm as defined by JIS Z 8801, wherein the dissolution rate of the detergent particles is calculated by Equation (1):

$$\text{Dissolution Rate (\%)} = [1 - (T/S)] \times 100 \qquad (1)$$

wherein S is a weight (g) of the detergent particles supplied; and
T is a dry weight of insoluble remnants of the detergent particles remaining on the sieve when an aqueous solution prepared under the above stirring conditions is filtered with the sieve.

4. The detergent particles according to claim 2 or 3, wherein a supported amount of an anionic surfactant is from 1 to 60 parts by weight, and a supported amount of a nonionic surfactant is from 1 to 45 parts by weight, based on 100 parts by weight of the base particle comprising from 5 to 90% by weight of the phosphate builder.

5. The detergent particles according to any one of claims 2 to 4, wherein in the base particle, the amount of the water-soluble polymer formulated is 2% by weight or more, and the amount of the amorphous silicate formulated is less than 3% by weight.

6. The detergent particles according to any one of claims 1 to 5, wherein a weight ratio of an anionic surfactant to a nonionic surfactant is from 4/1 to 1/3.

7. The detergent particles according to any one of claims 1 to 6, which comprise detergent particles each having a pore in the inner portion thereof having a size of 1/10 to 4/5 of the particle size.

8. The detergent particles according to any one of claims 1 to 7, wherein the detergent particles comprise a uni-core detergent particle.

9. A process for preparing the detergent particles as defined in any one of claims 1 to 8, comprising the steps of:

Step (a): preparing a slurry containing a phosphate builder, a water-soluble polymer, and a water-soluble salt excluding the phosphate builder, wherein 60% by weight or more of water-soluble components including the water-soluble polymer and the water-soluble salt are dissolved in the slurry;
Step (b): spray-drying the slurry obtained in Step (a) to prepare base particles; and
Step (c): adding a surfactant to the base particles obtained in Step (b) to support the surfactant thereby.

10. A detergent composition comprising the detergent particles as defined in any one of claims 1 to 8 in an amount of 50% by weight or more.

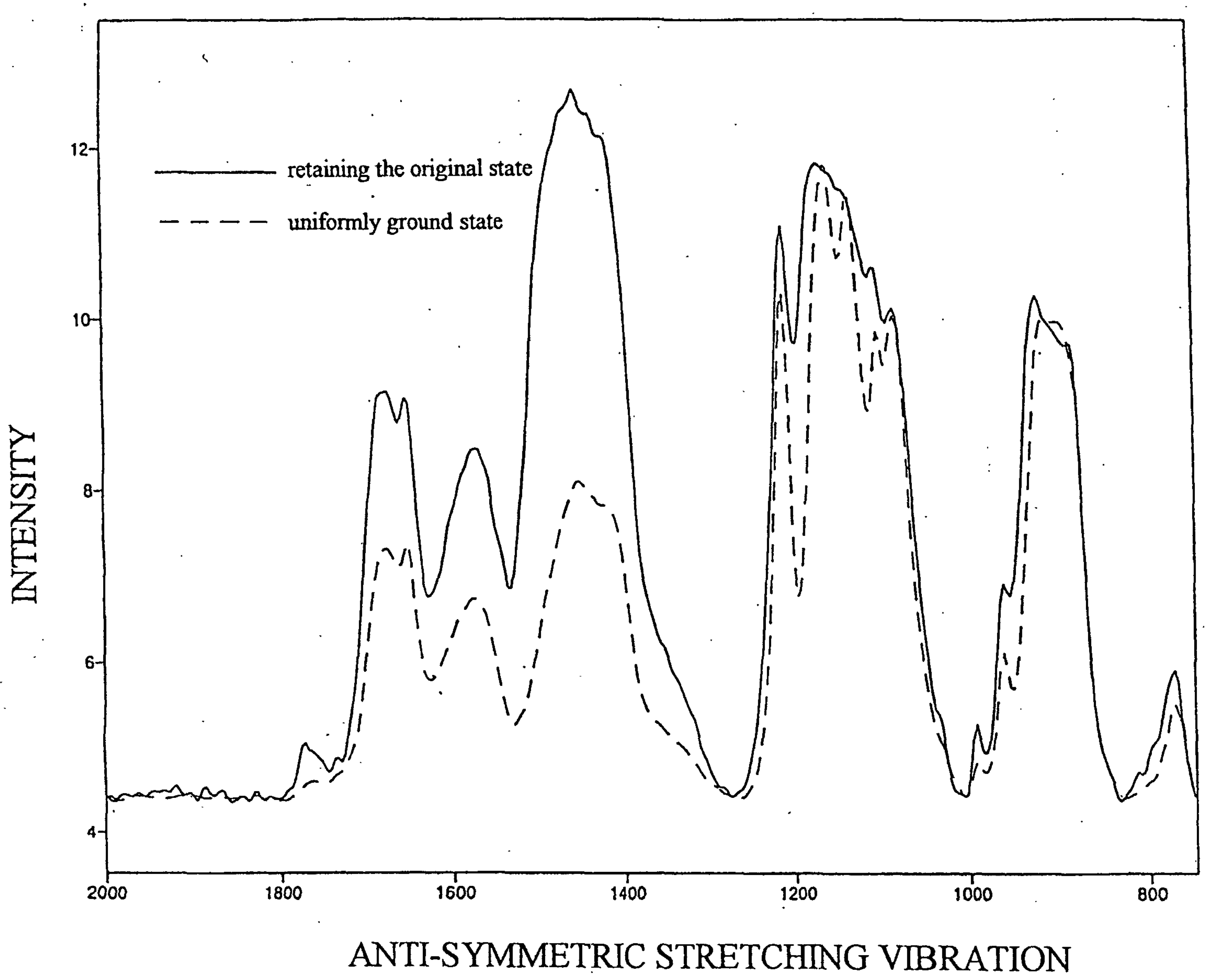
retaining the original state
uniformly ground state
INTENSITY
12
10
8
6
4
2000
1800
1600
1400
1200
1000
800
ANTI-SYMMETRIC STRETCHING VIBRATION

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/03872

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C11D17/06, C11D3/06, C11D3/37, C11D3/04, C11D11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^7 C11D17/06, C11D3/06, C11D3/37, C11D3/04, C11D11/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI(DIALOG)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO, 99/29830, A1 (Kao Corporation), 17 June, 1999 (17.06.99), whole document; especially claims; page 15, line 7; examples & EP, 969082, A1 & AU, 9915055, B	1-10
P,A	WO, 2000/23560, A1 (Kao Corporation), 27 April, 2000 (27.04.00), whole document; especially claims; pages 19-20; pages 25, line 19 to page 26 line 4; examples & JP, 2000-186300, A	1-10
A	JP, 10-176200, A (Kao Corporation), 30 June, 1998 (30.06.98), whole document; especially, claims; Par. Nos. [0031], [00620](3); examples (Family: none)	1-10
A	WO, 97/17422, A1 (Kao corporation), 15 May, 1997 (15.05.97), whole document; especially claim 29; page 31, line 8 to page 32 to line 15; examples & EP, 852611, A1 & JP, 9-94878, A	1-10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:
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"E"	earlier document but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&"	document member of the same patent family

Date of the actual completion of the international search 19 September, 2000 (19.09.00)	Date of mailing of the international search report 03 October, 2000 (03.10.00)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/03872

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 9-59699, A (Kao Corporation), 04 March 1997 (04.03.97), whole document; especially claim 28; page 8, column 14; examples (Family: none)	1-10
A	EP, 513824, A2 (Kao Corporation), 19 November, 1992 (19.11.92), whole document; especially claims; examples & AU, 9216334, B & JP, 5-209200, A & US, 5468516, A	1-10
A	EP, 342043, A1 (Procter & Gamble Co.), 15 November, 1989 (15.11.89), & JP, 2-64199, A & US, 5009804, A & CA, 1326623, A1	1-10
A	EP, 168102, A1 (Unilever NV.), 15 January, 1986 (15.01.86), & DE, 3424987, A1 & AU, 8544538, B & JP, 61-26698, A & US, 4639326, A & CA, 1236368, A1	1-10
A	GB, 2156870, A (Colgate Palmolive Co.), 16 October, 1985 (16.10.85), & DE, 3509331, A1 & FR, 2562085, A1 & AU, 8540714, B & JP, 61-298, A & US, 4741851, A & US, 4857223, A & CA, 1276091, A1	1-10
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A	JP, 6-207199, A (Kao Corporation), 26 July, 1994 (26.07.94) (Family: none)	1-10
A	JP, 2000-192084, A (Kao Corporation), 11 July, 2000 (11.07.00) (Family: none)	1-10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/03872

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	GB, 2159531, A (Colgate Palmolive Co.), 04 December, 1985 (04.12.85), & DE, 3516548, A1 & FR, 2565241, A1 & AU, 8542846, B & JP, 60-262896, A & US, 4725455, A & CA, 1278234, A1	1-10
A	JP, 58-213099, A (Kao Corporation), 10 December, 1983 (10.12.83) (Family: none)	1-10
A	WO, 92/18596, A1 (Procter & Gamble Co.), 29 October, 1992 (29.10.92), & AU, 9217803, B & EP, 581857, A1 & US, 5338476, A & JP, 6-506716, A	1-10
A	WO, 91/17234, A1 (Procter & Gamble Co.), 14 November, 1991 (14.11.91), & JP, 5-507745, A	1-10
A	EP, 330060, A1 (Colgate Palmolive Co.), 30 August, 1989 (30.08.89), & AU, 8930050, B & JP, 1-304200, A & CA, 1326621, A1	1-10
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A	US, 3925234, A (Henkel & Cie GmbH), 09 December, 1975 (09.12.75), & DE, 2338412, A1 & FR, 2194772, A1 & JP, 49-45107, A & GB, 1441416, A & CA, 1003160, A1	1-10

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