



(11) **EP 2 450 428 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
09.05.2012 Bulletin 2012/19

(51) Int Cl.:
C11D 11/00 ^(2006.01) **C11D 1/14** ^(2006.01)
C11D 3/10 ^(2006.01) **C11D 17/06** ^(2006.01)

(21) Application number: **10794135.3**

(86) International application number:
PCT/JP2010/061038

(22) Date of filing: **29.06.2010**

(87) International publication number:
WO 2011/001966 (06.01.2011 Gazette 2011/01)

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO SE SI SK SM TR**

(30) Priority: **30.06.2009 JP 2009155157**

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(54) **METHOD FOR PRODUCING HIGH BULK DENSITY DETERGENT GRANULES**

(57) A method for producing detergent particles having a bulk density of 650 g/L or more, including the following steps 1 to 3: step 1: mixing powdery raw materials having an oil-absorbing ability of 0.4 mL/g or more; step 2: adding water or an aqueous binder solution to a mixed powder obtained by the step 1, and preparing base particles with a low-shearing granulator; and step 3: mixing the base particles obtained in the step 2, with a surfactant composition containing an anionic surfactant and water. By using a method of the present invention, some effects

such as high-density detergent particles generally having very small skin irritability, favorable biodegradability, and a sharp particle size distribution can also be produced in high yields are exhibited. Having a sharper particle size distribution would lead to exhibition of the effects that a detergent having not only improved external appearance but also favorable free flowability and excellent productivity can be efficiently obtained.

EP 2 450 428 A1

DescriptionTECHNICAL FIELD

[0001] The present invention relates to a method for producing high-bulk density detergent particles using base particles and a surfactant composition containing an anionic surfactant. Further, the present invention relates to a detergent composition containing the detergent particles.

BACKGROUND ART

[0002] In the recent years, powder detergent compositions and production methods are desired to meet the requirements of economic advantages and environmental friendliness.

[0003] One method of obtaining a powder detergent is a method including the step of supporting a liquid surfactant on particles for supporting a surfactant. In the method, the particles for supporting a surfactant are desired to have a high supporting ability of the liquid surfactant. In other words, the supporting abilities desired for the particles for supporting a surfactant are two factors of being capable of supporting a liquid surfactant in a large amount (supporting capacity), and being capable of firmly holding the liquid surfactant that is once absorbed in an inner portion of the particles without bleeding out (supporting ability). The supporting capacity is important from the viewpoint of blending a surfactant in a necessary amount for detergency performance, and the supporting ability is important from the viewpoint of suppressing bleed-out of the liquid surfactant, and from the viewpoint of preventing the lowering of free flowability of a powder detergent, caking, or migration of a liquid surfactant to a vessel or the surface.

[0004] On the other hand, as surfactants, there are various disclosures of powder detergents formulated with compounds of an anionic surfactant represented by the formula (1), for the purposes of improving high detergent activity capability and environmental friendliness, and the like.

[0005] Various studies have been so far made on detergent particles in which particles for supporting a surfactant and a surfactant are used as described above. For example, Patent Publication 1 discloses a method for producing detergent particles using particles for supporting a surfactant prepared by spray-drying a preparation liquid containing a water-soluble inorganic salt, and an anionic surfactant represented by the formula (1). However, in this production of the particles, spray-drying is essential, and a method for production without employing spray-drying is desired, from the viewpoint of economic advantages.

[0006] On the other hand, for example, a method for producing a high-density detergent composition using an anionic surfactant according to a non-spray-drying method is disclosed. Patent Publication 2 discloses a method for producing a detergent composition with a surfactant paste and dried detergent materials in a high-speed mixer/moderate speed mixer/dryer continuously. Patent Publication 3 discloses a method for producing a detergent composition with a surfactant paste and dried detergent materials in a high-speed mixer/moderate speed mixer/conditioning apparatus continuously while recirculating the fine particles. However, in the method of Patent Publication 2, it is difficult to adjust particle sizes, and in the method of Patent Publication 3, a method of recirculating fine particles is used in order to solve this problem, thereby making its productivity low. Therefore, a method of obtaining high-density detergent particles having a necessary particle size in a good yield in an even more simple manner is in demand.

PRIOR ART REFERENCESPATENT PUBLICATIONS

[0007]

Patent Publication 1: JP-A-2006-137925
 Patent Publication 2: JP-A-Hei-10-500716
 Patent Publication 3: JP-A- Hei-10-506141

SUMMARY OF THE INVENTIONMEANS TO SOLVE THE PROBLEMS

[0008] Specifically, the gist of the present invention relates to:

[1] a method for producing detergent particles having a bulk density of 650 g/L or more, including the following steps 1 to 3:

step 1: mixing powdery raw materials having an oil-absorbing ability of 0.4 mL/g or more;
 step 2: adding water or an aqueous binder solution to a mixed powder obtained by the step 1, and preparing
 base particles with a low-shearing granulator; and
 step 3: mixing the base particles obtained in the step 2, with a surfactant composition containing the following
 component a) and component b):

a) an anionic surfactant represented by the following formula (1):



wherein R is an alkyl group or alkenyl group having 10 to 18 carbon atoms, and M is an alkali metal atom or an amine; and

b) water in an amount of 25 to 70 parts by weight, based on 100 parts by weight of the above component a);

[2] detergent particles obtained by the method as defined in the above [1]; and

[3] a detergent composition containing detergent particles obtained by the method as defined in the above [1].

EMBODIMENTS FOR CARRYING OUT THE INTENTION

[0009] The present invention relates to a method for producing detergent particles with favorable yields of high-density detergent particles having a necessary particle size, using base particles for supporting a surfactant composition obtained by a method without including spray-drying, and a surfactant composition containing an anionic surfactant. Further, the present invention relates to a detergent composition containing the detergent particles.

[0010] By using a method of the present invention including the step of mixing base particles obtained by a method without including a spray-drying step, and a compound of an anionic surfactant represented by the formula (1), some effects such as high-density detergent particles generally having very small skin irritability, favorable biodegradability, and a sharp particle size distribution can also be produced in favorable yields are exhibited. Having a sharper particle size distribution would lead to exhibition of the effects that a detergent having not only improved external appearance but also favorable free flowability and excellent productivity can be efficiently obtained.

[0011] In the present invention, a base particle refers to a particle containing at least a powder raw material having an oil-absorbing ability of 0.4 mL/g or more, and water or an aqueous binder solution. Preferably, a base particle is a particle obtained by adding water or an aqueous binder solution to a mixed powder containing a powder raw material having an oil-absorbing ability of 0.4 mL/g or more, and forming into particles with a low-shear granulator, and the particle is used for supporting a liquid surfactant composition. A collective of the particles is referred to as base particles. A detergent particle refers to a particle containing a surfactant and a builder or the like, in which a liquid surfactant composition is supported by the base particle, and detergent particles mean a collective thereof. A detergent composition means a composition containing the detergent particles and further containing separately added detergent components other than the detergent particles (for example, a builder particle, a fluorescer, an enzyme, a perfume, a defoaming agent, a bleaching agent, a bleaching activator, or the like).

[0012] Water solubility means that a degree of solubility in water at 25°C is 0.5 g/100 g or more, and water insolubility means that a degree of solubility in water at 25°C is less than 0.5 g/100 g.

[0013] A liquid surfactant composition refers to a composition containing a surfactant in the form of a liquid or paste upon supporting the surfactant to the base particles, and the liquid surfactant composition also includes a composition containing an anionic surfactant represented by the formula (1).

< Composition of Base Particles >

1. Powder Raw Material Having Oil-Absorbing Ability of 0.4 mL/g or More

[0014] An essential component in the present invention includes a powder raw material having an oil-absorbing ability of 0.4 mL/g or more. The oil-absorbing ability of raw material, base particles, and the like refers to a value determined by a method described in the Evaluation Methods of Qualities described later. A powder raw material having an oil-absorbing ability that satisfies an oil absorbing ability of 0.4 mL/g or more refers to a substantially porous substance having fine micropores of 10 μm or less in an inner portion of the powder, the substances being capable of supporting a surfactant in fine micropores thereof. The upper limit of the oil-absorbing ability is not particularly limited, and it is desired that the upper limit is, for example, 1.0 mL/g or less. The powder raw material may be constituted by one component, or may be constituted by plural components. By carrying out the step 1 of mixing the powder raw materials, a mixed powder is prepared.

[0015] The powder raw materials have an average particle size of preferably from 50 to 250 μm , more preferably from 50 to 200 μm , and even more preferably from 80 to 200 μm , from the viewpoint of formation of particles.

[0016] In addition, it is preferable that the powder raw material is a water-soluble substance, from the viewpoint of dissolubility. Examples of the powder raw material include porous powder prepared by drying soda ash prepared by baking sodium bicarbonate (for example, light ash and dense ash), sodium sulfate, or sodium triphosphate hydrate, and the like. The light ash is preferred from the viewpoint of easiness in handling and easy availability.

[0017] In a case where light ash is used as a powder raw material, a surfactant-supporting ability can be even more improved by adjusting a temperature upon baking sodium carbonate. The baking temperature is preferably from 120° to 250°C, preferably from 150° to 220°C, and even more preferably from 150° to 200°C, from the viewpoint of supporting ability.

[0018] The powder raw material is contained in an amount of preferably from 40 to 95% by weight, more preferably from 45 to 90% by weight, even more preferably from 50 to 85% by weight, and even more preferably from 50 to 80% by weight, of the base particles, from the viewpoint of supporting ability. Here, in a case where the components are adjusted to the above composition by a drying step, the powder raw material is contained in an amount of preferably from 25 to 80% by weight, more preferably from 30 to 77% by weight, even more preferably from 32 to 77% by weight, and even preferably from 32 to 73% by weight, of the particles before carrying out the drying step.

2. Binder

[0019] In the present invention, the base particles are prepared by adding water or an aqueous binder solution to a mixed powder, and forming particles from the mixed powder by using a low-shearing granulator. In a case where a clay mineral is used as one component of the powder raw material, a mixture of the clay mineral and a powder raw material other than the clay mineral is formed into particles. In a case where water is used, a bonding property generated by partly dissolving a powder raw material in water or bonding property of a clay mineral is utilized in formation of particles. In a case where an aqueous binder solution is used, a bonding property ascribed to the binder can be further utilized, so that the formation of particles is more facilitated.

[0020] In addition, in a case where a drying step is included, when water is used, there is a concern in the lowering of particle strength with drying; however, when an aqueous binder solution is used, an effect ascribed to the binder can be expected even after drying. Therefore, it is preferable to use an aqueous binder solution.

[0021] The binder is not particularly limited, so long as the binder has an ability of binding the components constituting the particle in the powder raw material with each other, and has a property of dissolving and/or dispersing in water quickly. The binder includes, for example, polyethylene glycols, polypropylene glycols, polyoxyethylene alkyl ethers and derivatives thereof, polyvinyl alcohols and derivatives thereof, water-soluble cellulose derivatives (derivatives thereof including ether compounds, and the like); organic polymers such as carboxylate polymers, starch, and saccharides, inorganic polymers such as amorphous silicate; and the like.

[0022] The water-soluble cellulose derivatives, saccharides, and carboxylate polymers are preferred, and a salt of acrylic acid-maleic acid copolymer and a salt of polyacrylic acid are more preferred, from the viewpoint of bonding property and detergency. The salt is preferably a sodium salt, a potassium salt, or an ammonium salt. Here, the carboxylate polymer has a weight-average molecular weight of preferably from 1,000 to 100,000, and more preferably from 2,000 to 80,000.

[0023] The binder is contained in the base particles in an amount of preferably from 0 to 35% by weight, more preferably from 5 to 30% by weight, even more preferably from 8 to 20% by weight, and even more preferably from 10 to 20% by weight, of the base particles, from the viewpoint of bonding property and oil-absorbing ability. Here, in a case where the amount of the binder is adjusted to the above components by a drying step, the binder is contained in an amount of preferably from 0 to 30% by weight, more preferably from 3 to 25% by weight, even more preferably from 5 to 17% by weight, and even more preferably from 7 to 17% by weight, of the particles before carrying out the drying step.

[0024] The concentration of the aqueous binder solution is not particularly limited. Since the particle sizes upon the formation of particles are greatly affected by the volume of the aqueous binder solution, the concentration may be determined from a necessary amount of the binder and a desired particle size of the particles.

3. Clay Mineral

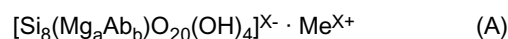
[0025] The clay mineral has a layered structure, and is capable of supporting a liquid surfactant between the layers. Therefore, by blending with a clay mineral as one component of the powder raw materials, supporting capacity of a liquid surfactant can be increased and at the same time supporting ability can be improved.

[0026] In addition, the clay mineral exhibits bonding property by containing water, so that the particle size of the base particles can be controlled by adjusting the amount of the clay mineral to be blended.

[0027] The clay mineral as mentioned above includes, for example, talc, pyrophyllites, smectites such as saponite,

hectorite, sauconite, stevensite, montmorillonite, beidellite and nontronite, vermiculites, micas such as phlogopite, biotite, zinnwaldite, muscovite, paragonite, celadonite and glauconite, chlorites such as clinochlore, chamosite, nimitzite, pennantite, sudoite and donbassite, brittle micas such as clintonite and margarite, thulite, serpentines such as antigorite, lizardite, chrysotile, amesite, cronstedtite, berthierine, greenalite and garnierite, kaolin minerals such as kaolinite, dickite, nacrite and halloysite, and the like. Among them, talc, smectites, swellable micas, vermiculites, chrysotile, the kaolin minerals and the like are preferable, the smectites are more preferable, and the montmorillonite is even more preferable, from the viewpoint of softening property. These clay minerals can be used alone or appropriately in a combination of two or more kinds.

[0028] In addition, from the viewpoint of surfactant-supporting ability, it is preferable that the clay mineral contains as a main component a clay mineral represented by the following general formula (A):



wherein each of **a**, **b** and **x** satisfies $0 < \mathbf{a} \leq 6$, $0 < \mathbf{b} \leq 4$, $x = 12 - 2\mathbf{a} - 3\mathbf{b}$, and Me is at least one ion selected from Na, K, Li, Ca^{1/2}, Mg^{1/2} and NH₄.

[0029] Examples of the clay mineral represented by the above general formula (A) include "Laundrosil DGA212," "Laundrosil PR414," "Laundrosil DG214," "Laundrosil DGA Powder," "EXM0242," "HULA SOFT-1 Powder" manufactured by Süd-Chemie; "Detersoft A," "Detersoft GIS," "Detersoft GIB," "Detersoft GISW" manufactured by Laviosa; Pure Bentonite, Standard Bentonite, and Premium Bentonite, manufactured by CSM, and the like. Among those given as the examples of the clay mineral listed above, some of them are in the form of particles in which a binder component is added and formed into particles, or the binder component may be added so long as the effects of the present invention would not be impaired.

[0030] In a case where a clay mineral listed above is used in the present invention, the shape of the clay mineral is preferably in the form of powder, from the viewpoint of formation of particles, and in a case of a granular product, it is preferable that the granular product is disintegrated beforehand to a suitable granularity. The pulverizer that can be utilized for disintegration includes impact crushers such as hammer crusher; impact pulverizers such as atomizers and pin mills; shearing rough pulverizers such as flash mills. These pulverizers may be used in a single-step procedure, or in a multi-step procedures with the same or different pulverizers.

[0031] The clay mineral powder has an average particle size of preferably 100 μm or less, more preferably 50 μm or less, and even more preferably 30 μm or less.

[0032] In addition, in the clay mineral represented by the general formula (A), a total of the alkali metal ions, i.e. Na ions, K ions, and Li ions, and a total of the alkaline earth metal ions, i.e. Ca ions and Mg ions, are in a molar ratio, i.e. [(Na + K + Li)/(Ca + Mg)] of preferably 1.0 or more, more preferably 1.5 or more, and even more preferably 2.0 or more, from the viewpoint of supporting ability and dissolubility.

[0033] In order to obtain a clay mineral having a high proportion of the alkali metal ions, if the clay mineral is a natural product, the producing region may be selected, or in a case where the clay granules are produced, an alkali metal salt can be added to prepare granules. In addition, in a case where the clay mineral is a synthesized product, the product can be prepared in any manner by a known method.

4. Water

[0034] The base particles in the present invention contain water in a proper amount that is used in the production steps. The smaller the amount of water as measured with an infrared moisture meter, the more preferred, from the viewpoint of increasing capacity of supporting a surfactant composition by the particles. The amount of water is preferably 1S% by weight or less, more preferably 10% by weight or less, and even more preferably 5% by weight or less.

5. Other Components

[0035] Here, the base particles in the present invention can be properly blended with a substance other than the 1 to 4 listed above as occasion demands. However, the amount of these substances blended is preferably 20% by weight or less, more preferably 10% by weight or less, and even more preferably 5% by weight or less, from the viewpoint of supporting ability. Examples of substances that can be blended are given hereinbelow.

- Chelating Agent

[0036] The chelating agent can be blended for the purpose of suppressing the inhibition of detergent action by metal ions. A water-soluble chelating agent is not particularly limited, so long as the chelating agent is a substance that holds a metal ion sequestering ability, and a crystalline silicate, a tripolyphosphate, an orthophosphate, a pyrophosphate, or

the like can be used. Among them, the crystalline silicate and the tripolyphosphate are preferred. A water-insoluble chelating agent is preferably particles that have an average particle size of from 0.1 to 20 μm , from the viewpoint of dispersibility in water. The preferred water-insoluble chelating agent includes crystalline aluminosilicates, including, for example, A-type zeolite, P-type zeolite, X-type zeolite, and the like, and the A-type zeolite is preferred from the viewpoint of metal ion sequestering ability and economic advantages.

- Water-Soluble Inorganic Salt

[0037] It is preferable that a water-soluble inorganic salt is added, for the purpose of enhancing an ionic strength of a washing liquid, and improving an effect such as sebum dirt washing.

[0038] The water-soluble inorganic salt is not particularly limited, so long as the inorganic salt is a substance that has favorable dissolubility and does not give a disadvantageous influence on detergency. The water-soluble inorganic salt includes, for example, alkali metal salts, ammonium salts, and the like, each having a sulfate group or a sulfite group.

[0039] Among them, it is preferable that sodium sulfate, sodium sulfite, or potassium sulfate, each having a high degree of ionic dissociation is used as an excipient. Also, its combined use with magnesium sulfate is preferred from the viewpoint of improving dissolution rate.

- Water-Insoluble Excipient

[0040] The water-insoluble excipient is not particularly limited, so long as the water-insoluble excipient is a substance that has favorable dispersibility in water and does not give a disadvantageous influence on detergency. The water-insoluble excipient includes, for example, crystalline or amorphous aluminosilicates, silicon dioxide, hydrated silicic acid compounds, and the like. The water-insoluble excipient preferably has an average primary particle size of from 0.1 to 20 μm , from the viewpoint of dispersibility in water.

- Other Auxiliary Components

[0041] Other auxiliary components include fluorescers, pigments, dyes, and the like.

[0042] Here, the average particle size of the above components can be measured in accordance with the methods described in the Measurement Methods of Physical Properties described later.

[0043] The method for producing detergent particles of the present invention includes the following steps 1 to 3. Base particles are prepared through the step 1 and the step 2, and detergent particles are prepared through the step 3.

< Method for Producing Base Particles >

[0044] The base particles in the present invention can be prepared by a method including the step of stirring or mixing at least a powder raw material having an oil-absorbing ability of 0.4 mL/g or more, without including a spray-drying step, and the step of adding water or an aqueous binder solution to the mixed powder obtained, and preparing particles with a low-shearing granulator.

1. Step 1

[0045] In the step of mixing a powder raw material having an oil-absorbing ability of 0.4 mL/g or more, any methods may be employed so long as the components can be substantially homogeneously mixed. For example, the mixing may be carried out with a low-shearing granulator used in the step 2, or the mixing may be previously carried out using a different mixer, and thereafter transferred to a low-shearing granulator. The different mixer to be used in powder mixing includes, for example, rotary drum mixers, pan mixers, ribbon mixers, Nauta mixers, Shugi Mixers, Lödige mixers, High-Speed Mixers, and the like.

[0046] Here, the clay mineral is contained in an amount of preferably from 0 to 45% by weight, more preferably from 0 to 40% by weight, even more preferably from 0 to 35% by weight, and even more preferably from 0 to 30% by weight, of the base particles, from the viewpoint of supporting ability and particle size control. Here, after the formation of particles, the particles may be dried as desired, and in a case where the components are adjusted to the above components by the drying step as described above, the clay mineral is contained in an amount of preferably from 0 to 40% by weight, 0 to 35% by weight, even more preferably from 0 to 30% by weight, and even more preferably from 0 to 25% by weight, of the particles before carrying out the drying step.

[0047] In addition, the clay mineral and the powder raw material are in a weight ratio, i.e. clay mineral/powder raw material, of preferably from 0/1 to 0/30, more preferably from 0/1 to 0/20, and even more preferably from 0/2 to 0/20.

2. Step 2

[0048] The step is a step of adding water or an aqueous binder solution to a mixed powder obtained by the step 1, and preparing base particles with a low-shearing granulator. In this step, a particle having a structure in which the powder raw material is loosely aggregated is formed. Also, the step 1 and the step 2 can be carried out simultaneously.

[0049] The low-shearing granulator usable in this step may be any apparatus that do not greatly densify the particles by giving a strong shearing force to the particles. For example, even in a vertical or horizontal granulator equipped with a main blade and a disintegration blade that can give a high shearing force, the granulator can be utilized in the production of the particle of the present invention by setting a rotational speed or a Froude number described below to a low value, thereby controlling densification. In other words, the low-shearing granulator as used herein encompasses a granulator which can be operated by lowering a shearing force by setting or the like of operating conditions, even if the granulator is capable of giving a high shearing force to a particle.

[0050] As the low-shearing granulator, vessel rotary drum granulators, in which the formation of particles progresses with the rotation of the body of the granulator, are preferred, among which a pan granulator and a rotary drum granulator are more preferred, from the viewpoint of easiness in formation of particles and improvement in supporting ability. These apparatuses can be used in both methods of a batch process and continuous process. Here, it is preferable that the low-shearing granulator is provided with baffles for assisting mixing in the pan or the rotary drum, from the viewpoint of powder miscibility and liquid-solid miscibility.

[0051] Also, in order to use a granulator as a low-shearing granulator, the granulator is set to have a Froude number as defined in the following formula of preferably 1.0 or less, more preferably 0.8 or less, even more preferably 0.6 or less, and even more preferably 0.4 or less, from the viewpoint of supporting ability.

[0052]

$$\text{Froude number: } Fr = V^2 / (R \times g)$$

wherein

V: peripheral speed [m/s],

R: a radius [m] from the center of rotation to the circumference of the rotated object, and

g: a gravitational acceleration rate [m/s²].

[0053] The granulator is set to have a Froude number of preferably 0.001 or more, more preferably 0.005 or more, even more preferably 0.01 or more, and still even more preferably 0.05 or more, from the viewpoint of homogeneously adding water or an aqueous binder solution to a mixed powder.

[0054] Here, it is supposed that in a vertical or horizontal granulator equipped with a main blade and a disintegration blade, the values of the main shaft are used for V and R, and that in a pan granulator or a rotary drum granulator in which the formation of particles is progressed by the rotation of the body of the granulator, the values of the body of the granulator are used for V and R. In addition, in a pan granulator equipped with a disintegration blade, it is supposed that the values for disintegration blade are used for V and R.

[0055] In the present invention, it is preferable that water or an aqueous binder solution is added while homogeneously dispersing. As a method for serving this purpose, there is a method of forming fine particles from the liquid component as mentioned above by using a one-fluid nozzle, or a multi-fluid nozzle such as a two-fluid nozzle.

[0056] The multi-fluid nozzle refers to a nozzle that allows to flow a liquid component and a gas for formation fine particles, such as the air or nitrogen, in independent pathways, to communicate to a portion in the vicinity of a tip end portion of the nozzle, and mixing and forming fine particles. As the multi-fluid nozzle, a two-fluid nozzle, a three-fluid nozzle, a four-fluid nozzle, or the like can be used. In addition, a mixing portion of the liquid component and the gas for forming fine particles may be any one of an internal mixing type where the mixing is carried out within a tip end portion of the nozzle, or an external mixing type where the mixing is carried out in the external of a tip end portion of the nozzle.

[0057] In the present invention, it is preferred to add a liquid component by using a multi-fluid nozzle to form fine liquid droplets, and it is more preferred to use a two-fluid nozzle. As the multi-fluid nozzle mentioned above, for example, a wide-angled round type two-fluid nozzle (manufactured by Spraying Systems Japan K.K.), a full-cone type two-fluid nozzle (manufactured by Atomax Co., Ltd.), or a four-fluid nozzle (manufactured by Fujisaki Denki K.K.), or the like can be used.

[0058] In addition, when it is intended to increase a rate of adding a binder, it is also effective to use plural number of these one-fluid nozzles or multi-fluid nozzles, thereby increasing the rate of adding the binder, while maintaining the formation of fine droplets.

[0059] By using the method as described above, a homogenous dispersion can be achieved even in an aqueous binder solution having a high viscosity, so that base particles having an improved yield and a sharp particle size distribution are obtained.

[0060] In this step, the procedures of drying the base particles obtained may be further carried out. By carrying out the procedures, gaps in the particles constituting the base particles are increased, so that supporting capacity of the base particles can be even more improved.

[0061] A drying method that does not give a strong shearing force as much as possible is preferred, from the viewpoint of suppressing the lowering of supporting capacity caused by the disintegration of the particles. For example, in a batch process, the drying method includes a method including placing the particles in a vessel, and drying the particles with an electric dryer or a hot air dryer; and a method of drying with a batch-type fluidized bed; or the like. In a continuous process, the drying method employs a fluidized bed, a rotary dryer, a steam tube dryer, or the like.

[0062] A drying temperature is preferably 80°C or more, more preferably 120°C or more, even more preferably 150°C or more, and even more preferably 180°C or more, from the viewpoint of drying rate. In addition, in a case where an organic binder is used as a binder, and a drying temperature is preferably 300°C or less, more preferably 250°C or less, and more preferably 220°C or less, from the viewpoint of suppressing the degradation of the binder.

< Physical Properties of Base Particles >

[0063] The base particles in the present invention are particles having a structure in which at least a powder raw material having an oil-absorbing ability of 0.4 mL/g or more is loosely aggregated. For this reason, the particles have two supporting sites: (1) large gaps between the powder raw materials, and (2) small gaps within the powder raw material (for example, gaps having sizes of 10 μm or less). Among them, both (1) and (2) greatly influence supporting capacity and supporting ability, and (1) greatly influences supporting rate. By adjusting the two supporting sites, base particles having a desired supporting ability can be obtained.

[0064] In addition, in a case where a clay mineral is blended, a liquid surfactant composition can be supported between the layers, so that improvement in supporting ability are possibly found.

[0065] The base particles in the present invention have a bulk density of preferably from 400 to 550 g/L, and more preferably from 400 to 500 g/L, from the viewpoint of obtaining a supporting capacity of a liquid surfactant composition and from the viewpoint of obtaining a high bulk density after the liquid surfactant composition is supported. It is considered that a relatively low bulk density of the base particles in the present invention is accomplished by formation of particles with a low-shearing granulator mentioned above.

[0066] Also, the base particles have an average particle size of preferably from 140 to 600 μm, more preferably from 200 to 500 μm, and even more preferably from 200 to 400 μm, from the viewpoint of powder dust property and dissolubility upon the use of a detergent composition containing detergent particles containing base particles and a liquid surfactant composition supported thereto.

[0067] The liquid surfactant composition of the base particles has an oil-absorbing ability of preferably 0.4 mL/g or more, even more preferably 0.45 mL/g or more, and even more preferably 0.5 mL/g or more, from the viewpoint of increasing an allowable range of the amount of the liquid surfactant composition blended. It is considered that a relatively high oil-absorbing ability of the base particles in the present invention is accomplished by formation of particles with a low-shearing granulator mentioned above.

[0068] Here, the bulk density, the average density, the oil-absorbing ability of the liquid surfactant composition, and the amount of water can be measured in accordance with the methods described in the Measurement Methods of Physical Properties described later.

[Components in Surfactant Composition]

[0069] In an anionic surfactant represented by:



R is an alkyl group or alkenyl group having 10 to 18 carbon atoms, preferably 12 to 16 carbon atoms. M is preferably an alkali metal atom such as Na or K, or an amine such as monoethanolamine or diethanolamine, and Na and K are preferred, from the viewpoint of improving detergency of a detergent composition.

Physical. Properties of Surfactant Composition]

[0070] In a surfactant composition containing an anionic surfactant represented by the formula (1) and a given amount of water, in an operable temperature region of the surfactant composition, it is desired that the surfactant composition

has a temperature range satisfying a viscosity of 10 Pa·s or less, and more preferably 5 Pa·s or less, from the viewpoint of handling property upon the production. It is preferable that the temperature range mentioned above exists preferably up to 70°C, and more preferably up to 60°C, from the viewpoint of stability of the surfactant composition. Here, the viscosity is determined with a coaxial double cylindrical rotary viscometer (manufactured by HAAKE, sensor: SV-DIN) at a shearing rate of 50 [1/s].

[0071] The surfactant composition usable in the step 3 greatly varies in viscosity depending upon the water content. For example, in the preparation of a surfactant composition by neutralizing an acid precursor of the component a) with an alkali compound, it is preferable that a surfactant composition having a desired water content, in other words, a desired viscosity, is prepared by adjusting a water content of the alkali compound used. It is generally known that when a surfactant composition contains water in an amount of from 25 to 70 parts by weight, based on 100 parts by weight of the component a), i.e. water content of the surfactant composition being from about 20 to about 40%, the viscosity is lowered, thereby making its handling easy. In the present invention, it is preferable to use a surfactant composition of which amount of water is adjusted within this range. The amount of water in the surfactant composition is in the range of preferably from 30 to 70 parts by weight, and more preferably from 35 to 65 parts by weight, based on 100 parts by weight of the component a), from the viewpoint of handling.

[0072] In addition, since the acid precursor of the component a) is very unstable and more likely to be degraded, it is preferable that the surfactant composition is adjusted so that the degradation can be suppressed. The method of adjustment is not particularly limited, and a known method can be used. For example, the method may be carried out by removing heat of neutralization with a heat exchanger or the like using a loop reactor, while cautiously temperature-controlling the acid precursor of the component and the surfactant composition. A temperature range during production includes a temperature of from 30° to 60°C, and a temperature range for storage after the production includes a temperature of 60°C or lower. In addition, the surfactant composition may be used by optionally elevating the temperature upon use.

[0073] In addition, it is preferable that the resulting anionic surfactant composition has excess alkalinity, from the viewpoint of suppressing degradation.

[0074] In addition, the surfactant composition usable in the step 3 may contain an unreacted alcohol or an unreacted polyoxyethylene alkyl ether upon the production of the acid precursor of the component a), sodium sulfate, which is a by-product of the neutralization reaction, or a pH buffering agent, which can be added during the neutralization reaction, a decolorizing agent, or the like.

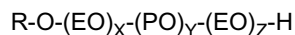
[0075] Here, the component a) is contained in an amount in the range of preferably from 10 to 45% by weight, and more preferably from 15 to 40% by weight, of the detergent particles obtainable in the present invention, from the viewpoint of detergency and dissolubility.

[0076] In the surfactant composition, the component a) as the surfactant can be used alone, or the component may also be used as a mixture with a nonionic surfactant. Especially, in a case where a nonionic surfactant having a melting point of 30°C or lower is used, it is preferable to use the nonionic surfactant together with a water-soluble nonionic organic compound having a melting point of from 45° to 100°C and a molecular weight of from 1,000 to 30,000, the water-soluble nonionic organic compound having an action of elevating a melting point of a surfactant (hereinafter referred to as a "melting-point elevating agent"), or an aqueous solution thereof. Here, the melting-point elevating agent which can be used in the present invention includes, for example, polyethylene glycols, polypropylene glycols, polyoxyethylene alkyl ethers, Pluronic nonionic surfactants, and the like. Also, an amphoteric surfactant or a cationic surfactant can be used together, depending upon the purposes. In addition, an anionic surfactant other than the anionic surfactant represented by the formula (1), such as a polyoxyethylene alkyl ether sulfate or an alkylbenzenesulfonate, can be used in an amount within the range of from 0 to 10% by weight, more preferably from 0 to 5% by weight, and even more preferably from 0 to 3% by weight, of the detergent particles, from the viewpoint of improving dispersibility of the detergent particles in low-temperature water. Specifically, it is more preferable that an anionic surfactant other than a nonionic surfactant and/or an anionic surfactant represented by the formula (1) is contained in the surfactant composition in the step 3. In such a case, the amount of the component is preferably from 0.1 to 10% by weight, more preferably from 0.2 to 5% by weight, and even more preferably from 0.5 to 3% by weight.

[0077] Further, in order to obtain defoaming effects, a fatty acid salt can be used in together therewith.

[0078] The nonionic surfactants include polyoxyethylene alkyl or alkenyl ethers, polyoxyethylene alkyl- or alkenylphenyl ethers, polyoxyethylene-polyoxypropylene alkyl or alkenyl ethers, polyoxyethylene-polyoxypropylene glycols as represented by the trade name "Pluronic," polyoxyethylene alkylamines, higher fatty acid alkanolamides, alkyl glucosides, alkyl glucosamides, alkylamine oxides, and the like. Among them, those having high hydrophilicity and those having a low forming ability of liquid crystals or having no formation of liquid crystals when mixed with water are preferable, and the polyoxyalkylene alkyl or alkenyl ethers are even more preferable. Preferably, the nonionic surfactant is preferably ethylene oxide (hereinafter simply referred to as "EO") adducts of alcohols, and the EO adducts and propylene oxide (hereinafter simply referred to as "PO") adducts of alcohols. As the order of addition, there can be employed embodiments including an embodiment of adding EO, and thereafter adding PO; an embodiment of adding PO, and thereafter adding

EO; or an embodiment of adding randomly EO and PO. More preferable order of addition includes an embodiment of adding EO in a block form, thereafter adding PO in a block form, and further adding EO in a block form to give a compound represented by the general formula:



wherein R is a hydrocarbon group, preferably an alkyl group or an alkenyl group; EO is an oxyethylene group; PO is an oxypropylene group; and X, Y and Z are each average number of moles thereof, among which even more preferable average number of moles have the relations of $X > 0$; $Z > 0$; $X + Y + Z = 6$ to 14 ; $X + Z = 5$ to 12 ; and $Y = 1$ to 4 .

[0079] The nonionic surfactant is blended in the detergent particles in an amount preferably within the range of from 0 to 10% by weight, more preferably from 0 to 5% by weight, and even more preferably from 0 to 3% by weight, of the detergent particles, from the viewpoint of improving detergency, improving anti-caking property, and suppressing the choking upon formation of powder dusts.

[0080] Upon the mixing of the surfactant composition and the base particles, a powder raw material other than the above powder raw material may be added as desired, and the amount thereof is preferably from 0 to 150 parts by weight, based on 100 parts of the particles. The powder raw material includes, for example, aluminosilicates, crystalline silicates such as PREFEED (manufactured by Tokuyama Siltex), and the like.

< Physical Properties of Detergent Particles >

[0081] According to the method of the present invention, detergent particles having desired properties can be obtained. The detergent particles obtained according to the method of the present invention are also embraced by the present invention. The preferred physical properties of the detergent particles according to the present invention are as follows.

[0082] The bulk density is 650 g/L or more, preferably from 650 to 1,000 g/L, more preferably from 650 to 950 g/L, even more preferably from 650 to 900 g/L. The average particle size is preferably from 150 to 600 μm , more preferably from 180 to 550 μm , and even more preferably from 250 to 500 μm .

[0083] Here, the bulk density and the average particle size mentioned above can be measured in accordance with the Measurement Methods of Physical Properties described later.

[0084] In addition, as an index of the preferred particle size distribution of the detergent particles according to the present invention, Rosin-Rammler number can be used. In the calculation for the Rosin-Rammler number, the following formula is used.

[0085]

$$\log (\log (100/R (D_p)))=n \log (D_p/D_e)$$

R (D_p): a cumulative percentage [%] of powder having particle sizes of D_p μm or more;

D_p : a particle size [μm]

D_e : an absolute particle size constant [μm]

n: a Rosin-Rammler number [-]

[0086] The larger the Rosin-Rammler number n, the sharper the particle size distribution. n is preferably 1.0 or more, more preferably 1.3 or more, more preferably 1.5 or more, even more preferably 1.8 or more, and still even more preferably 2.0 or more.

[0087] A preferred yield of particle sizes of the detergent particles according to the present invention, as expressed by a proportion of the particles passing through a sieve opening of from 250 to 500 μm , is preferably 35% or more, more preferably 40% or more, even more preferably 45% or more, even more preferably 50% or more, and still even more preferably 60% or more. In addition, a proportion of the particles passing through a sieve opening of from 125 to 500 μm is preferably 45% or more, more preferably 50% or more, even more preferably 55% or more, even more preferably 60% or more, and still even more preferably 70% or more.

[0088] As the amount of water of the detergent particles according to the present invention, the smaller the amount of water, the more preferred, from the viewpoint of a high blending ratio of the component a), Specifically, in a case where an amount of water in the detergent particles is measured with an infrared moisture meter, the amount of water is preferably 20% by weight or less, more preferably 15% by weight or less, even more preferably 10% by weight or less, and still even more preferably 5% by weight or less.

< Method for Producing Detergent Particles >

[0089] A preferred method for obtaining detergent particles includes the following step 3, and may further optionally include the step 4 or the step 5 as occasion demands.

3. Step 3

[0090] This step is a step of mixing the base particles obtained in the step 2, with a surfactant composition containing the following component a) and component b).

[0091] In the method of the present invention, the component a) is an anionic surfactant represented by the formula (1), and the component b) is water in an amount of from 25 to 70 parts by weight, and preferably from 25 to 65 parts by weight, based on 100 parts by weight of the above component a).

[0092] Here, in this step, at least the base particles obtained by the step 2 may be used. In other words, in this step, other particles having an ability of supporting a surfactant, for example, particles obtained by another methods, including, for example, spray-drying, may be used together with the base particles. Here, in cases where the base particles are used together with the other particles, a mixture of the base particles and the particles obtained by other methods can be handled as base particles.

[0093] The ratio of the present base particles is preferably 50% by weight or more, more preferably 70% by weight or more, and even more preferably 90% by weight or more, of the overall base particles, from the viewpoint of oil-absorbing ability.

3-1. Step 3

[0094] In this step, by mixing base particles and a surfactant composition, the surfactant composition is supported by the base particles. The method includes, for example, a method including mixing base particles with a surfactant composition by using a mixer for a batch process or a continuous process. In a case of carrying out according to a batch process, as a method of supplying to a mixer, there can be employed such a method as (1) a method including previously supplying base particles, and thereafter adding thereto a surfactant composition; (2) a method including repeatedly supplying base particles and a surfactant composition in the mixer in small amounts at a time; (3) a method including repeatedly supplying a part of base particles in a mixer, and thereafter supplying the remaining base particles and a surfactant composition in the mixer in small amounts at a time, and the like.

[0095] In the addition of the surfactant composition to the base particles, the larger the amount of the surfactant composition blended, the more important the rate of addition. Specifically, it is preferable that a rate of adding a surfactant composition is equal to or lower than a rate of absorbing oil in the base particles. By carrying out addition of the surfactant composition at a rate of addition as mentioned above, oil absorption of the surfactant composition can be made possible even to an inner portion of the base particles, whereby consequently the aggregation of the detergent particles due to adhesiveness of the surfactant can be suppressed, so that the particle size distribution of the resulting detergent particles can be made sharp.

[0096] The surfactant composition has a specific rate of addition of preferably 35 parts by weight/minute or lower, more preferably 20 parts by weight/minute or lower, even more preferably 10 parts by weight/minute or lower, and still even more preferably 7.5 parts by weight/minute or lower, based on 100 parts by weight of the base particles.

[0097] The surfactant composition is added to the base particles in an amount of, for example, preferably from 30 to 100 parts by weight, based on 100 parts by weight of the base particles. The surfactant composition is added to the base particles in an amount of preferably 30 parts by weight or more, more preferably 40 parts by weight or more, and even more preferably 50 parts by weight or more, based on 100 parts by weight of the base particles, from the viewpoint of detergency. In addition, the surfactant composition is added to the base particles in an amount of preferably 100 parts by weight or less, more preferably 80 parts by weight or less, and even more preferably 60 parts by weight or less, based on 100 parts by weight of the base particles, from the viewpoint of dissolubility.

[0098] Preferable mixers specifically include as follows. In a case of mixing by a batch process, those of (1) to (3) are preferable: (1) 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.); mixers disclosed in JP-A-Hei 10-296064, mixers disclosed in JP-A-Hei 10-296065, and the like; (2) Ribbon Mixer (manufactured by Nichiwa Kikai Kogyo K.K.); Batch Kneader (manufactured by Satake Kagaku Kikai Kogyo K.K.); Ribocone (manufactured by K.K. Okawahara Seisakusho), and the like; (3) Nauta Mixer (manufactured by Hosokawa Micron Corp.), SV Mixer (Shinko Pantec Co., Ltd.), and the like. Among the above-mentioned mixers, preferable are Lödige Mixer, PLOUGH SHARE Mixer, and the mixers disclosed in JP-A-Hei 10-296064, mixers disclosed in JP-A-Hei 10-296065, and the like. Since step 4 described below can be carried out by the same mixer, these mixers are preferable from the viewpoint of simpli-

fication of equipments. Among them, the mixers disclosed in JP-A-Hei 10-296064 and the mixers disclosed in JP-A-Hei 10-296065 are preferable, because the moisture and temperature of the mixture can be regulated by ventilation, whereby the disintegration of the base particles can be suppressed. In addition, mixers, such as Nauta Mixer, SV Mixer and Ribbon Mixer, which are capable of mixing powders with liquids without applying a strong shearing force, are preferable from the viewpoint that the disintegration of the base particles can be suppressed.

[0099] Also, the base particles may be mixed with a surfactant composition by using the above-mentioned continuous process-type mixer. Also, the continuous process-type mixer other than those listed above includes Flexo Mix (manufactured by Powrex Corp.), Turbulizer (manufactured by Hosokawa Micron Corporation), and the like.

[0100] In addition, in this step, when a nonionic surfactant is used, it is preferable that a melting point-elevating agent or an aqueous solution thereof, which has a function of elevating a melting point of this nonionic surfactant, is added before adding a surfactant composition, simultaneously with adding a surfactant composition, in the course of adding a surfactant composition, or after adding a surfactant composition, or previously mixed with a surfactant composition. By adding the melting point-elevating agent, the caking property of the detergent particles and the bleed-out property of the surfactants in the detergent particles can be suppressed. Here, as these melting point-elevating agents, the same ones as those exemplified in the melting point-elevating agent in the components of the detergent particles described above can be used. The amount of the melting point-elevating agent used is preferably from 0.5 to 8 parts by weight, more preferably from 0.5 to 5 parts by weight, and even more preferably from 1 to 3 parts by weight, based on 100 parts by weight of the base particles. The above range is preferable from the viewpoint of the suppression of the aggregation between the particles of the detergent particle contained in the detergent particles, the fast dissolubility, and the suppression of the bleed-out property and the caking property. A method of adding the melting point-elevating agent, including adding by previously mixing the melting point-elevating agent with a surfactant by an arbitrary process, or a method including adding a surfactant, and thereafter adding the melting point-elevating agent, is advantageous for the suppression of the bleed-out property and the caking property of the detergent particles.

[0101] It is preferable that the temperature within the mixer in this step is adjusted so that the degradation of the anionic surfactant can be suppressed, and the temperature range during the production is preferably from 30° to 60°C, and the storage temperature range after the production is preferably 60°C or lower.

[0102] 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 30 minutes, more preferably from 2 to 25 minutes, and even more preferably from 3 to 20 minutes.

[0103] In the step 3, the mixing of base particles and a surfactant composition may be carried out under ventilation. More specifically, in the step 3, the ventilation includes the procedures of blowing a gas such as the air into a mixing vessel of a mixing apparatus. By carrying out the procedures, base particles can further support a surfactant composition, so that the resulting detergent particles contain a surfactant composition in a high blending ratio.

[0104] The reasons why the effects as described above are exhibited are deduced to be due to the fact that by carrying out the procedures, water in the surfactant composition existing on the surface of the base particles is removed. As a result, the adhesiveness of the detergent particles is reduced, thereby suppressing the aggregation of the detergent particles, leading to a sharp particle size distribution of the resulting detergent particles.

[0105] The blowing conditions are, for example, such that a gas to be blown in is at a temperature of preferably from 10° to 65°C, more preferably from 30° to 60°C, and even more preferably from 50° to 60°C.

[0106] The blowing amount is preferably from 1 to 15 parts by weight/min, preferably from 2 to 10 parts by weight/min, and even more preferably from 3 to 8 parts by weight/min, based on 100 parts by weight of the detergent particles.

[0107] A powdery surfactant and/or a powdery builder can also be added before adding a surfactant composition, simultaneously with adding a surfactant composition, in the course of adding a surfactant composition, or after adding a surfactant composition. By adding the powdery builder, the particle size of the detergent particles can be controlled, and an improvement in detergency can be achieved. In a case where the acid precursor of an anionic surfactant is added, it is more 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" as referred to herein refers to an agent for enhancing detergency other than surfactants which is in a powdery form, concretely, including base materials showing metal ion sequestering ability, such as zeolite and citrates; base materials showing alkalizing ability, such as sodium carbonate and potassium carbonate; base materials having both metal ion sequestering ability and alkalizing ability, such as crystalline silicates; other base materials enhancing ionic strength, such as sodium sulfate; and the like.

[0108] Here, as crystalline silicates, crystalline silicates described in JP-A-Hei 5-279013, column 3, line 17 (those prepared by a process comprising calcinating and crystallizing at a temperature of from 500° to 1,000°C being preferable); JP-A-Hei 7-89712, column 2, line 45; and JP-A-Sho 60-227895, page 2, lower right column, line 18 (the silicates in Table 2 being preferable) can be used as preferred powdery builders. Here, the alkali metal silicates having an $\text{SiO}_2/\text{M}_2\text{O}$ ratio, wherein M is an alkali metal, of from 0.5 to 3.2, preferably from 1.5 to 2.6, are more favorably used.

[0109] The amount of the powdery builder used is preferably from 0 to 12 parts by weight, more preferably from 0 to

6 parts by weight, based on 100 parts by weight of the base particles, When the amount of the powdery builder for detergents used is in the above range, they are excellent in dissolubility.

[0110] Further, subsequent to the step 3, it is preferable to add a step 4 of surface-modifying the detergent particles. step 4: surface-modifying the detergent particles obtained in the step 3 with a surface-coating agent.

Here, in the step 3, disintegration may be progressed concurrently.

step 5: drying the detergent particles obtained in the step 3 or 4.

3-2. Step 4

[0111] In this step, the particle surface of the detergent particles obtained in the step 3 is modified. In order to carrying this out, the embodiments for addition may include a process comprising the step 4 of adding various surface coating agents such as (1) fine powder, and (2) a liquid material. The number of times for the step 4 may be one or more times.

[0112] The free flowability and the anti-caking property of the detergent particles are likely to be improved by modifying the particle surface of the detergent particles with a surface coating agent. Therefore, it is preferable to provide a surface-modifying step in the method of the present invention. The apparatuses to be used in the step 4 are preferably those equipped with both agitation blades and disintegration blades among the mixers exemplified in the step 3. Each of the surface coating agents will be explained below.

(1) Fine Powder

[0113] As the fine powder, it is preferable that the average particle size of its primary particle is preferably 10 μm or less, more preferably from 0.1 to 10 μm . When the particle size is in the above range, it is favorable from the viewpoints of the improvement in the coating ratio of the particle surface of the detergent particles, and improvements in free flowability and anti-caking property of the detergent particles. The average particle size of the fine powder is 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. Further, it is preferable that the fine powder has a high ion exchange capacity or a high alkalizing ability from the aspect of detergency. The fine powder may be constituted by one component, or the fine powder may be constituted by plural components.

[0114] The fine powder is desirably aluminosilicates, which may be any of crystalline or amorphous forms. Besides the aluminosilicates, fine powders of sodium sulfate, calcium silicate, silicon dioxide, bentonite, talc, clay, amorphous silica derivatives, crystalline silicates, and the like are preferable. In addition, a metal soap of which primary particles have an average particle size of from 0.1 to 10 μm , a powdery surfactant (for instance, an alkyl sulfate, or the like), or a water-soluble organic salt can be also similarly used. In addition, when a crystalline silicate is used, it is preferably used in admixture with fine powder other than the crystalline silicate for the purpose of preventing deterioration owing to aggregation of the crystalline silicates by moisture absorption and carbon dioxide absorption, and the like.

[0115] 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, and even more preferably from 2 to 20 parts by weight, based on 100 parts by weight of the detergent particles. When the amount of the fine powder used is in the above range, the free flowability is improved, thereby giving a good sense of feel to consumers.

(2) Liquid Materials

[0116] The liquid materials include water-soluble polymers, fatty acids, and the like, which can be added in the form of aqueous solutions and molten states. The liquid materials may be constituted by one component, or the liquid materials may be constituted by plural components.

(2-1) Water-Soluble Polymer

[0117] The water-soluble polymer includes carboxymethyl celluloses, polyethylene glycols, polycarboxylates such as sodium polyacrylate and copolymers of acrylic acid and maleic acid and salts thereof, and the like. The amount of the water-soluble polymer used is preferably from 0 to 10 parts by weight, more preferably from 0 to 8 parts by weight, and even more preferably from 0 to 6 parts by weight, based on 100 parts by weight of the detergent particles. When the amount of the water-soluble polymer used is in the above range, the detergent particles exhibiting excellent dissolubility and excellent free flowability and anti-caking properties can be obtained.

(2-2) Fatty Acid

[0118] The fatty acid includes, for instance, fatty acids having 10 to 22 carbon atoms, and the like, The amount of the

fatty acid used is preferably from 0 to 5 parts by weight, and more preferably from 0 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 exhibiting free flowability, and then supplied to the detergent particles by spraying.

3-3. Step 5

[0119] In this step, the procedures of drying the resulting detergent particles may be further carried out. By carrying out the above procedures, water derived from a surfactant composition or the like can be removed from the detergent particles.

This step is an optional step of drying the detergent particles obtained in the step 3 or the step 4. By removing water, an active agent component in the detergent particles can be improved.

[0120] A drying method that does not give a strong shearing force as much as possible is preferred, from the viewpoint of suppressing the disintegration of the particles. For example, in a batch process, the drying method includes a method including placing the particles in a vessel, and drying the particles with an electric dryer or a hot air dryer; and a method of drying with a batch-type fluidized bed; or the like. In a continuous process, the drying method employs a fluidized bed, a rotary dryer, a steam tube dryer, or the like.

[0121] The drying temperature is preferably from 40° to 110°C, more preferably from 50° to 100°C, and even more preferably from 60° to 90°C, from the viewpoint of the suppression of degradation of the anionic surfactant and the drying speed.

< Detergent Composition >

[0122] The detergent composition of the present invention is a composition containing the detergent particles described above, and the composition further comprises 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).

[0123] The detergent particles are contained in an amount of preferably 50% by weight or more, more preferably 60% by weight or more, even more preferably 70% by weight or more, and still even more preferably 80% by weight or more and 100% by weight or less, of the detergent composition, from the viewpoint of detergency.

[0124] The detergent components other than the detergent particles are contained in an amount of preferably 50% by weight or less, more preferably 40% by weight or less, even more preferably 30% by weight or less, and still even more preferably 20% by weight or less, of the detergent composition.

< Method for Producing Detergent Composition >

[0125] The method for producing a detergent composition is not particularly limited, and the method includes, for example, a method of mixing the detergent particles and separately added detergent components. Since the detergent composition obtained in the manner described above contains a detergent particle having a large supporting capacity of the surfactant, sufficient detergent effects can be exhibited even with a small amount. The application of such a detergent composition is not particularly limited, as long as it is applied to powder detergent, including, for example, laundry powder detergents, detergents for automatic dishwashers, and the like.

< Measurement Methods of Physical Properties >

1. Bulk Density

[0126] Bulk density is measured in accordance with a method prescribed in JIS K 3362.

Here, in the present invention, the bulk density of the base particles is considered to be a bulk density after excluding particles having sizes of 2000 μm or more, and the bulk density of the detergent particles is considered to be a bulk density after excluding particles having sizes of 1180 μm or more.

2. Degree of Increase in Bulk Density

[0127] In the method for producing detergent particles using the base particles, a degree of increase in bulk density as defined by the following formula can be used as an index showing oil-absorbing ability of the detergent particles. The larger the value of the degree of increase in bulk density, the higher the oil-absorbing ability of the detergent particles. In the present invention, the detergent particles have a degree of increase in bulk density of preferably from 1.2 to 1.7,

and more preferably from 1.3 to 1.6.

Degree of Increase in Bulk Density

$$= \frac{(\text{Bulk Density of Detergent Particles})}{(\text{Bulk Density of Base Particles})}$$

3. Average Particle Size

[0128] Average particle sizes are determined in accordance with the following two methods.

(1) For those having an average particle size of 80 μm or more, an average particle size is obtained by vibrating particles for 5 minutes using standard sieves of JIS K 8801 (sieve openings from 2000 to 125 μm), and calculating a median size from weight percentages according to the sizes of the sieve openings. More specifically, nine-step sieves having sieve openings of 125 μm , 180 μm , 250 μm , 355 μm , 500 μm , 710 μm , 1,000 μm , 1,400 μm , and 2,000 μm and a receiving tray are used, and the sieves are stacked on the receiving tray in the order beginning from those sieves having smaller sieve openings, and 100 g of particles are added from above the uppermost sieve having a size of 2,000 μm , and a lid is placed over the particles, and attached to a rotating and tapping shaker machine (manufactured by HEIKO SEISAKUSHO, tapping: 156 times/min, rolling: 290 times/min). The particles are vibrated for 5 minutes, and the weights of the particles remaining on each of the sieves and the receiving tray are measured, and weight proportions (%) of the particles on each sieve is calculated. The weight proportions of the particles in the order beginning from the receiving tray to those sieves having smaller sieve openings are cumulated, and a particle size at which a total is 50% is defined as an average particle size.

[0129] Here, as to those products having an average particle size of 125 μm or less, similar measurements are carried out using 12-step sieves having sieve openings of 45 μm , 63 μm , 90 μm , 125 μm , 180 μm , 250 μm , 355 μm , 500 μm , 710 μm , 1,000 μm , 1,400 μm , and 2,000 μm , and a receiving tray, and an average particle size is calculated.

Here, in the present invention, the average particle size of the base particles is considered to be an average particle size after excluding the particles having sizes of 2,000 μm or more, and the average particle size of the detergent particles is considered to be an average particle size of the entire particles.

[0130] (2) As to those having an average particle size of less than 80 μm , a laser diffraction/scattering type particle size analyzer LA-920 (manufactured by Horiba, LTD.) is used, and particles are dispersed in a solvent that does not dissolve the particles, and a median size measured is defined as an average particle size. Incidentally, regarding (2), those particles having a size of 150 μm or less can be also measured.

4. Rosin-Rammler Number

[0131] The weights of the particles remaining on each of the sieves and the receiving tray are measured in accordance with a method similar to that of the measurement of the above average particle size to calculate the weight proportions of the particles on each sieve (opening D_p [μm]) (cumulative proportion $R(D_p)$ [μm]). Moreover, a slope n of a least square approximation linear line when plotting $\log(\log(100/R(D_p)))$ against each of $\log D_p$ is defined as a Rosin-Rammler number.

5. Water (Content)

[0132] Water content is measured in accordance with an infrared moisture meter method. Specifically, a 3 g sample is weighed and placed on a weighing dish of a known weight, and the sample is heated at 200°C for the base particles, or at 105 °C for the detergent particles with an infrared moisture meter (FD-240, manufactured by Kett Kagaku Kenkyujo K.K.). A time point at which there is not weight change for 30 seconds is defined as a termination of drying. Thereafter, a water content is calculated from the weight after drying and the weight before drying.

6. Free Flowability

[0133] A flow time is defined as a time period required for flowing 100 mL of powder from a hopper used in a measurement of bulk density as prescribed in JIS K 3362. The free flowability as expressed by the flow time is preferably 10

seconds or less, more preferably 8 seconds or less, and even more preferably 7 seconds or less.

[0134] Here, in the present invention, the free flowability of the base particles is considered to be flowability after excluding particles having sizes of 2000 μm or more, and the free flowability of the detergent particles is considered to be free flowability after excluding particles having sizes of 1180 μm or more.

< Evaluation Methods for Qualities >

1. Oil-Absorbing Ability

[0135] A 30 to 35g powder is supplied into an absorption amount measurement apparatus (S410, manufactured by ASAHISOUKEN), and driving blades are rotated at 200 rpm. To this powder a liquid nonionic surfactant (EMULGEN 108, manufactured by Kao Corporation) is added dropwise at a liquid feeding rate of 4 mL/min, and a point that reaches a maximum torque is probed thoroughly. The amount of the liquid at a point satisfying 70% of the torque of this maximum torque is divided by an amount of the powder supplied, and the resultant value is defined as an oil-absorbing ability.

2. Yield of Base Particles

[0136] The yield of the particles in the present invention is expressed by a weight proportion of the base particles having a particular particle size range in the resulting base particles.

3. Yield of Detergent

[0137] The yield of detergent in the present invention is expressed by a weight proportion of detergent particles having sizes between 250 and 500 μm , or a weight proportion of detergent particles having sizes between 125 and 500 μm .

The following examples further describe and demonstrate embodiments of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention.

EXAMPLES

[0138] In the present examples, the following raw materials were used, unless specified otherwise.

Light Ash: Average particle size: 100 μm (manufactured by Central Glass Co., Ltd., oil-absorbing ability: 0.45 mL/g)

Clay Mineral: Detersoft A (manufactured by Laviosa)

Sodium Polyacrylate: Weight-average molecular weight: 10,000 (manufactured by Kao Corporation)

[0139] The present invention will be further explained on the basis of the following Examples.

< Production of Base Particles 1 >

[0140] Base Particles 1 used in Examples 1 to 7 were produced according to the following procedures.

[0141] The amount 4.2 kg of Light Ash and 0.3 kg of Clay Mineral were mixed in a 75-L rotary drum granulator (ϕ 40 cm x L 60 cm, rotational speed: 30 rpm, Froude number: 0.2) having baffles. After mixing the components for 10 seconds, 2.5 kg of a 35% aqueous solution of sodium polyacrylate was added thereto in 7 minutes with one internal mixing-style two-fluid nozzle (manufactured by Spraying System Japan K.K., pressure for spraying a binder: 0.15 MPa, air spraying pressure for forming fine particles: 0.3 MPa). After the addition, the mixture was formed into particles for 3 minutes, and the particles were then discharged from the rotary drum granulator, and dried at 200°C for 2 hours with an electric dryer. The water content after the drying was 0.5% by weight.

[0142] The resulting particles 1 had physical properties such that the particles had an average particle size of 336 μm and a bulk density of 486 g/L, and had an oil absorbing ability of 0.48 mL/g. Also, the particles had an yield of particles having sizes less than 2000 μm of 96%.

< Production of Base Particles 2 >

[0143] Base Particles 2 used in Examples 8 to 13 were produced according to the following procedures.

[0144] The amount 11.6 kg of Light Ash was mixed in a 122-L rotary drum granulator (ϕ 50 cm x L 62 cm, rotational speed: 18.5 rpm, Froude number: 0.1) having baffles. After mixing the components for 10 seconds, 6.4 kg of a 35% aqueous solution of sodium polyacrylate was added thereto in 7 minutes with two external mixing-style two-fluid nozzles (manufactured by ATMAX INC., air spraying pressure for forming fine particles: 0.3 MPa). After the addition, the mixture

was formed into particles for 1 minute, and the particles were then discharged from the rotary drum granulator, and dried at 200°C for 3 hours with an electric dryer. The water content after the drying was 1.9% by weight.

[0145] The resulting particles 2 had physical properties such that the particles had an average particle size of 305 μm and a bulk density of 487 g/L, and had an oil absorbing ability of 0.56 mL/g. Also, the particles had an yield of particles having sizes less than 2000 μm of 94%.

Production Example 1

[0146] Incidentally, spray-dried particles used in Comparative Examples 1 to 4 were produced according to the following procedures.

[0147] A mixing vessel was charged with 375 parts by weight of water. After the water temperature reached 35°C, 127 parts by weight of sodium sulfate, 5 parts by weight of sodium sulfite, and 1 part by weight of a fluorescer were added thereto, and the components were stirred for 10 minutes. One-hundred and twenty-seven parts by weight of sodium carbonate were added to the mixture, 75 parts by weight of a 40% by weight aqueous solution of sodium polyacrylate were added to the mixture, and the components were stirred for 10 minutes, to provide a first preparation liquid. A fine crystal precipitating agent sodium chloride was added to the first preparation liquid in an amount of 24 parts by weight, and the mixture was stirred for 10 minutes. Further, 266 parts by weight of zeolite were added thereto, and the mixture was stirred for 30 minutes, to provide a homogeneous second preparation liquid (water content of slurry: 42% by weight).

[0148] The second preparation liquid was fed to a spray-drying tower (countercurrent type) with a pump, and sprayed from a pressure spraying nozzle arranged near the top of the tower at a spraying pressure of 2.5 MPa. A high-temperature gas to be fed to a spray-drying tower was supplied at 200°C from the lower part of the tower, and discharged at 90°C from the top of the tower. The resulting spray-dried particles had a water content of 4% by weight, an average particle size of 304 μm and a bulk density of 494 g/L.

Example 1

[0149] A surfactant composition containing an anionic surfactant (R-OSO₃Na, C12/C14/C16 = 64/24/12 (weight ratio); water content: 33% by weight, hereinafter referred to as "Composition A") was heated to 60°C. Next, 100 parts by weight of Base Particles 1 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 60 parts by weight of the above Composition A in 8 minutes, and thereafter the mixture was stirred for 3 minutes. The detergent particles were discharged from the mixer, and dried at 100°C for 2 hours with an electric dryer, to discharge Detergent Particles 1.

[0150] The resulting Detergent Particles 1 had a water content of 0.6%, an average particle size of 353 μm , a Rosin-Rammler number of 1.65, an yield of detergent having sizes from 250 to 500 μm of 52%, an yield of detergent having sizes from 125 to 500 μm of 73%, a bulk density of 755 g/L, and a free flowability of 6.0 s.

Example 2

[0151] Composition A was heated to 60°C. Next, 100 parts by weight of Base Particles 1 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 60 parts by weight of the above Composition A in 8 minutes. Further, after 1 minute from the beginning of supplying of the above Composition A, blowing was started in the mixer. Here, the blowing was carried out under the conditions of a temperature of 60°C, and an amount blown of 7.3 parts by weight/minute based on 100 parts by weight of the detergent particles. After the termination of addition of the above Composition A, the mixture was stirred for 3 minutes, to discharge Detergent Particles 2.

[0152] The resulting Detergent Particles 2 had a water content of 9.2%, an average particle size of 376 μm , a Rosin-Rammler number of 2.04, an yield of detergent having sizes from 250 to 500 μm of 61%, an yield of detergent having sizes from 125 to 500 μm of 76%, a bulk density of 696 g/L, and a free flowability of 5.5 s.

Example 3

[0153] Composition A was heated to 60°C. Next, 100 parts by weight of Base Particles 1 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed

to flow through a jacket at a rate of 10 L/min. Thereto were added 60 parts by weight of the above Composition A in 8 minutes. Further, after 1 minute from the beginning of supplying of the above Composition A, blowing was started in the mixer. Here, the blowing was carried out under the conditions of a temperature of 60°C, and an amount blown of 7.3 parts by weight/minute based on 100 parts by weight of the detergent particles. After the termination of addition of the above Composition A, the mixture was stirred for 3 minutes. The detergent particles were discharged, and dried at 100°C for 2 hours with an electric dryer, to discharge Detergent Particles 3.

[0154] The resulting Detergent Particles 3 had a water content of 0.5%, an average particle size of 374 μm , a Rosin-Rammler number of 2.10, an yield of detergent having sizes from 250 to 500 μm of 61%, an yield of detergent having sizes from 125 to 500 μm of 76%, a bulk density of 688 g/L, and a free flowability of 5.9 s.

Example 4

[0155] Composition A was heated to 60°C. Next, 100 parts by weight of Base Particles 1 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 96.7 parts by weight of the above Composition A in 13 minutes. Further, after 1 minute from the beginning of supplying of the above Composition A, blowing was started in the mixer. Here, the blowing was carried out under the conditions of a temperature of 60°C, and an amount blown of 5.9 parts by weight/minute based on 100 parts by weight of the detergent particles. After the termination of addition of the above Composition A, the mixture was stirred for 3 minutes. The detergent particles were discharged, and dried at 100°C for 2 hours with an electric dryer, to discharge Detergent Particles 4.

[0156] The resulting Detergent Particles 4 had a water content of 0.3%, an average particle size of 447 μm , a Rosin-Rammler number of 1.81, an yield of detergent having sizes from 250 to 500 μm of 47%, an yield of detergent having sizes from 125 to 500 μm of 57%, a bulk density of 716 g/L, and a free flowability of 6.2 s.

Comparative Example 1

[0157] Detergent Particles 5 were obtained in the same manner as in Example 1 using the spray-dried particles obtained in Production Example 1.

[0158] The resulting Detergent Particles 5 had a water content of 0.5%, an average particle size of 441 μm , a Rosin-Rammler number of 2.40, an yield of detergent having sizes from 250 to 500 μm of 58%, an yield of detergent having sizes from 125 to 500 μm of 69%, a bulk density of 562 g/L, and a free flowability of 6.0 s.

Comparative Example 2

[0159] Detergent Particles 6 were obtained in the same manner as in Example 2 using the spray-dried particles obtained in Production Example 1.

[0160] The resulting Detergent Particles 6 had a water content of 10.6%, an average particle size of 423 μm , a Rosin-Rammler number of 2.51, an yield of detergent having sizes from 250 to 500 μm of 58%, an yield of detergent having sizes from 125 to 500 μm of 67%, a bulk density of 559 g/L, and a free flowability of 5.5 s.

Comparative Example 3

[0161] Detergent Particles 7 were obtained in the same manner as in Example 3 using the spray-dried particles obtained in Production Example 1.

[0162] The resulting Detergent Particles 7 had a water content of 0.4%, an average particle size of 410 μm , a Rosin-Rammler number of 2.38, an yield of detergent having sizes from 250 to 500 μm of 59%, an yield of detergent having sizes from 125 to 500 μm of 70%, a bulk density of 544 g/L, and a free flowability of 5.9 s.

Comparative Example 4

[0163] Detergent Particles 8 were obtained in the same manner as in Example 4 using the spray-dried particles obtained in Production Example 1.

[0164] The resulting Detergent Particles 8 had a water content of 0.4%, an average particle size of 454 μm , a Rosin-Rammler number of 2.57, an yield of detergent having sizes from 250 to 500 μm of 53%, an yield of detergent having sizes from 125 to 500 μm of 60%, a bulk density of 565 g/L, and a free flowability of 6.2 s.

Comparative Example 5

[0165] Detergent Particles 9 were obtained in the same manner as in Example 1 using Light Ash in place of Base Particles 1.

[0166] The resulting Detergent Particles 9 had a water content of 0.5%, an average particle size of 321 μm , a Rosin-Rammler number of 1.40, an yield of detergent having sizes from 250 to 500 μm of 42%, an yield of detergent having sizes from 125 to 500 μm of 71%, a bulk density of 627 g/L, and a free flowability of 6.1 s.

Comparative Example 6

[0167] Detergent Particles 10 were obtained in the same manner as in Example 2 using Light Ash in place of Base Particles 1.

[0168] The resulting Detergent Particles 10 had a water content of 9.7%, an average particle size of 291 μm , a Rosin-Rammler number of 0.92, an yield of detergent having sizes from 250 to 500 μm of 17%, an yield of detergent having sizes from 125 to 500 μm of 49%, a bulk density of 761 g/L, and a free flowability of 5.6 s.

Comparative Example 7

[0169] Detergent Particles 11 were obtained in the same manner as in Example 3 using Light Ash in place of Base Particles 1.

[0170] The resulting Detergent Particles 11 had a water content of 0.7%, an average particle size of 278 μm , a Rosin-Rammler number of 0.90, an yield of detergent having sizes from 250 to 500 μm of 17%, an yield of detergent having sizes from 125 to 500 μm of 49%, a bulk density of 712 g/L, and a free flowability of 6.4 s.

Comparative Example 8

[0171] Detergent Particles 12 were obtained in the same manner as in Example 4 using Light Ash in place of Base Particles 1.

[0172] The resulting Detergent Particles 12 had a water content of 0.3%, an average particle size of 728 μm , a Rosin-Rammler number of 1.29, an yield of detergent having sizes from 250 to 500 μm of 20%, an yield of detergent having sizes from 125 to 500 μm of 32%, a bulk density of 655 g/L, and a free flowability of 6.7 s.

Example 5

[0173] Composition A was heated to 60°C. Next, 100 parts by weight of Base Particles 1 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 60 parts by weight of the above Composition A in 2 minutes, and thereafter the mixture was stirred for 3 minutes. The detergent particles were discharged from the mixer, and dried at 105°C for 2 hours with an electric dryer, to discharge Detergent Particles 13.

[0174] The resulting Detergent Particles 13 had a water content of 0.5%, an average particle size of 508 μm , a Rosin-Rammler number of 1.89, an yield of detergent having sizes from 250 to 500 μm of 38%, an yield of detergent having sizes from 1.25 to 500 μm of 48%, a bulk density of 663 g/L, and a free flowability of 6.3 s.

Example 6

[0175] Composition A was heated to 60°C. Next, 100 parts by weight of Base Particles 1 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 60 parts by weight of the above Composition A in 4 minutes, and thereafter the mixture was stirred for 3 minutes. The detergent particles were discharged from the mixer, and dried at 105°C for 2 hours with an electric dryer, to discharge Detergent Particles 14.

[0176] The resulting Detergent Particles 14 had a water content of 0.7%, an average particle size of 475 μm , a Rosin-Rammler number of 1.63, an yield of detergent having sizes from 250 to 500 μm of 38%, an yield of detergent having sizes from 125 to 500 μm of 51%, a bulk density of 679 g/L, and a free flowability of 5.9 s.

Example 7

[0177] Composition A was heated to 60°C. Next, 100 parts by weight of Base Particles 1 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 60 parts by weight of the above Composition A in 4 minutes. Further, after 1 minute from the beginning of supplying of the above Composition A, blowing was started in the mixer. Here, the blowing was carried out under the conditions of a temperature of 60°C, and an amount blown of 7.2 parts by weight/minute based on 100 parts by weight of the detergent particles. After the termination of addition of the above Composition A, the mixture was stirred for 3 minutes. The detergent particles were discharged, and dried at 105°C for 2 hours with an electric dryer, to discharge Detergent Particles 15.

[0178] The resulting Detergent Particles 15 had a water content of 0.4%, an average particle size of 353 µm, a Rosin-Rammler number of 1.88, an yield of detergent having sizes from 250 to 500 µm of 57%, an yield of detergent having sizes from 125 to 500 µm of 75%, a bulk density of 687 g/L, and a free flowability of 5.9 s.

Example 8

[0179] A surfactant composition containing an anionic surfactant (R-OSO₃Na, C12/C14/C16 = 64/24/12 (weight ratio); water content: 35% by weight, hereinafter referred to as "Composition B") was heated to 60°C. Next, 100 parts by weight of Base Particles 2 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 60 parts by weight of the above Composition B in 8 minutes. Further, after 1 minute from the beginning of supplying of the above Composition B, blowing was started in the mixer. Here, the blowing was carried out under the conditions of a temperature of 60°C, and an amount blown of 7.5 parts by weight/minute based on 100 parts by weight of the detergent particles. After the termination of addition of the above Composition B, the mixture was stirred for 3 minutes, to discharge Detergent Particles 16.

[0180] The resulting Detergent Particles 16 had a water content of 9.7%, an average particle size of 358 µm, a Rosin-Rammler number of 1.74, an yield of detergent having sizes from 250 to 500 µm of 48%, an yield of detergent having sizes from 125 to 500 µm of 71%, a bulk density of 665 g/L, and a free flowability of 5.6 s.

Example 9

[0181] Sixty parts by weight of Composition B and 5 parts by weight of sodium polyoxyethylene lauryl ether sulfate (manufactured by Kao Corporation, EMULGEN 270J) were mixed (the mixture hereinafter referred to as "Composition C"), and the mixture was heated to 60°C. Next, 100 parts by weight of Base Particles 2 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 65 parts by weight of the above Composition C in 8.7 minutes. Further, after 1 minute from the beginning of supplying of the above Composition C, blowing was started in the mixer. Here, the blowing was carried out under the conditions of a temperature of 60°C, and an amount blown of 7.3 parts by weight/minute based on 100 parts by weight of the detergent particles. After the termination of addition of the above Composition C, the mixture was stirred for 3 minutes, to discharge Detergent Particles 17.

[0182] The resulting Detergent Particles 17 had a water content of 9.7%, an average particle size of 429 µm, a Rosin-Rammler number of 1.93, an yield of detergent having sizes from 250 to 500 µm of 44%, an yield of detergent having sizes from 125 to 500 µm of 59%, a bulk density of 706 g/L, and a free flowability of 6.3 s.

Example 10

[0183] Composition C was heated to 60°C. Next, 100 parts by weight of Base Particles 2 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 65 parts by weight of the above Composition C in 8.7 minutes. Further, after 1 minute from the beginning of supplying of the above Composition C, blowing was started in the mixer. Here, the blowing was carried out under the conditions of a temperature of 60°C, and an amount blown of 7.3 parts by weight/minute based on 100 parts by weight of the detergent particles. After the termination of addition of the above Composition C, the mixture was stirred for 3 minutes. The detergent particles were discharged, and dried at 105°C for 2 hours with an electric dryer, to discharge Detergent Particles 18.

[0184] The resulting Detergent Particles 18 had a water content of 0.5%, an average particle size of 380 μm , a Rosin-Rammler number of 1.54, an yield of detergent having sizes from 250 to 500 μm of 42%, an yield of detergent having sizes from 125 to 500 μm of 64%, a bulk density of 706 g/L, and a free flowability of 5.9 s.

5 Example 11

[0185] Sixty parts by weight of Composition B and 10 parts by weight of sodium polyoxyethylene lauryl ether sulfate (manufactured by Kao Corporation, EMULGEN 270J) were mixed (the mixture hereinafter referred to as "Composition D") , and the mixture was heated to 60°C. Next, 100 parts by weight of Base Particles 2 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 70 parts by weight of the above Composition D in 9.3 minutes. Further, after 1 minute from the beginning of supplying of the above Composition D, blowing was started in the mixer. Here, the blowing was carried out under the conditions of a temperature of 60°C, and an amount blown of 7.1 parts by weight/minute based on 100 parts by weight of the detergent particles. After the termination of addition of the above Composition D, the mixture was stirred for 3 minutes. The detergent particles were discharged, and dried at 105°C for 2 hours with an electric dryer, to discharge Detergent Particles 19.

[0186] The resulting Detergent Particles 19 had a water content of 0.6%, an average particle size of 421 μm , a Rosin-Rammler number of 1.56, an yield of detergent having sizes from 250 to 500 μm of 40%, an yield of detergent having sizes from 125 to 500 μm of 58%, a bulk density of 728 g/L, and a free flowability of 5.7 s.

Example 12

[0187] Sixty parts by weight of Composition B and 5 parts by weight of polyoxyethylene lauryl ether (manufactured by Kao Corporation, EMULGEN 106) were mixed (the mixture hereinafter referred to as "Composition E"), and the mixture was heated to 60°C. Next, 100 parts by weight of Base Particles 2 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 65 parts by weight of the above Composition E in 8.7 minutes. Further, after 1 minute from the beginning of supplying of the above Composition E, blowing was started in the mixer. Here, the blowing was carried out under the conditions of a temperature of 60°C, and an amount blown of 7.3 parts by weight/minute based on 100 parts by weight of the detergent particles. After the termination of addition of the above Composition E, the mixture was stirred for 3 minutes, to discharge Detergent Particles 20.

[0188] The resulting Detergent Particles 20 had a water content of 9.0%, an average particle size of 435 μm , a Rosin-Rammler number of 1.86, an yield of detergent having sizes from 250 to 500 μm of 40%, an yield of detergent having sizes from 125 to 500 μm of 58%, a bulk density of 700 g/L, and a free flowability of 7.1 s.

Example 13

[0189] Composition E was heated to 60°C. Next, 100 parts by weight of Base Particles 2 obtained were supplied into a Lödige mixer (manufactured by Matsuzaka Giken, volume: 20 L, equipped with a jacket), and stirring of the main shaft (agitation blade, rotational speed: 60 rpm, peripheral speed: 0.9 m/s) was started. Here, a hot water at 60°C was allowed to flow through a jacket at a rate of 10 L/min. Thereto were added 65 parts by weight of the above Composition E in 8.7 minutes. Further, after 1 minute from the beginning of supplying of the above Composition E, blowing was started in the mixer. Here, the blowing was carried out under the conditions of a temperature of 60°C, and an amount blown of 7.3 parts by weight/minute based on 100 parts by weight of the detergent particles. After the termination of addition of the above Composition E, the mixture was stirred for 3 minutes. The detergent particles were discharged, and dried at 105°C for 2 hours with an electric dryer, to discharge Detergent Particles 21.

[0190] The resulting Detergent Particles 21 had a water content of 0.6%, an average particle size of 412 μm , a Rosin-Rammler number of 1.65, an yield of detergent having sizes from 250 to 500 μm of 41%, an yield of detergent having sizes from 125 to 500 μm of 60%, a bulk density of 697 g/L, and a free flowability of 6.8 s.

[0191] Conditions and results of Examples and the like mentioned above are shown in the following tables.

[0192]

[Table 1]

Table-1

		Ex. 1	Ex. 2	Ex. 3	Ex. 4
	Detergent Particles No.	1	2	3	4
	Base Particles/Powder Raw Material	Base Particles 1	Base Particles 1	Base Particles 1	Base Particles 1
	b) Water Content based on 100 parts by weight of Component a) [parts by weight]	49	49	49	49
	Rate of Adding Surfactant Composition [parts by wt/min]	7.5	7.5	7.5	7.4
	Blowing Procedures During Adding/Mixing Step	not conducted	conducted	conducted	conducted
	Procedures of Drying Detergent Particles	conducted	not conducted	conducted	conducted
	Amount of Base Particles/ Powder Raw Material [parts by weight]	100	100	100	100
	Amount of Surfactant Composition (Composition A) [parts by weight]	60	60	60	97
	Amount of Surfactant Composition (Composition B) [parts by weight]	-	-	-	-
	Amount of Surfactant Composition (Composition C) [parts by weight]	-	-	-	-
	Amount of Surfactant Composition (Composition D) [parts by weight]	-	-	-	-
	Amount of Surfactant Composition (Composition E) [parts by weight]	-	-	-	-
	Physical Properties of Detergent Particles				
	Average Particle Size [μm]	353	376	374	447
	Rosin-Rammler Number [-]	1.65	2.04	2.10	1.81
	Yield of Detergent (250-500 μm) [%]	52	61	61	47
	Yield of Detergent (125-500 μm) [%]	73	76	76	57
	Water Content [%]	0.6	9.2	0.5	0.3
	Detergent Particles (Product of less than 1180 μm)				
	Bulk Density [g/L]	755	696	688	716
	Degree of Increase in Bulk Density [-]	1.55	1.43	1.42	1.47
	Free Flowability [s]	6.0	5.5	5.9	6.2

(Continued)

(Continued)

		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
	Detergent Particles No.	5	6	7	8
	Base Particles/Powder Raw Material	Particles in Production Example	Particles in Production Example	Particles in Production Example	Particles in Production Example
	b) Water Content based on 100 parts by weight of Component a) [parts by weight]	49	49	49	49
	Rate of Adding Surfactant [parts by Composition wt/min]	7.5	7.5	7.5	7.4
	Blowing Procedures During Adding/Mixing Step	not conducted	conducted	conducted	conducted
	Procedures of Drying Detergent Particles	conducted	not conducted	conducted	conducted
	Amount of Base Particles/ Powder Raw Material [parts by weight]	100	100	100	100
	Amount of Surfactant Composition [parts by (Composition A) weight]	60	60	60	97
	Amount of Surfactant Composition [parts by (Composition B) weight]	-	-	-	-
	Amount of Surfactant Composition [parts by (Composition C) weight]	-	-	-	-
	Amount of Surfactant Composition [parts by (Composition D) weight]	-	-	-	-
	Amount of Surfactant Composition [parts by (Composition E) weight]	-	-	-	-
	Physical Properties of Detergent Particles				
	Average Particle Size [μm]	411	423	410	454
	Rosin-Rammler Number [-]	2.40	2.51	2.38	2.57
	Yield of Detergent (250-500 μm) [%]	58	58	59	53
	Yield of Detergent (125-500 μm) [%]	69	67	70	60
	Water Content [%]	0.5	10.6	0.4	0.4
	Detergent Particles (Product of less than 1180 μm)				
	Bulk Density [g/L]	562	559	544	565
	Degree of Increase in Bulk Density [-]	1.14	1.13	1.10	1.14
	Free Flowability [s]	6.0	5.5	5.9	6.2

[0193]

[Table 2]

Table-2

		Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Detergent Particles No.		9	10	11	12
Base Particles/Powder Raw Material		Light Ash	Light Ash	Light Ash	Light Ash
b) Water Content based on 100 parts by weight of Component a)	[parts by weight]	49	49	49	49
Rate of Adding Surfactant Composition	[parts by wt/min]	7.5	7.5	7.5	7.4
Blowing Procedures During Adding/Mixing Step		not conducted	conducted	conducted	conducted
Procedures of Drying Detergent Particles		conducted	not conducted	conducted	conducted
Amount of Base Particles/ Powder Raw Material	[parts by weight]	100	100	100	100
Amount of Surfactant Composition (Composition A)	[parts by weight]	60	60	60	97
Amount of Surfactant Composition (Composition B)	[parts by weight]	-	-	-	-
Amount of Surfactant Composition (Composition C)	[parts by weight]	-	-	-	-
Amount of Surfactant Composition (Composition D)	[parts by weight]	-	-	-	-
Amount of Surfactant Composition (Composition E)	[parts by weight]	-	-	-	-
<u>Physical Properties of Detergent Particles</u>					
Average Particle Size	[μm]	321	291	278	728
Rosin-Rammler Number	[-]	1.40	0.92	0.90	1.29
Yield of Detergent (250-500 μm)	[%]	42	17	17	20
Yield of Detergent (125-500 μm)	[%]	71	49	49	32
Water Content	[%]	0.5	9.7	0.7	0.3
<u>Detergent Particles (Product of less than 1180 μm)</u>					
Bulk Density	[g/L]	627	761	712	655
Degree of Increase in Bulk Density	[-]	-	-	-	-
Free Flowability	[s]	6.1	5.6	6.4	6.7

(Continued)

(Continued)

		Ex. 5	Ex. 6	Ex. 7
5	Detergent Particles No.	13	14	15
	Base Particles/Powder Raw Material	Base Particles 1	Base Particles 1	Base Particles 1
10	b) Water Content based on 100 [parts by weight] parts by weight of Component a)	49	49	49
	Rate of Adding Surfactant Composition [parts by wt/min]	30	15	15
15	Blowing Procedures During Adding/Mixing Step	not conducted	not conducted	conducted
	Procedures of Drying Detergent Particles	conducted	conducted	conducted
20	Amount of Base Particles/ Powder Raw Material [parts by weight]	100	100	100
	Amount of Surfactant Composition (Composition A) [parts by weight]	60	60	60
25	Amount of Surfactant Composition (Composition B) [parts by weight]	-	-	-
	Amount of Surfactant Composition (Composition C) [parts by weight]	-	-	-
30	Amount of Surfactant Composition (Composition D) [parts by weight]	-	-	-
	Amount of Surfactant Composition (Composition E) [parts by weight]	-	-	-
35	Physical Properties of Detergent Particles			
	Average Particle Size [μm]	508	475	353
40	Rosin-Rammler Number [-]	1.89	1.63	1.88
	Yield of Detergent (250-500 μm) [%]	38	38	57
	Yield of Detergent (125-500 μm) [%]	48	51	75
45	Water Content [%]	0.5	0.7	0.4
	Detergent Particles (Product of less than 1180 μm)			
	Bulk Density [g/L]	663	679	687
	Degree of Increase in Bulk Density [-]	1.36	1.40	1.41
50	Free Flowability [s]	6.3	5.9	5.9

[0194]

[Table 3]

Table-3

		Ex. 8	Ex. 9	Ex. 10
Detergent Particles No.		16	17	18
Base Particles/Powder Raw Material		Base Particles 2	Base Particles 2	Base Particles 2
b) Water Content based on 100 parts by weight of Component a)	[parts by weight]	54	54	54
Rate of Adding Surfactant Composition	[parts by wt/min]	7.5	7.5	7.5
Blowing Procedures During Adding/Mixing Step		conducted	conducted	conducted
Procedures of Drying Detergent Particles		not conducted	not conducted	conducted
Amount of Base Particles/ Powder Raw Material	[parts by weight]	100	100	100
Amount of Surfactant Composition (Composition A)	[parts by weight]	-	-	-
Amount of Surfactant Composition (Composition B)	[parts by weight]	60	-	-
Amount of Surfactant Composition (Composition C)	[parts by weight]	-	65	65
Amount of Surfactant Composition (Composition D)	[parts by weight]	-	-	-
Amount of Surfactant Composition (Composition E)	[parts by weight]	-	-	-
<u>Physical Properties of Detergent Particles</u>				
Average Particle Size	[μm]	358	429	380
Rosin-Rammler Number	[-]	1.74	1.93	1.54
Yield of Detergent (250-500 μm)	[%]	48	44	42
Yield of Detergent (125-500 μm)	[%]	71	59	64
Water Content	[%]	9.7	9.7	0.5
<u>Detergent Particles (Product of less than 1180 μm)</u>				
Bulk Density	[g/L]	665	706	706
Degree of Increase in Bulk Density	[-]	1.37	1.45	1.45
Free Flowability	[s]	5.6	6.3	5.9

(Continued)

(Continued)

		Ex. 11	Ex. 12	Ex. 13
5	Detergent Particles No.	19	20	21
	Base Particles/Powder Raw Material	Base Particles 2	Base Particles 2	Base Particles 2
10	b) Water Content based on 100 parts by weight of Component a) [parts by weight]	54	54	54
	Rate of Adding Surfactant Composition [parts by wt/min]	7.5	7.5	7.5
15	Blowing Procedures During Adding/Mixing Step	conducted	conducted	conducted
	Procedures of Drying Detergent Particles	conducted	not conducted	conducted
20	Amount of Base Particles/ Powder Raw Material [parts by weight]	100	100	100
	Amount of Surfactant Composition (Composition A) [parts by weight]	-	-	-
25	Amount of Surfactant Composition (Composition B) [parts by weight]	-	-	-
	Amount of Surfactant Composition (Composition C) [parts by weight]	-	-	-
30	Amount of Surfactant Composition (Composition D) [parts by weight]	70	-	-
	Amount of Surfactant Composition (Composition E) [parts by weight]	-	65	65
35	Physical Properties of Detergent Particles			
	Average Particle Size [μm]	421	435	412
40	Rosin-Rammler Number [-]	1.56	1.86	1.65
	Yield of Detergent (250-500 μm) [%]	40	40	41
	Yield of Detergent (125-500 μm) [%]	58	58	60
45	Water Content [%]	0.6	9.0	0.6
	Detergent Particles (Product of less than 1180 μm)			
	Bulk Density [g/L]	728	700	697
	Degree of Increase in Bulk Density [-]	1.49	1.44	1.43
50	Free Flowability [s]	5.7	7.1	6.8

[0195] It was clarified from Examples 1 to 7 that high-density detergent particles having a bulk density of 650 g/L or more can be obtained in a good yield by mixing Base Particles 1 prepared without using spray-drying method and a composition containing an anionic surfactant represented by the formula (1). Also, it was clarified from Examples 8 to 13 that high-density detergent particles having a bulk density of 650 g/L or more can be obtained in a good yield by mixing Base Particles 2 prepared without using spray-drying method and a composition further containing sodium poly-

oxyethylene lauryl ether sulfate or polyoxyethylene lauryl ether in a composition containing an anionic surfactant represented by the formula (1).

[0196] In addition, it was shown by comparison between Examples 1 to 4 and Comparative Examples 1 to 4 that detergent particles having a sharp particle size distribution are obtained by mixing particles obtained by using spray-drying method, and a composition containing an anionic surfactant represented by the formula (1), but high-density detergent particles having a bulk density of 650 g/L or more cannot be stably obtained.

[0197] In addition, it was clarified from the comparison between Examples 1 to 4 and Comparative Examples 5 to 8 that in a case where Light Ash was used place of Base Particles 1, there are some cases where high-density detergent particles having a bulk density of 650 g/L or more are obtained by mixing with a compound of an anionic surfactant represented by the formula (1), but their particle size distribution is broad and yield is low.

INDUSTRIAL APPLICABILITY

[0198] According to the present invention, high-density detergent particles having a necessary particle size can be produced in a high yield by using base particles obtained by a method that does not include spray-drying and a compound of an anionic surfactant represented by the formula (1).

Claims

1. A method for producing detergent particles having a bulk density of 650 g/L or more, comprising the following steps 1 to 3:

step 1: mixing powdery raw materials having an oil-absorbing ability of 0.4 mL/g or more;

step 2: adding water or an aqueous binder solution to a mixed powder obtained by the step 1, and preparing base particles with a low-shearing granulator; and

step 3: mixing the base particles obtained in the step 2, with a surfactant composition comprising the following component **a)** and component **b)**:

a) an anionic surfactant represented by the following formula (1):



wherein R is an alkyl group or alkenyl group having 10 to 18 carbon atoms, and M is an alkali metal atom or an amine; and

b) water in an amount of 25 to 70 parts by weight, based on 100 parts by weight of the above component **a)**.

2. The method according to claim 1, wherein the low-shearing granulator in the step 2 is a pan granulator or a rotary drum granulator.

3. The method according to claim 1 or 2, wherein the surfactant composition in the step 3 further comprises a nonionic surfactant and/or an anionic surfactant other than the anionic surfactant represented by the formula (1).

4. The method according to any one of claims 1 to 3, wherein the surfactant composition is mixed in an amount of 30 to 100 parts by weight, based on 100 parts by weight of the base particles.

5. The method according to any one of claims 1 to 4, further comprising the following step 4:

step 4: surface-modifying the detergent particles obtained in the step 3 with a surface-coating agent.

6. The method according to any one of claims 1 to 5, further comprising the following step 5:

step 5: drying the detergent particles obtained in the step 3 or the step 4.

7. The method according to any one of claims 1 to 6, wherein the step 2 further comprises the procedures of drying the base particles obtained in the step.

8. The method according to any one of claims 1 to 7, wherein the step 3 comprises mixing the base particles and the

surfactant composition under ventilation.

9. The method according to any one of claims 1 to 8, wherein the step 2 comprises adding water or an aqueous binder solution with a multi-fluid nozzle.

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10. The method according to claim 9, wherein the multi-fluid nozzle is a two-fluid nozzle.

11. The method according to any one of claims 1 to 10, wherein the powdery raw materials in the step 1 are powdery raw materials comprising light ash.

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12. Detergent particles obtained by the method as defined in any one of claims 1. to 11.

13. A. detergent composition comprising detergent particles obtained by the method as defined in any one of claims 1 to 11.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/061038

A. CLASSIFICATION OF SUBJECT MATTER <i>C11D11/00</i> (2006.01) i, <i>C11D1/14</i> (2006.01) i, <i>C11D3/10</i> (2006.01) i, <i>C11D17/06</i> (2006.01) i 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) <i>C11D11/00</i> , <i>C11D1/14</i> , <i>C11D3/10</i> , <i>C11D17/06</i> Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2010 Kokai Jitsuyo Shinan Koho 1971-2010 Toroku Jitsuyo Shinan Koho 1994-2010 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 8-73888 A (Lion Corp.), 19 March 1996 (19.03.1996), claims; paragraph [0039]; examples (Family: none)	12, 13 1-11
A	JP 2006-137925 A (Kao Corp.), 01 June 2006 (01.06.2006), claims; examples & EP 1788071 A1 & WO 2006/013982 A1 & CN 101001943 A	1-13
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent 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 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 03 September, 2010 (03.09.10)		Date of mailing of the international search report 14 September, 2010 (14.09.10)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/061038

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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P, A	WO 2009/142135 A1 (Kao Corp.), 26 November 2009 (26.11.2009), claims; paragraphs [0072], [0073]; examples & JP 2010-1460 A	1-13

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