METHOD OF MANUFACTURING WATER-ABSORBENT RESIN AGGLOMERATES, AND WATER-ABSORBENT RESIN AGGLOMERATES

The subject invention provides water-absorbent resin agglomerates having high strength and superior absorbency, and a method of producing water-absorbent resin agglomerates which can prevent agglomeration of hydrated water-absorbent resin, allowing the resin agglomerates to be efficiently dried and cured. A method of producing water-absorbent resin agglomerates according to the present invention comprises the steps of: (a) mixing first water-absorbent resin particles and an aqueous solution so as to produce a hydrated water-absorbent resin; and (b) mixing the hydrated water-absorbent resin with second water-absorbent resin particles or fine particles.
DESCRIPTION

METHOD OF MANUFACTURING WATER-ABSORBENT RESIN
AGGLOMERATES, AND WATER-ABSORBENT RESIN
AGGLOMERATES

5 TECHNICAL FIELD

The present invention relates to a manufacturing method of particle water absorbing agent, and water-absorbent resin agglomerates.

More specifically, the present invention relates to a manufacturing method of water-absorbent resin agglomerates containing a water-absorbent resin as a main component. This manufacturing method produces water-absorbent resin agglomerates which have less fine particles and high granulation strength. The resulting particle water-absorbent resin is generally used extensively as a component of sanitary articles, such as paper (disposable) diapers, sanitary napkins, and so-called incontinence pads, as a component of a waste fluid solidification agent, or as a water block agent.

To be more precise, the present invention provides water-absorbent resin agglomerates and a manufacturing method thereof in which the water-absorbent resin particles are first mixed with an aqueous solution, and then another kind of fine particles are mixed to the mixture. The method
ensures efficient production of water-absorbent resin agglomerates.

BACKGROUND ART

Recently, water-absorbent resins have been used extensively as a component of sanitary articles, such as paper diapers, sanitary napkins, and incontinence pads, to absorb body fluids. The water-absorbent resins are also used for other kinds of product, such as agricultural/gardening tools, for example, a water retention agent, ameliorant etc.

Such a water absorbent resin has been required to have certain properties, including an ability to absorb a sufficient amount of liquid at a sufficient speed when in contact with an aqueous fluid like a body fluid. Other required properties include gel strength, liquid permeability, and absorbing power for absorbing liquid from a base material containing an aqueous fluid. However, these properties are not positively proportional to each other. For example, as the absorbency increases, the liquid permeability, gel strength, and absorption speed decrease.

In view of this problem, a surface cross-linking technology, which cross-links the vicinity of surface of water-absorbing resin, has been known as a method of ensuring high and proportionate water absorbing characteristics of water-absorbent resin. Many different
methods have been disclosed as methods of carrying out this surface cross-linking (Documents 1 to 8 below disclose some examples of the method).

On the other hand, the quality of general water-absorbent resin is regarded superior when the content of powder less than 200μm in particle diameter (fine particle) is smaller. The fine particles cause plugging of absorbent article, such as a paper diaper, thereby decreasing the liquid permeability. The fine particles also cause dust in handling the products, or decrease in production yield. The demands for water-absorbent resin less in content of fine particles have therefore arisen.

There have been some conventional methods of producing a water-absorbent resin less in content of fine particles. Typical methods include (i) a method of controlling agglomeration size by adjusting degree of polymerization, pulverization etc., and (ii) a method of classify/remove the produced fine particles by a sieve or airflow. However, the method (i) still produces a large amount of fine particles, that is about several % to several 10 %. On the other hand, the method (ii) in which the produced fine particles are discarded decreases yield and requires abolishment cost.

In view of this defect, there have been technologies of reusing the fine particles inevitably produced in the
manufacturing process of water-absorbent resin, for example, by reprocessing them into agglomerates. Apart from the re-granulation, there is a method of mixing the fine particles with a polymerization gel (or a substance with high viscosity) so that the particles are reused, as described in Documents 9 to 11. However, these methods cannot ensure sufficient effect of reducing the amount of fine particles.

Further, Documents 12 to 13 suggest a granulation method by mixing the fine particle with water. This method reproduces agglomerates with a high yield, however cannot ensure sufficient reduction of the amount of fine particles of the agglomerate product.

Further, Document 14 – 17 disclose another granulation method in which the water-absorbent resin and an aqueous solution are mixed in the presence of a mixing facilitating agent, such as an inorganic salt compound, water-insoluble inorganic fine powder, a polymer compound, or a metal-ion contained compound. The methods however have different defects, such as increase in cost because of the use of mixing facilitating agent, generation of dust from the water-insoluble inorganic fine powder, or decrease in absorbency of the resulting water-absorbent resin.

Further, in the method of Document 12, the amount of fine particles is reduced by the granulation from the water-absorbent resin powder, but the agglomerates are
damaged (destruction of agglomerates) in the process of transporting the water-absorbent resin or the process of completing the final product (e.g. into paper diaper), and the fine particles are generated again. As a result, properties of resin are often reduced because of decrease in absorption speed, increase of water-soluble content (impurity), or decrease of absorbency against pressure. In view of this, the document mentions necessity of a certain strength of the resulting agglomerates.

Another factor which may affect the properties of the water-absorbent resin is a particle diameter. That is, to ensure the various properties of water-absorbent resin, adjustment of particle diameter is an important factor in the granulation.

Granulation generally designates a process of agglomerating plural particles together so as to form an agglomeration matter having a certain diameter. Many granulation methods of producing water-absorbent resins have been attempted, and most of them use some kind of additives, such as an aqueous solution (water, metallic salt aqueous solution etc.) into a water-absorbent resin, and mix them together by stirring. Meanwhile, in general manufacturing of water-absorbent resin, the content of water-absorbent resin particles less than 200μm in particle diameter (hereinafter referred to as “fine powder”),
particularly of resin powder mainly constituted of particles less than 150μm in particle diameter, is preferably reduced as much as possible.

The fine powder causes plugging of the water-absorbent resin article (such as paper diaper), and decreases liquid permeability of the article. Further, it causes dust in handling the products, or decrease in production yield. Therefore, the demands for water-absorbent resin less in content of fine powder have arisen.

In view of this defect, there have been technologies of reusing the fine powder inevitably produced in the manufacturing process of water-absorbent resin, for example, by reprocessing them into agglomerates. Apart from the re-granulation, there is a method of mixing the fine powder with a polymerization gel, and drying the resulting gel, as described in Documents 9 to 14. The fine powder is thus reprocessed into larger agglomerates. However, in these methods, the fine powder is first processed into gel, and then dried and pulverized. The amount of fine powder is not particularly reduced in the resulting water-absorbent resin.

As to the amount of aqueous solution added to the resin, it is generally either very small (5 - 10 mass %) or very large (100% or more). This is because a water-absorbent resin has a characteristic such that the adhesion of the hydrate water-absorbent resin powder becomes greatest when its solid
content is in a range of 60-80% (content of aqueous solution = 20-40%), with which the powder becomes aggregates. Though it is not relevant to the scope of the present invention, the adhesion property is considered to derive from the hydrogen bond of polyacrylic acid (salt), which is a raw material of the water-absorbent resin. This adhesion property is necessary to change the powder into agglomerates, but if the property is excessively large, it makes the powder to be aggregates.

Meanwhile, a mixture of water-absorbent resin powder and aqueous solution (hydrated water-absorbent resin powder) generally has poor fluidity, and therefore the whole body tends to be agglomerated into a big aggregate. To improve fluidity, the moisture in the surfaces, or in the vicinity of the surfaces, of the hydrated water-absorbent resin powder is scattered to the outside of the system (evaporation/drying), or is diffused into the hydrate water-absorbent resin (curing).

Further, there has been still another manufacturing method of water-absorbent resin, which mixes the resin not only with an aqueous solution, but also with inorganic particles. For example, one of the methods (Document 19) mixes the resin first with an ethylene-acrylic acid co-polymer and inorganic particles, and then with water, so as to ensure certain strength and absorption speed of the resulting resin
(agglomerate). Another method (Document 20) mixes the resin with an aqueous solution and a dispersion solution of inorganic powder, so as to improve the blocking property in moisture absorption.

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[Document 1]
US patent No. 4666983

[Document 2]
US patent No. 4734478

[Document 3]

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US patent No. 5422405

[Document 4]
US patent No. 5140076

[Document 5]
US patent No. 6071976

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[Document 6]
US patent No. 6720389

[Document 7]
US patent No. 5164459

[Document 8]

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US patent No. 6254990

[Document 9]
EP patent No. 463388A

[Document 10]
EP patent No. 417761A

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[Document 11]
EP patent No. 496594A
[Document 12]
US patent No. 6228930
[Document 13]
US patent No. 6458921
[Document 14]
US patent No. 4970267
[Document 15]
EP patent No. 644224

[Document 16]
US patent No. 5002986
[Document 17]
EP patent No. 318989B
[Document 18]

EP patent No. 496594
[Document 19]

Japanese Unexamined Patent Publication *Tokukaihei* 8-113653 (Published on May 7, 1996)
[Document 20]


**DISCLOSURE OF INVENTION**

As described above, many modification of water-absorbent resin were attempted with an aim of reducing
the content of fine particles. However, there has been no easy and reliable method of significantly reducing the fine particle content.

Further, in the conventional method of using an aqueous solution which is mixed with resin by stirring, the particles became aggregates due to the great adhesion force, and the aqueous solution was not evenly mixed with powder. As a result, the mixing by stirring becomes difficult, and the mixture results in a large aggregate (several cm to several 10cm in diameter). If production of resin agglomerates unified in particle diameter is attempted using this highly-adhesive aggregate of hydrated water-absorbent resin, it would be required to stir it with a great power and for a long time (long granulation process is required), and also required to pulverize it with a great force. Therefore, this method likely to increase the manufacturing cost of resin agglomerates (for example, 1mm to 0.15mm in diameter) and decrease physicalities of the resulting agglomerates due to pulverization with a great force.

Further, in the conventional method of mixing an aqueous solution with resin by stirring, the hydrated water-absorbent resin tends to be a large aggregate, which is not easily dried. This is because the heat in the drying process is not likely to be easily transferred to the hydrated water-absorbent resin, and also the moisture is not easily
shifted. As a result, extra heat energy is required in the drying process, but still the sufficient drying is not ensured. This causes defects, such as a decrease in physicalities, and the granulation becomes inefficient.

More specifically, with the conventional method the formation of aggregate cannot be avoided, and therefore the hydrated water-absorbent resin is not sufficiently dried or cured. Consequently, the production of fluid resin agglomerates unified in particle diameter becomes insufficient.

Further, as described above, Document 19 discloses a method in which the resin is first mixed with an ethylene-acrylic acid co-polymer and inorganic particles, and then with more water. This method efficiently produces resin agglomerates having certain strength, absorption speed, and small particle distribution. This method however has no effect of preventing the formation of agglomeration of the hydrated water-absorbent resin, or ensuring efficient drying or curing.

Also, Document 20 discloses a method in which the resin is mixed with an aqueous solution and an inorganic powder dispersion solution. This method has an effect of improving the blocking property in moisture absorption. The method of Document 20 however has no effect of preventing the formation of agglomeration of the hydrated
water-absorbent resin, or ensuring efficient drying or curing, as with the method of Document 19. Besides, this method does not perform the drying process etc. after mixing the water-absorbent resin, aqueous solution and inorganic powder dispersion solution. Therefore the effect of producing fluid resin agglomerates cannot be ensured.

The present invention is made in view of the foregoing conventional problems and an object is to clear away the various defects of a water-absorbent resin caused by the fine particles contained therein, and provide a production method of water-absorbent resin agglomerates with less content of fine particles. This method ensures high granulation strength, and does not cause a decrease in physicalities of agglomerates due to granulation process. Also, the method of the present invention has an effect of preventing agglomeration of hydrated water-absorbent resin, thereby allowing the resin to be dried and cured efficiently.

A method of producing water-absorbent resin agglomerates according to the present invention comprises the steps of (a) mixing first water-absorbent resin particles and an aqueous solution so as to produce a hydrated water-absorbent resin; and (b) mixing the hydrated water-absorbent resin with second water-absorbent resin particles.

The method of producing water-absorbent resin
agglomerates according to the present invention is preferably arranged so that: in the step (b), the hydrated water-absorbent resin is mixed with the second water-absorbent resin particles, and a moisture content of the hydrated water-absorbent resin is not less than 20 mass % but not more than 99 mass %.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: the first water-absorbent resin particles containing the aqueous solution is a hydrated gel.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: the first water-absorbent resin particles have a smaller mass average particle diameter than a mass average particle diameter of the second water-absorbent resin particles.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: the first water-absorbent resin particles each have a cross-linked surface.

The method of producing water-absorbent resin agglomerates according to the present invention preferably further comprises the step of: (c) heating and drying a mixture of (i) the first water-absorbent resin particles containing the aqueous solution and (ii) the second
water-absorbent resin particles.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: a mass ratio of the first water-absorbent resin particles to the second water-absorbent resin particles is in a range of 1/99 to 50/50.

With this arrangement, the aqueous solution is evenly distributed in the water-absorbent resin particles, and therefore a sufficient adhesion force can be given to the water-absorbent resin particles. This makes the resulting agglomerates strong, and thereby facilitates granulation of water-absorbent resin particles in the step (a).

The method of producing water-absorbent resin agglomerates according to the present invention preferably further comprises the step of: (d) classifying the mixture of (i) the first water-absorbent resin particles containing the aqueous solution and (ii) the second water-absorbent resin particles, or a product resulting from the step (c).

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: the water-absorbent resin agglomerates are constituted of the first water-absorbent resin particles and the second water-absorbent resin particles.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably
arranged so that: each of the first water-absorbent resin particles and the second water-absorbent resin particles is a polyacrylic acid based water-absorbent resin.

The water-absorbent resin agglomerates of the present invention are manufactured through special processes which clear away the various conventional defects of a water-absorbent resin caused by the fine particles contained in the water-absorbent resin particles. The method of the present invention ensures reduction in content of fine particle, and high granulation strength, and does not cause a decrease in physicalities of agglomerates due to granulation process.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: in the step (b), the hydrated water-absorbent resin is mixed with fine particles so as to produce a hydrated water-absorbent resin composite, the method further comprises the step of: (i) curing the hydrated water-absorbent resin composite, and/or (ii) drying the hydrated water-absorbent resin composite.

With this method in which the water-absorbent resin particles and an aqueous solution are mixed, the mixture has an adhesion force, with which the particles become agglomerates, i.e., a hydrate water-absorbent resin. Further, the mixture is further mixed with fine particles so that the fine particles are provided on the plane where the hydrate
water-absorbent resin particles are adhered to each other. As a result, the hydrate water-absorbent resin particles are separated, and the fine particles are inserted between the resin particles. In this state, it is likely that only a point of the surface of each resin particles is in contact with the fine particle.

The excessively-grown agglomeration of hydrate water-absorbent resin is thus divided, converted into agglomerates (water-absorbent resin hydrated composite). In this manner, the hydrate water-absorbent resin becomes fluid in a short time. Further, the division of excessively-grown agglomeration of hydrate water-absorbent resin results in a increase in surface area per particle volume, thereby enlarging the gap between the agglomerates. This allows the drying/curing process to be carried out in a short time at a low temperature. In this way, water-absorbent resin agglomerates are manufactured with significantly high efficiency.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: in the step (i), the second water-absorbent resin particles are mixed with a system created by mixing the first water-absorbent resin particles and an aqueous solution so as to produce a hydrated water-absorbent resin.
With this method, plural doses of the water-absorbent resin particles are supplied so that the water-absorbent resin particles, which require an aqueous solution, are unevenly mixed with the aqueous solution.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: in the step (a), an amount of the aqueous solution is not less than 1 part by mass and not more than 150 parts by mass with respect to 100 parts by mass of the first water-absorbent resin particles.

With this method, a desired amount of aqueous solution can be added to the resin particles so that the resin particles have a great adhesion force. This facilitates the granulation of water-absorbent resin particles in the step (a).

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: the first water-absorbent resin particles mainly contain particles less than 200μm in diameter (hereinafter referred to as fine powder), and the second water-absorbent resin particles mainly contain particles not less than 200μm and less than 850μm in diameter (hereinafter referred to as coarse particles), and the hydrated water-absorbent resin is obtained by mixing the coarse particles with a hydrated fine powder which is produced by mixing the fine powder and an aqueous solution.
It is known that the water-absorbent resin powder is constituted of particles of varied diameters, and the easiness of distribution of aqueous solution to the particles depends on the particle diameter. Therefore, when the water-absorbent resin particles are mixed with an aqueous solution, the surface cross-linked powder which contains large-diameter particles may not be fully mixed with the aqueous solution, and therefore the aqueous solution may not be sufficiently distributed to the particles. As a result, the strength of resulting agglomerates would become lower than the desired level. Consequently, a larger amount of particles would remain powder instead of becoming agglomerates, making the resulting agglomerates non-unified in diameter. Further, this may also result in decrease in working environment or decrease in water-absorbent property of the water-absorbent resin agglomerates because of the dust generated from the fine powder.

However, in the foregoing method, the water-absorbent resin particles are classified in advance into two groups: particles less than 200μm in diameter and particles equal to or greater than 200μm in diameter. Then, the fine powder less than 200μm in diameter are first processed into agglomerates, and then the rest of the particles are added to the agglomerates. In this way, fine powder may be efficiently processed into agglomerates, and therefore it is possible to
efficiently obtain agglomerates unified in diameter while reducing the amount of residue fine powder.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: the first water-absorbent resin particles each have a cross-linked surface.

Through the surface cross-linking, the properties, such as liquid permeability, of the water-absorbent resin particles increase. Therefore it is possible to obtain water-absorbent resin agglomerates with superior properties.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: the amount of the fine particles is not less than 0.01 part by mass and not more than 10 parts by mass with respect to 100 parts by mass of the water-absorbent resin particles.

With this arrangement, the amount of fine particles is adjusted to a desired level, allowing the separated particles to be connected again via the fine particles in such a manner that only a point of the surface of each resin particles is in contact with the fine particle. With this state, the hydrated resin powder will not be agglomerated into a aggregate. This method therefore efficiently produces agglomerates relatively uniform in diameter.

The method of producing water-absorbent resin
agglomerates according to the present invention is preferably arranged so that: the fine particles are water-insoluble inorganic fine particles.

With this arrangement, the agglomerated water-absorbent resin agglomerates may be dispersed by a small amount of aqueous solution. Therefore, it is possible to efficiently produce agglomerates relatively uniform in diameter.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: in the steps (i) and/or (ii), the hydrated water-absorbent resin composite is kept at a same temperature or heated up under a temperature range of 30°C to 250°C.

With the temperature range of not less than 30°C and not more than 250°C, the curing and/or drying process is more efficiently carried out compared to the conventional method, and the heating can be performed in a short time by a drier having a small heating capability. Therefore, the foregoing arrangement is very useful for reduction in production time, production cost, power consumption etc.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: the steps (i) and/or (ii) are carried out by way of either or both of still-placement and aeration.
In the case where the curing and/or drying process involves still-placement (no stirring, illiquid state), the curing/drying process is performed without stirring the mixture, which is placed still. In this manner, there is little possibility that the produced agglomerates are destroyed during the curing/drying process, and the physicality of the resulting water-absorbent resin particles will not deteriorate. Further, the process in which the mixture is placed still can be performed at a low energy cost.

Further, in the case where the curing and/or drying process involves aeration, the evaporated moisture moves out of the system. Therefore, the curing/drying process can be performed with high efficiency.

Water-absorbent resin agglomerates according to the present invention are manufactured through one of the foregoing methods of producing water-absorbent resin agglomerates, the water-absorbent resin agglomerates are preferably arranged so that: the water-absorbent resin agglomerates contain moisture in an amount of not less than 5 parts by mass and not more than 20 parts by mass, and contain inorganic fine particles in an amount of not less than 0.01 parts by mass and not more than 10 parts by mass when a total amount of the water-absorbent resin agglomerates is 100 parts by mass,

(1) a centrifuge retention capacity of the water-absorbent
resin agglomerates with respect to a 0.90 mass % of sodium chloride aqueous solution is 27g/g;

(2) an absorption against pressure of 1.9kPa of the water-absorbent resin agglomerates with respect to a 0.90 mass % of sodium chloride aqueous solution is 20g/g;

(3) an absorption against pressure of 4.8kPa of the water-absorbent resin agglomerates with respect to a 0.90 mass % of sodium chloride aqueous solution is 10g/g;

(4) an absorption speed of the water-absorbent resin agglomerates with respect to a 0.90 mass % of sodium chloride aqueous solution is not less than 20 seconds and not more than 50 seconds;

(5) the water-absorbent resin agglomerates contains particles which pass through a JIS standard sieve 150 μm in mesh size in an amount of not less than 0 parts by mass and not more than 5 parts by mass.

In the case of the water-absorbent resin agglomerates with such characteristics are used for a paper diaper or the like, leakage or rewet of the absorbed liquid hardly occurs. The product therefore ensures high physicalities.

The method of producing water-absorbent resin agglomerates according to the present invention is preferably arranged so that: the inorganic fine particles are water-insoluble inorganic fine particles.

With this arrangement, the agglomerated
water-absorbent resin agglomerates may be dispersed by a small amount of fine particles. Therefore, it is possible to efficiently produce agglomerates relatively uniform in diameter.

Additional objects, features, and strengths of the present invention will be made clear by the description below. Further, the advantages of the present invention will be evident from the following explanation in reference to the drawings.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a schematic view showing respective flows of a process of adding aqueous solution and a process of adding fine particles, according to the present invention.

Fig. 2 is a schematic view showing respective flows of a process of adding aqueous solution and a process of adding fine particles, according to a plural-step granulation of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[First Embodiment]

(1) Water-absorbent resin powder

The following explains a manufacturing method of water-absorbent resin powder used for the present invention.

The water-absorbent resin agglomerates of the present
invention can otherwise be expressed as a particle water absorbing agent. The water-absorbent resin particle of the present invention can otherwise be expressed as a water-absorbent resin powder. A publicly-known conventional water-absorbent resin powder is often used for manufacturing of the particle water absorbing agent, particularly one having a carboxyl group. A typical powder (abbreviated name: acrylate water absorbent resin) is produced through polymerization/cross-linking of a hydrophilic unsaturated monomer which contains an acrylic acid and/or the salt thereof as a main component. The powder absorbs a large amount of water, 50 times to 3000 times of its mass, and forms a hydrogel. The water-absorbent resin preferably contains a water-soluble component (specified by Parallel Extraction Polymer (US reissue patent Re 32649)) in an amount of 40 mass % or lower (down to 0 mass %), more preferably 30 mass % or lower, further preferably 20 mass % or lower, still further preferably 15 mass % or lower. Note that, in the present specification, the "powder" has a moisture content (specified in Examples) of 0-30 mass%, preferably 0-20 mass%, more preferably 0-10 mass %.

The acrylate substance may be acrylic acid alkali metallic salt, ammonium salt, amine salt or the like. The water-absorbent resin preferably has a composition of: acrylic
acid = 10-40 mol %, acrylic acid salt = 60-90 mol% (their total amount = 100%). The neutralization of the acrylic acid or its polymer can be carried out with an unsaturated monomer, or can be carried out during/after the polymerization.

The resulting water-absorbent resin may contain other unsaturated monomer than the acrylic acid in addition to the acrylic acid and/or its salt. The unsaturated monomer other than the acrylic acid is not limited, but typical examples include an anionic unsaturated monomer such as (meth)acrylic acid, maleic acid, 2-(meth)acrylamide-2-methylpropane sulfonic acid, 2-(meth)acyloylethane sulfonic acid or the salt thereof; a nonionic unsaturated monomer containing a hydrophilic group such as (meth)acrylamide, 2-hydroxypropyl(meth)acrylate, (methoxy)polyethyleneglycol(meth)acrylate; or a cationic unsaturated monomer of quaternary salt etc. such as N,N-dimethylaminoethyl (meth)acrylate; and the like. Among these, only one monomer may be used, or plural of them may be mixed together. The amount of unsaturated monomer other than acrylic acid is generally 0-30 mol %, preferably 0-10 mol % with respect to the total amount of the acrylic acid and the salt thereof, which are main components of the resin.

Further, as to the polymerization of the foregoing
hydrophilic unsaturated monomer containing acrylic acid and/or the salt thereof during the manufacturing of water-absorbent resin powder used for the present invention, a bulk polymerization or precipitation polymerization may be suitably used. However, a polymerization method using an aqueous solution as the hydrophilic unsaturated monomer, such as aqueous solution polymerization, or reversed phase suspension polymerization, is more preferable in terms of performance and easiness of control of polymerization condition.

examples of unsaturated monomer, cross-linking agent, initiator etc., which are all applicable to the present invention.

Note that, in the case of using the foregoing hydrophilic unsaturated monomer, the concentration of the monomer in the aqueous solution (hereinafter referred to as a monomer aqueous solution) is not particularly limited, however the concentration is preferably in a range of 10-70 mass %, more preferably in a range of 20-40 mass %. Further, in the case of carrying out the aqueous solution polymerization or the reversed phase suspension polymerization, another kind of solvent may be used together with water as required. Any kind of solvent may be used as this additional solvent.

To induce the polymerization, various radical polymerization initiators may be used. As the polymerization initiator, for example, a radical polymerization initiator such as potassium persulfate, ammonium persulfate, sodium persulfate, potassium peracetic, sodium peracetic, potassium percarbonate, sodium percarbonate, t-butylhydroperoxide, hydrogen peroxide, and 2,2'-azobis (2-amidino-propane) dihydrochloride. Further, a reductant may be used to facilitate decomposition of the polymerization initiator. The examples of the reductant include (bi) sulfurous acid (salt) such as sodium sulfite, sodium hydrogen sulfite; or reducing metal such as L-ascorbic acid (salt), or ferrous salt; or
various amines. The reductant is however not limited to these substances. In terms of physicality, the amount of polymerization initiator is generally in a range of 0.001-2 mol %, preferably in a range of 0.01-0.05 mol % with respect to the amount of unsaturated monomer.

Further, polymerization reaction may be induced by irradiating the reaction system with an active energy ray, such as radial ray, electron ray, or ultraviolet light. Note that, the reaction temperature in the polymerization reaction is not particularly limited, but is generally in a range of 10-130°C, preferably in a range of 20-120°C. Further, the reaction time is not particularly limited either, it however should be determined in consideration of types of the hydrophilic unsaturated monomer and polymerization initiator, reaction temperature etc.

The water-absorbent resin used for the present invention may be a self-crosslinking resin, which does not require a cross-linking agent. However, a preferable resin is one obtained by co-polymerization or reaction with an internal cross-linking agent which containing two or more polymerization unsaturated group or two or more reaction groups within a molecule. The examples of internal cross-linking agent include N,N'-methylenebis(meth)acrylamide, (poly)ethyleneglycol(meth)acrylate, (poly)propyleneglycol
di(meth)acrylate, trimethylolpropanetri(meth)acrylate, glyceroltri(meth)acrylate, glycerolacrylatemethacrylate, ethyleneoxide denatured trimethylolpropanetri(meth)acrylate, pentaerythritolhexa(meth)acrylate, triallyl cyanurate, triallyl isocyanurate, triallyl phosphate, triallyl amine, poly(meth)allyloxyalkane, (poly)ethyleneglycoldiglycidylether, glyceroldiglycidylether, ethylene glycol, polyethylene glycol, propylene glycol, glycerine, pentaerythritol, ethylenediamine, ethylene carbonate, propylene carbonate, polyethyleneimine, and glycidyl(meth)acrylate, and the like.

These internal-cross-linking agents may be used either individually or in a suitable combination of two or more kinds. The internal-cross-linking agent may be added to the reaction system either at once or in separate doses. It is however preferable that a cross-linking monomer including not less than two polymerizable unsaturated groups is always used for the polymerization, taking into account the absorption properties or other properties of the product water-absorbing agent. The amount of internal-cross-linking agent used is preferably 0.005 to 2 mol %, more preferably 0.01 to 1 mol % with respect to the content of unsaturated monomer.

Note that, in the polymerization, the following substances may be added to the reaction system: a blowing agent such as (hydrogen) carbonate salt, carbon dioxide, azo compound, inactive organic solvent etc.; a hydrophilic
polymer such as starch and cellulose, a derivative of starch and cellulose, polyvinyl alcohol, polyacrylic acid (polyacrylate), and crosslinked polyacrylic acid (crosslinked polyacrylate); a surfactant; a chain transfer agent such as hypophosphorous acid; a chelating agent or the like. The amount of these agents is preferably in a range of 0-30 mass %, more preferably in a range of 0-10 mass % with respect to the amount of monomer.

When the polymer resulted from the polymerization is a gel, the gel polymer is generally pulverized before/after drying, to become water-absorbent resin.

The method of drying gel polymer is not particularly limited, and a general dryer or a heating oven may be used. The drying is generally performed at a temperature of 80-250°C, preferably of 100-220°C, more preferably of 120-200°C. The drying time is determined to ensure a desired moisture content, taking the surface area of the gel polymer, moisture content, and the types of drier/heatng oven into account.

The water-absorbent resin powder used for the present invention may be particles not processed for particle size after the pulverization, or may be particles processed for particle size according to the usage. Further, in terms of agglomeration strength, each water-absorbent resin particle preferably has an irregular form resulting from the aqueous
solution polymerization rather than the sphere form resulting from the reversed phase suspension polymerization. Further, the water-absorbent resin powder as the material of the water-absorbent resin agglomerate is preferably cross-linked in the surface. However, the resin powder not cross-linked in the surface may also be used. The mass average particle diameter of the water-absorbent resin powder before/after the surface cross-linking is generally in a range of 50-1000μm. The particle size may be adjusted according to the particle size distribution of the two kinds (first, second) of water-absorbent resin powder (described later).

(2) Surface cross-linking process

The following more specifically explains the surface cross-linking process. Various publicly known surface cross-linking methods used for many different purposes in this field (for example, Documents 1 through 8) are also suitable for the present invention.

Examples of the surface cross-linking agent include polyhydric alcohol compounds, such as ethylene glycol, diethylene glycol, propylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, 1,3-propanediol, dipropylene glycol, 2,2,4-trimethyl-1,3-pentanediol, polypropylene glycol, glycerin, polyglycerin, 2-butene-1,4-diol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-cyclohexanediol, 1,2-cyclohexanediol,
trimethylolpropane, diethanolamine, triethanolamine, polyoxypropylene, oxyethylene-oxypropylene block copolymer, pentaerythritol, and sorbitol; epoxy compounds, such as (poly) ethylene glycol diglycidyl ether, (poly, di, or mono) glycerol polyglycidyl ether, (poly) propylene glycol diglycidyl ether, or glycidol; polyamine compounds, such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyethylene-imine or the organic/inorganic salt thereof (aziridinium salt etc.); polyisocyanate compounds, such as 2,4-trilene diisocyanate; polyoxazoline compounds, such as 1,2-ethylenebisoxazoline; carbonate compounds, such as 1,3-dioxolan-2-one; haloepoxy compounds, such as epichlorohydrin, epibromohydrin, or α-methylepichlorohydrin; polyvalent metal compounds, such as hydroxide and chloride, such as zinc, calcium, magnesium, alminium, iron, and zirconium. These substances may be used either individually or in a suitable combination of two or more kinds in consideration of reaction property. Preferably, the cross-linking agent is constituted of at least one kind selected from a polyhydric alcohol compound, an epoxy compound, a polyamine compound and the salt thereof, and an alkylene carbonate compound.

In the case where the foregoing surface cross-linking agents which reacts with a carboxyl group is, as suggested in
US patent No. 5422405 publication, constituted of a first surface cross-linking agent and a second surface cross-linking agent which are different in solubility parameter (SP value), it is possible to produce an absorbing agent further superior in absorbency against pressure. The first surface cross-linking agent is preferably made of a compound not less than 12.5 \((\text{cal/cm}^3)^{1/2}\), more preferably not more than 13.0 \((\text{cal/cm}^3)^{1/2}\) in solubility parameter, which can be reacted with the carboxyl group. The second surface cross-linking agent is preferably made of a compound less than 12.5 \((\text{cal/cm}^3)^{1/2}\), more preferably in a range of 9.5 \((\text{cal/cm}^3)^{1/2}\) to 12.0 \((\text{cal/cm}^3)^{1/2}\) in solubility parameter, which can be reacted with the carboxyl group.

The amount of the surface cross-linking agent with respect to the water-absorbent resin varies depending on the kind of compound used as the material or the combination of the materials. However, the amount is preferably within a range of 0.001 parts by mass to 10 parts by mass, more preferably from 0.01 parts by mass to 5 parts by mass, based on 100 parts by mass of the solid content of water-absorbent resin powder.

Upon mixing the water-absorbent resin with the surface cross-linking agent, it is preferable to use water as the solvent. The amount of water is preferably not less than 0 and not more than 20 parts by mass, more preferably in a
range of 0.5 to 10 parts by mass, based on 100 parts by mass of the water-absorbent resin powder.

Further, upon mixing the water-absorbent resin with the surface cross-linking agent, a hydrophilic organic solvent (aqueous solution) may be used as the solvent as required. Examples of the hydrophilic organic solvent include: lower alcohols, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, or isobutyl alcohol; ketones, such as acetone; ethers, such as dioxane, or tetrahydrofuran. The amount of the hydrophilic organic solvent with respect to the water-absorbent resin is preferably not larger than 20 parts by mass, more preferably not larger than 0-10 parts by mass, based on 100 parts by mass of the water-absorbent resin powder.

Further, to ensure reliable mixing and reaction of the substances, 0-5 parts by mass of basic compound such as surfactant, inactive inorganic powder, organic acid (salt), inorganic acid (salt), caustic soda may be added to 100 parts by mass of water absorbent resin powder.

After mixing the water-absorbent resin powder with the surface cross-linking agent, the resulting mixture is heated to cause the vicinity of the surface of the water-absorbent resin powder to be cross-linked. In consideration of reaction property of cross-linking agent, and of simplicity and productivity of manufacturing device, the cross-linking of the
vicinity of the surface of the water-absorbent resin powder is preferably performed by heating. The temperature of this heating process varies depending on the kind of surface cross-linking agent. However, the temperature of this heating process is preferably set in a range of 80-250°C, more preferably in a range of 100-200°C (heating medium temperature). The heating process can be performed using an ordinary dryer or heating oven. Examples of the heating oven includes a groove-type mixing dryer, a rotary dryer, a disk dryer, a fluidized-bed dryer, a pneumatic conveyor dryer, and an infrared dryer.

(3) Addition of aqueous solution

A manufacturing method of particle water absorbing agent of the present invention includes a (a) step of mixing a first water-absorbent resin powder and an aqueous solution, and a (b) step of mixing the first water-absorbent resin powder having been mixed with the aqueous solution, and a second water-absorbent resin powder.

It is both allowable the first water-absorbent resin powder and the second water-absorbent resin powder are made of the same component, or different component. Similarly, the two kinds of water-absorbent resin powder materials (first, second) of the present invention may have the same particle size distribution, or different particle size distribution. As one preferable combination, polyacrylirate
resin is used for both the first water-absorbent resin powder and second water-absorbent resin powder, but the first water-absorbent resin powder is smaller in particle size diameter than the second water-absorbent resin powder. Further, in addition to the two (first and second) kinds of water-absorbent resin powder, a third or more kinds of water-absorbent resin powder may be used. Further, to be securely mixed with an aqueous solution, at least the first, preferably also the second water-absorbent resin powder, are processed by cross-linking.

The mass average particle diameter of the first water-absorbent resin powder is preferably smaller than 200μm. Further, the content of water-absorbent resin powder 150μm or smaller in particle diameter in the first water-absorbent resin powder is preferably at least 30 mass % (up to 100 mass %), more preferably 50 mass %, further preferably 70 mass %, still further preferably 90 mass %.

The mass average particle diameter of the second water-absorbent resin powder is preferably in a range of 200-800μm, more preferably in a range of 230-600μm, further preferably in a range of 260-500μm.

The second water-absorbent resin powder is preferably dry powder. The dry powder in the present invention does not necessarily mean water content of 0 mass %, as long as in a range of 0-15 mass %, preferably 0-10 mass %.
The ratio of the first water-absorbent resin powder to the second water-absorbent resin powder is not particularly limited, but the mass ratio of the first water-absorbent resin powder to the second water-absorbent resin powder, in other words, the relative percentage of the first water-absorbent resin powder and the second water-absorbent resin powder is generally in a range of 1/99 - 50/50, preferably in a range of 2/98 - 40/60, further preferably in a range of 3/97 - 30/70.

The first water-absorbent resin powder and the second water-absorbent resin powder may be manufactured through any one of the foregoing methods. They may be individually subjected to polymerization, drying, pulverization, and, if required, particle size adjustment and/or surface cross-linking. Otherwise, the first water-absorbent resin powder and the second water-absorbent resin powder may be obtained by classifying water-absorbent resin powder produced through polymerization, drying, pulverization, and, if required, particle size adjustment and/or surface cross-linking. To securely mix the powder with an aqueous solution, at least the first water-absorbent resin powder, preferably also the second water-absorbent resin powder, has a cross-linked surface.

The temperature of the two kinds of water-absorbent resin powder is not an issue to ensure the effect of the
present invention. The temperature is generally 5°C or greater, more preferably 20°C or greater. A temperature greater than 100°C does not make a significant difference, and therefore the process is generally performed at a temperature up to 100°C.

In the present invention, any kind of aqueous solution may be used as an aqueous solution to be mixed with the first water-absorbent resin powder is not limited. Preferable examples include water or an aqueous solution containing water-soluble salt or hydrophilic organic solvent. To ensure various properties or the granulation strength of the powder, the content of water in the aqueous solution is adjusted within a range of 90-100 mass %, preferably in a range of 95-100 mass %, more preferably in a range of 99-100 mass %.

The aqueous solution may contain a small amount of cross-linking agent (e.g. surface cross-linking agent) or a surfactant. Use of cross-linking agent with an aqueous solution may provide effect of reducing water-soluble component, an effect of improving granulation strength etc.

The temperature of the aqueous solution is not an issue to ensure the effect of the present invention. The temperature is generally not less than 5°C up to the boiling point, preferably not less than 20°C. A temperature greater than 100°C does not make a significant difference, and therefore the process is generally performed at a temperature
up to 100°C.

The amount of aqueous solution is generally 1-50 parts by mass, preferably 5-30 parts by mass, more preferably 10-20 parts by mass, all with respect to 100 parts by mass of total amount of the first water-absorbent resin powder and the second water-absorbent resin powder. When the amount of aqueous solution exceeds 50 parts by mass, it becomes difficult to treat the resin as agglomerates, and it requires extra cost of drying process. On the other hand, when the amount of aqueous solution is less than 1 parts by mass, the granulation strength becomes insufficient, and the characteristics of grain cannot be ensured in the resulting product. Besides, the powder and the aqueous solution cannot be securely mixed, and agglomerates may not be produced.

The first water-absorbent resin powder containing the aqueous solution according to the present invention is preferably a hydrated gel. The moisture content (specified in Examples) of the hydrated gel is generally not less than 20 mass %, more preferably in a range of 30-95 mass %, further preferably in a range of 40-90 mass %. With this high hydration, the strength of the resulting agglomerates increases.

In the present invention, the step (a) of mixing the first water-absorbent resin powder with an aqueous solution is not
particularly limited, as long as they are evenly mixed until the agglomerates becomes fine without large agglomerates. In a common method, the aqueous solution is poured into the first water-absorbent resin powder, but it is also allowable that the first water-absorbent resin powder is supplied into the aqueous solution.

The way/condition of pouring an aqueous solution into the first water-absorbent resin powder is not particularly limited. For example, the aqueous solution may be poured at once into the first water-absorbent resin powder being stirred; or, the aqueous solution may be gradually supplied into the first water-absorbent resin powder by, for example, spraying the solution into the resin powder. However, if the supply of the aqueous solution into the first water-absorbent resin powder takes too long, the first water-absorbent resin powder may form a large agglomerate during the mixture, or may be kneaded, thus decreasing quality of water-absorbent resin. The supply of aqueous solution into the resin powder is therefore preferably carried out within 60 seconds, more preferably within 30 seconds, further preferably within 10 seconds.

The way/condition of supplying the first water-absorbent resin powder into an aqueous solution is not particularly limited either. For example, the first water-absorbent resin powder containing an aqueous solution which ensures the
effect of the present invention may be produced by supplying the first water-absorbent resin powder into an aqueous solution being stirred. In this case, the supply of the first water-absorbent resin powder into the aqueous solution is preferably carried out within 60 seconds, more preferably within 30 seconds, further preferably within 10 seconds. Further, the first water-absorbent resin powder containing an aqueous solution which ensures the effect of the present invention may also be produced by supplying the first water-absorbent resin powder and an aqueous solution to a mixer at once. In this case, the supply of two materials is preferably carried out within 60 seconds, more preferably within 30 seconds, further preferably within 10 seconds. Further, the two materials may be supplied together but as several doses so that the first water-absorbent resin powder containing an aqueous solution which ensures the effect of the present invention may be sequentially produced.

If there is a long interval before the mixing of the first water-absorbent resin powder and aqueous solution is actually started after addition of aqueous solution into the first water-absorbent resin powder or addition of the first water-absorbent resin powder into an aqueous solution, the aqueous solution and the first water-absorbent resin powder may not be evenly mixed, and the powder would become a large agglomerate. Therefore the mixing should be started as
soon as possible, preferably within 1 minute, more preferably within 30 seconds after the addition of the first water-absorbent resin powder/aqueous solution. The aqueous solution may be poured into the first water-absorbent resin powder being stirred; or, the first water-absorbent resin powder may be supplied into the aqueous solution being stirred. It is also allowable that the first water-absorbent resin powder and the aqueous solution may be supplied to a mixer at once but as several doses, so as to sequentially produce the first water-absorbent resin powder containing an aqueous solution of the present invention.

In the present invention, the step (b) of mixing the first water-absorbent resin powder containing an aqueous solution with the second water-absorbent resin powder is not particularly limited, as long as they are evenly mixed until the agglomerates becomes fine without large agglomerates. In a common method, the second water-absorbent resin powder is supplied into the first water-absorbent resin powder containing an aqueous solution, but it is also allowable that the first water-absorbent resin powder containing an aqueous solution is supplied into the second water-absorbent resin powder. If there is a long interval before the mixing of the first water-absorbent resin powder containing an aqueous solution and the second
water-absorbent resin powder is actually started after addition of the first water-absorbent resin powder containing an aqueous solution into the first water-absorbent resin powder or addition of the second water-absorbent resin powder into the first water-absorbent resin powder containing an aqueous solution, they may not be evenly mixed, and the mixture would not become the water-absorbent resin agglomerates of the present invention but become a large agglomerate. Therefore the mixing should be started as soon as possible, preferably within 1 minute, more preferably within 30 seconds after the addition of the first water-absorbent resin powder/aqueous solution. The second water-absorbent resin powder may be poured into the first water-absorbent resin powder containing an aqueous solution being stirred; or, the first water-absorbent resin powder containing an aqueous solution may be supplied into the second water-absorbent resin powder being stirred. It is also allowable that the first water-absorbent resin powder containing an aqueous solution and the second water-absorbent resin powder may be supplied to a mixer at once but as several doses, so as to sequentially produce the water-absorbent resin agglomerates of the present invention.

In the present invention, the step (a) of adding an aqueous solution, and the step (b) of adding the second water-absorbent resin powder are preferably carried out
within 60 minutes.

The actual mixing time in the step (a) of adding an aqueous solution and in the step (b) of adding the second water-absorbent resin powder is not restricted. However, when the mixing is performed too long, it may cause degradation of the first water-absorbent resin powder and the second water-absorbent resin powder. The mixing is therefore preferably within 5 minutes, more preferably within 1 minute. A long time mixing may cause degradation of the resulting water-absorbent resin, such as a decrease in absorbency against pressure.

As long as the desired mixing can be performed, any kinds of mixer may be used. However, a mixer with a stationary container, particularly a stirring machine is preferred. Suitable examples include a turbulizer (Hosokawa micron Co. Ltd.), Loedige mixer (M-5R type: product of Loedige Co. Ltd.), and mortar-type mixer (product of Nishi-Nihon Shiken-ki Seisakusho). A batch-type mixer and a continuous mixer are both suitable. Because of its stable performance, the batch-type mixer is preferred in some cases.

The water-absorbent resin agglomerates of the present invention may be further dried to increase agglomeration strength. Therefore, the step (b) is preferably followed by a step (c) of thermal drying of the mixture of the first water-absorbent resin powder and the second water-absorbent
resin powder.

With this thermal drying process, each fine particle becomes integrate, and reproduced as a particle with the same strength of the primary water-absorbent resin powder. The resulting water-absorbent resin agglomerates are superior in shock resistance, and contain less amount of fine particles, and therefore serve as a high-quality particle water absorbing agent. The water-absorbent resin dry agglomerates of the present invention designate resin agglomerates obtained by subjecting the water-absorbent resin agglomerates to a thermal drying process (described later), and are not defined by its moisture content etc. The thermal drying process of the water-absorbent resin agglomerates of the present invention is not particularly limited, and a common drier or an oven may be used. To avoid excessive degradation of the water-absorbent resin agglomerates, the drying process is preferably performed at 40-150°C, more preferably at 60-100°C. The drying has to be carried on for a certain time in consideration of physicalities, generally 1 minute to 10 hour, preferably 3 minutes to 3 hours.

Further, after the step (b) and step (c), the present invention preferably carries out another step (d) for pulverizing/classifying the mixture of the first water-absorbent resin powder containing an aqueous solution and the second water-absorbent resin powder, or the dried
agglomerates. In the pulverization process, excessively large agglomerates (eg. 850μm or greater) are crushed. The pulverization may be carried out for the whole agglomerates or only for large agglomerates.

Further, if necessary, the water-absorbent resin agglomerates or the dried and pulverized/classified water-absorbent resin agglomerates may be further subjected to cross-linking in the vicinities of the agglomeration surfaces. Specifically, water-absorbent resin powder is processed into the water-absorbent resin agglomerates through the foregoing granulation method, and the agglomerates are then dried by heat to be water-absorbent resin dry agglomerates. As a result, a particle water absorbing agent containing small amount of fine particles is produced. The water-absorbent resin agglomerates or the water-absorbent resin dry agglomerates may be further subjected to cross-linking in the vicinities of the agglomeration surfaces to be completed as a particle water absorbing agent.

As described, the water-absorbent resin dry agglomerates of the present invention designate the water-absorbent resin agglomerates and/or the water-absorbent resin dry agglomerates. Further, the water-absorbent resin dry agglomerates of the present invention designate the water-absorbent resin dry agglomerates having been through surface cross-linking.
In contrast to the present invention, a method in which the two kinds (first, second) of water-absorbent resin powder are first mixed together, and the mixture is then mixed with an aqueous solution (single-step granulation) has a difficulty in producing the water-absorbent resin agglomerates or the water-absorbent resin dry agglomerates according to the present invention which ensure high agglomeration strength. Therefore, the water-absorbent resin agglomerates containing small amount of fine particles cannot be produced by this method.

On the other hand, in the foregoing method in which the first water-absorbent resin powder and an aqueous solution are first mixed together, and the mixture is then mixed with the second water-absorbent resin powder, it is possible to produce a particle water absorbing agent containing a small amount of fine particles, which is constituted of resin agglomerates as a mixture of the first water-absorbent resin powder and the second water-absorbent resin powder, without using a special mixer. The particle water absorbing agent of the present invention is not always 100% of agglomerations (agglomerates) constituted of water-absorbent resin particles, and may be a mixture of agglomerations (agglomerates) of water-absorbent resin particles and water-absorbent resin fine particles (primary particles). This fact that the particle water absorbing agent of the present invention is
agglomerations (agglomerates) constituted of plural water-absorbent resin particles may be confirmed by observation of the particle water absorbing agent with an optical microscope, with which the state where a plurality of particles, each of which maintains its original form, is agglomerated is clearly shown. When the particulate water-absorbent resin agent of the present invention absorbs liquid, it is swollen in a unit of plural discontinuous particles. This also proves the alleged structure.

Note that, the production of the particle water absorbing agent of the present invention, that is the resin agglomerates constituted of the first water-absorbent resin powder and the second water-absorbent resin powder, may be easily confirmed by the increase in mass average particle diameter of the raw material, that is water-absorbent resin particles, and/or the decrease in content of fine particles in the resulting resin agglomerates.

(4) Particle water absorbing agent

The absorbency under no pressure (CRC) of the particle water absorbing agent according to the present invention with respect to physiological saline is not less than 27g/g, preferably not less than 30g/g, more preferably not more than 33g/g, further preferably not more than 36g/g. If the absorbency under no pressure is less than 20g/g, the sufficient physicality is not ensured when the particle water
absorbing agent is used for a diaper. The upper limit of CRC is not limited, but is preferably around 60g/g to avoid an increase in cost due to manufacturing complication.

The absorbency against pressure (AAP) of 1.9kPa of the particle water absorbing agent according to the present invention is not less than 20g/g, preferably not less than 22g/g, more preferably not more than 24g/g, further preferably not more than 26g/g. If the absorbency against pressure is less than 20g/g, the sufficient physicality is not ensured when the particle water absorbing agent is used for a diaper. The upper limit of AAP is not limited, but is preferably around 40g/g to avoid an increase in cost due to manufacturing complication.

The mass average particle diameter (D50) of the particle water absorbing agent according to the present invention is preferably 200-800μm, more preferably 250-600μm, further preferably 300-500μm. The content of fine particle (less than 150μm in diameter) is preferably very low. Specifically, the content is preferably 0-5 mass %, more preferably not more than 3 mass %, further preferably not more than 1 mass % before the shock-resistant test, which will be described later in Examples. After the shock resistant test, the content is preferably 0-5 mass %, more preferably not more than 3 mass %. The logarithm standard deviation (σlog) is adjusted within a range of 0.25-0.50, more preferably
within a range of 0.30-0.45.

The production process of the particle water absorbing agent according to the present embodiment may include the step for giving various functions, for example, the step of adding deodorant, antibacterial agent, fragrant materials, various inorganic powders, blowing agent, pigment, dyestuff, hydrophilic short fiber, fertilizer, oxidizer, reducer, water, saline, etc. The amount of these additives is 0-30 mass %, preferably 0-5 mass %. The particle water absorbing agent of the present invention is useful for the various conventional applications of water-absorbent resins. Particularly, with its superior absorbent property against pressure and absorbency speed, and low content of fine particles, the particle water absorbing agent of the present invention is particularly applicable to absorbent cores of various sanitary products, such as paper (disposable) diapers, sanitary napkins, incontinence pads, or absorbent articles, such as a waste fluid solidification agent, a water block agent etc.

[Second Embodiment]

A manufacturing method of particle water absorbing agent according to another embodiment of the present invention includes; a (a) aqueous solution adding process of producing a hydrate water-absorbent resin by mixing a water-absorbent resin powder and an aqueous solution; a (b) fine particle adding process of producing a hydrate
water-absorbent resin composite by mixing the hydrate water-absorbent resin and fine powder; a curing process of curing the hydrate water-absorbent resin composite; and/or a drying process of drying the hydrate water-absorbent resin composite. Note that, the method according to this embodiment is hereinafter referred to as “single-step granulation”. The following explains each process of the method.

<Process of adding aqueous solution>

A process of adding aqueous solution is a process in which the aqueous solution is added to the water-absorbent resin particles so as to obtain a hydrated water-absorbent resin. When the process is carried out, the aqueous solution acts so that the water-absorbent resin particles are granulated, thereby obtaining the hydrated water-absorbent resin.

The water-absorbent resin particles of the present invention are conventionally known water-absorbent resin. For example, the water-absorbent resin particles are a conventionally known cross-linked polymer which absorbs a large amount of water (50 to 1000 times) in ion exchanged water and constitutes anionic, nonionic, or cationic water-insoluble hydrogel.

It is essential that the water-absorbent resin particles are water-swelling and water-insoluble. An amount of
uncross-linked water-soluble component (water-soluble polymer) contained in the water-absorbent resin particles is preferably 0 wt% or more and 30 wt% or less, more preferably 1 wt% or more and 25 wt% or less, still more preferably 5 wt% or more and 20 wt% or less, particularly preferably 5 wt% or more and 15 wt% or less.

Generally, each of these types of the water-absorbent resin particles is obtained as follows: polymerization is carried out in a monomer solution phase, and the polymerized resultant is dried as required, and the resultant is subjected to ordinary pulverization before and/or after being dried. Note that, in the present invention, the water-absorbent resin particles are referred to also merely as a water-absorbent resin.

Specific examples of the cross-linked polymer include: a partially neutralized cross-linked polyacrylic acid polymer (U.S. Patent No. 4625001, U.S. Patent No. 4654039, U.S. Patent No. 5250640, U.S. Patent No. 5275773, European Patent No. 456136, and the like); a cross-linked partially neutralized starch-acrylic acid graft polymer (U.S. Patent No. 4076663); an isobutylene-maleic acid copolymer (U.S. Patent No. 4389513); a saponified vinyl acetate-acrylic acid copolymer (U.S. Patent No. 4124748); a hydrolyzed acrylamide (co)polymer (U.S. Patent No. 3959569); a hydrolyzed acrylonitril copolymer (U.S. Patent No. 3935099); and the
like.

It is preferable that the water-absorbent resin particles used in the present invention are particles of a water absorbent resin made of a cross-linked polyacrylic acid (salt) polymer, obtained by polymerizing a water-insoluble unsaturated monomer containing acrylic acid and/or a salt thereof, which cross-linked polyacrylic acid (salt) polymer contains acrylic acid and/or a salt thereof as a constitutional unit. It is preferable to use the foregoing monomer since the monomer allows further improvement of the obtained water-absorbent resin particles in terms of the water absorbing ability and the safety.

The cross-linked polyacrylic acid (salt) polymer is a cross-linked polymer obtained by polymerizing a monomer containing not less than 50 mol% and not more than 100 mol%, preferably not less than 70 mol% and not more than 100 mol%, more preferably not less than 90 mol% and not more than 100 mol% of acrylic acid and/or a salt thereof, with respect to all constitutional units. Further, preferably not less than 50 mol% and not more than 90 mol%, more preferably not less than 60 mol% and not more than 80 mol% of an acid group contained in the polymer is neutralized. Examples of the salt include: alkali metal salt such as sodium, potassium, and lithium; ammonium salt; and amine salt. The water-absorbent resin for forming salt may be neutralized in a
monomer phase before polymerization, or may be neutralized during and after polymerization, or these processes may be combined with each other.

The polyacrylic acid (salt) cross-linked polymer may be obtained by copolymerizing a monomer (acrylic acid and/or a salt thereof) used as a main component with other monomer as required.

Specific examples of other monomer include: an anionic unsaturated monomer such as methacrylic acid, maleic acid, vinyl sulfonic acid, styrene sulfonic acid, 2-(meth)acrylamide-2-methylpropane sulfonic acid, 2-(meth)acryloyloxyethane sulfonic acid, 2-(meth)acryloyloxypropane sulfonic acid, and salt thereof; a nonionic hydrophilic-group-containing unsaturated monomer such as acrylamide, methacrylamide, N-ethyl(meth)acrylamide, N-n-propyl(meth)acrylamide, N-isopropyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl (meth)acrylate, methoxypolyethyleneeglycol (meth)acrylate, polyethyleneeglycol mono (meth)acrylate, vinylpyridine, N-vinylpyrrolidone, N-acryloylpiperidine, N-acryloylpyrrolidine and N-vinylacetamide; and cationic unsaturated monomer such as N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylamide, and quaternary
salt thereof; and the like.

An amount of the monomer other than acrylic acid and/or a salt thereof is preferably not less than 0 mol% and not more than 30 mol%, more preferably not less than 0 mol% and not more than 10 mol%, with respect to the whole monomer.

The monomer composition may include other hydrophobic unsaturated monomer which is copolymerizable with the unsaturated monomer as long as the hydrophilicity of the obtained cross-linked copolymer is not inhibited. Specific examples of the copolymerizable monomer include: a (meth)acrylic ester such as methyl (meth)acrylate, ethyl (meth)acrylate, and butyl (meth)acrylate; a hydrophobic monomer, having an acid group, a hydroxyl group, or an amino group, such as vinyl acetate and vinyl propionate; and the like. These copolymerizable monomers may be independently used, or a combination of two or more kinds may be used as required.

In polymerizing the monomer to obtain the water-absorbent resin of the present invention, bulk polymerization or precipitation polymerization may be performed. However, in consideration for the performance of a resultant polymer, controllability of polymerization, and absorption characteristics of a swelling gel, more preferable methods of polymerization are aqueous polymerization and
reversed phase suspension polymerization, using an aqueous solution of the monomer.

Note that, when an aqueous solution of the monomer is used, the concentration of the monomer in the aqueous solution (hereinafter, referred to as monomer aqueous solution) is determined in accordance with a temperature of the solution and a type of the monomer and hence is not limited to any particular value. However, the concentration is preferably within 10 wt% to 70 wt%, and more preferably 20 wt% to 60 wt%. In polymerizing the aqueous solution, solvent other than water may be additionally used as required, and a type of the additionally used solvent is not particularly limited.

The reversed phase suspension polymerization is a polymerization method that is carried out by suspending the monomer aqueous solution in a hydrophobic organic solvent. For example, the reversed phase suspension polymerization is described in documents such as United States Patents No. 4093776, No. 4367323, No. 4446261, No. 4683274, and No. 5244735, for example. Further, the aqueous solution polymerization is a polymerization method in which the polymerization is carried out by using the monomer aqueous solution without using a dispersion solvent. For example, the aqueous solution polymerization is described in documents such as U.S. Patent No. 4625001, No. 4873299, No. 4286082,
No.4973632, No. 4985518, No. 5124416, No. 5250640, No. 5264495, No. 5145906, and No. 5380808, and documents such as European Patent No. 0811636, No. 0955086, and No. 0922717. The monomers and initiators used in the polymerization methods described in those patent publications may be used in the present invention.

Examples of the aqueous polymerization include: a method in which the monomer aqueous solution is polymerized in a double arm kneader while crushing a resultant hydrogel; a method in which the monomer aqueous solution is supplied on a belt which is driven in a predetermined vessel and a gel obtained by carrying out the polymerization is crushed by a meat chopper; and the like.

In initiating the polymerization, for example, it is possible to use: a radical polymerization initiator such as potassium persulfate, ammonium persulfate, sodium persulfate, t-butylhydroperoxide, hydrogen peroxide, 2,2'-azobis (2-amidino-propane) dihydrochloride; or a photo polymerization initiator such as 2-hydroxy-2-methyl-1-phenyl-propane-1-one.

Further, redox polymerization may be carried out by additionally using a reducer for promoting decomposition of the polymerization initiator. Examples of the reducer include: (bi)sulfite such as sodium sulfite and sodium bisulfite; reducing metal (salt) such as L-ascorbic acid and ferrous
sulfate; an amine; and the like. However, the reducer is not particularly limited.

An amount of polymerization initiators used is ordinarily within 0.001 to 2 mol%, preferably within 0.01 to 0.1 mol%, with respect to the whole monomer. In case where the amount of the polymerization initiators is less than 0.001 mol%, a larger amount of the monomer is unreacted under this condition, so that a larger amount of residual monomer exists in the resultant water-absorbent resin or the resultant water absorbing agent. Thus, such condition is not preferable. In case where the amount of the polymerization initiators exceeds 2 mol%, a larger amount of water-soluble content exists in the resultant water-absorbent resin or the resultant water absorbing agent. Thus, also such condition is not preferable.

Further, the polymerization reaction may be initiated by irradiating an active energy ray such as a radiant ray, an electron ray, and an ultraviolet ray to the reaction system. Also, the foregoing polymerization initiator may be used together. Note that, a reaction temperature in the polymerization reaction is not particularly limited, but an upper limit of the reaction system is preferably within 15°C to 130°C, more preferably within 20°C to 120°C. A reaction time and a polymerization pressure are not particularly limited, and these conditions may be suitably set in accordance with
types of the monomer and the polymerization initiator, a reaction temperature, and the like.

The cross-linked polymer may be a self cross-linking type obtained without using any cross-linking agent. However, it is preferable to use a cross-linked polymer obtained by copolymerizing or reacting a cross-linking agent having two or more polymerizable unsaturated groups and/or two or more reactive groups.

Examples of the cross-linking agent (referred to also as internal cross-linking agent) include:

N,N’-methylenebis(meth)acrylamide, (poly)ethyleneglycol di(meth)acrylate, (poly)propyleneglycol di(meth)acrylate, (ethylene oxide denaturalized) trimethylolpropanetri(meth)acrylate, trimethylolpropanedi(meth)acrylate, glycerinetri(meth)acrylate, (ethylene oxide denaturalized) glycerineacrylamethacrylate, pentaerythritoltetra(meth)acrylate, dipentaerythritolhexa(meth)acrylate, N,N-diallylacrylamide, triallyl cyanurate, triallyl isocyanurate, triallyl phosphate, triallyl amine, diallyloxy acetate, bis(N-vinylcarboxylic amide), (ethylene oxide denaturalized) tetraallyloxyethane, poly(meth)allyloxyalcane, (poly)ethyleneglycol diglycidyl ether, glycerol diglycidyl ether, ethyleneglycol, polyethyleneglycol, propyleneglycol, glycerine, pentaerythritol, ethylenediamine, polyethylenemine, glycidyl(meth)acrylate, and the like.
These internal cross-linking agents may be used either independently or in a suitable combination of two or more kinds. Particularly, it is preferable that a compound including not less than two polymerizable unsaturated groups is used as the internal cross-linking agent, taking into account the absorption characteristics or other properties of the resultant water-absorbent resin particles. An amount of internal cross-linking agent used is preferably within 0.001 mol% to 2 mol %, more preferably within 0.005 mol% to 0.5 mol %, still more preferably within 0.01 mol% to 0.2 mol %, with respect to a total number of moles of the whole monomer. In case where the amount of the internal cross-linking agent is less than 0.001 mol% and in case where the amount of the internal cross-linking agent is more than 2 mol%, it may be impossible to obtain sufficient absorption characteristics.

In case of introducing the cross-linking structure into the polymer by using the internal cross-linking agent, the internal cross-linking agent is added to the reaction system before, while or after polymerizing the monomer, or the internal cross-linking agent is added to the reaction system after carrying out neutralization.

Note that, in the polymerization, the following substances may be added to the reaction system: starch and cellulose; a derivative of starch and cellulose; 0 to 50 wt% (with respect to the monomer) of hydrophilic polymer such as
polyvinyl alcohol, polyacrylic acid (polyacrylate), and
cross-linked polyacrylic acid (cross-linked polyacrylate); 0 to
10 wt% of blowing agent such as (hydrogen) carbonate,
carbon dioxide, azo compound, and inactive organic solvent; a
starch; various kinds of surfactant; a chelating agent; and a
chain transfer agent such as hypophosphorous acid
(hypophosphate).

In case of the aqueous polymerization, it is general that
the cross-linked polymer obtained by carrying out the
polymerization becomes a aggregate, so that the cross-linked
polymer is pulverized into particles in or after the
polymerization. The pulverization can be carried out by using
each of or a combination of various cutting means such as a
roller type cutter, a guillotine cutter, a slicer, a roll cutter, a
shredder, scissors, and the like, but the cutting means is not
particularly limited. Note that, in case of the reversed phase
suspension polymerization, the polymerization is carried out
in the particulate phase, so that it is generally unnecessary to
carry out the pulverization.

In the water-absorbent resin particles, when the
cross-linked polymer is obtained by carrying out the aqueous
polymerization and is in the gelatinous phase, that is, in case
where the cross-linked polymer is a hydrogel cross-linked
polymer, the cross-linked polymer is dried as required, and
the cross-linked polymer is ordinarily pulverized before
and/or after being dried, thereby obtaining the water-absorbent resin. A drying time depends on a surface area size and a moisture content of the polymer and on a type of a dryer used. The drying time is set, for example, to one minute or more and 10 hours or less so that a desired moisture content is achieved.

The water-absorbent resin particles may be obtained by pulverizing the hydrogel cross-linked polymer into particles or may be obtained by pulverizing or classifying the hydrogel cross-linked polymer having been dried. A particle diameter of the water-absorbent resin particles is not particularly limited, but it is preferable that a particle diameter defined in classification using a standard sieve (using JIS Z8801-1 (2000) or a similar sieve: hereinafter, the particle diameter is defined through the same operation) is less than 850 μm. In case where the particle diameter defined in classification using a standard sieve is more than 850 μm, the particles are likely to be a aggregate while carrying out granulation, and properties such as absorption characteristics of the water-absorbent resin agglomerates are deteriorated. Thus, such particle diameter is not preferable.

As to the particle size of the water-absorbent resin, it is preferable that: particles whose particle diameter is within 600 μm to 850 μm account for not less than 0 wt% and less than 20 wt%, particles whose particle diameter is within 300
μm to 600 μm account for not less than 60 wt%, particles whose particle diameter is less than 200 μm account for less than 20 wt%. In case where the particles whose particle diameter is within 600 μm to 850 μm account for not less than 20 wt% and in case where the particles whose particle diameter is within 300 μm to 600 μm account for less than 60 wt% and the particles whose particle diameter is less than 200 μm account for not less than 20 wt%, a rate at which body fluid (urine, blood, and the like) is absorbed may significantly drop. Thus, such particle size is not preferable.

A logarithmic standard deviation (σ\(^2\)) indicative of a particle size distribution is preferably within 0.25 to 0.400, more preferably within 0.270 to 0.380. In case where the logarithmic standard deviation (σ\(^2\)) indicative of a particle size distribution is less than 0.250, the production cost significantly rises, so that such particle size distribution is not preferable. In case where the logarithmic standard deviation (σ\(^2\)) indicative of a particle size distribution exceeds 0.400, the particle size is likely to be uneven and the granulation strength is unstable, so that such particle size distribution is not preferable.

In the water-absorbent resin particles which can be used in the present invention, an absorbency under no pressure in absorbing 0.90 wt% of sodium chloride aqueous solution is preferably 10 g/g or more and 50 g/g or less, more
preferably 20 g/g or more and 45 g/g or less, still more preferably 25 g/g or more and 45 g/g or less. In case where the absorbency under no pressure in absorbing 0.90 wt% of sodium chloride aqueous solution is less than 10 g/g, it is necessary to add a large amount of cross-linking agent in producing the water-absorbent resin particles, so that an amount of the water-soluble components significantly decreases. As a result, the granulation strength drops and the water-absorbent resin insufficiently absorbs liquid. Thus, in an absorbent core of a diaper or the like, rewet of the absorbed liquid increases or a similar disadvantage occurs, so that the absorbent core becomes sticky.

In case where the absorbency under no pressure in absorbing 0.90 wt% of sodium chloride aqueous solution is more than 50 g/g, an amount of the water-soluble components increases, so that the water-absorbent resin particles are likely to be a aggregate and liquid absorption of the water-absorbent resin particles causes the gel strength of the swollen gel particles to drop. As a result, the gel particles under a pressure such as a body weight are deformed, so that a gel layer volume of the water-absorbent resin drops. Thus, liquid leakage from the absorbent core may occur.

In the water-absorbent resin particles which can be used in the present invention, an absorbency against pressure of 1.9 kPa in absorbing 0.90 wt% of sodium chloride
aqueous solution is preferably 10 g/g or more and 40 g/g or less, more preferably 20 g/g or more and 35 g/g or less. When an absorbent core of a diaper or the like is used, a pressure such as a body weight is always exerted onto the absorbent core. Thus, in case where the absorbency against pressure of 1.9 kPa in absorbing 0.90 wt% of sodium chloride aqueous solution is less than 10 g/g, the water-absorbent resin against pressure insufficiently absorbs liquid, and body fluid (blood, urine, or the like) may leak from the absorbent core and/or the absorbent core may be sticky.

In order to increase the absorbency against pressure of 1.9 kPa in absorbing 0.90 wt% of sodium chloride aqueous solution so that the absorbency is 40 g/g or more, the water-absorbent resin requires improvement. This raises the production cost, but it is impossible to obtain higher granulation strength and an effect corresponding to the improvement. Thus, it is not necessary that the absorbency against pressure of 1.9 kPa in absorbing 0.90 wt% of sodium chloride aqueous solution is 40 g/g or more.

The water-absorbent resin particles are not particularly limited, but it is preferable that the water-absorbent resin particles are subjected to a surface cross-linking treatment. The “surface cross-linking” is reaction between a functional group (particularly, a carboxyl group) in the water-absorbent resin surfaces and a compound (preferably, organic
cross-linking agent or the like) which is reactive with the functional group. By carrying out the surface cross-linking treatment, it is possible to further improve properties required in the water-absorbent resin.

As the surface cross-linking agent which can be used in the surface cross-linking treatment, it is possible to use an organic surface cross-linking agent or a multivalent metal component which can react with a functional group of the water-absorbent resin particles, particularly with a carboxyl group of the water-absorbent resin particles, so as to form a cross-linked structure. Particularly, it is preferable to use, for example, the following organic surface cross-linking agents: polyhydric alcohols such as ethyleneglycol, diethyleneglycol, propyleneglycol, triethyleneglycol, tetraethyleneglycol, polyethyleneglycol, 1,3-propanediol, dipropyleneglycol, 2,2,4-trimethyl-1,3-pentandiol, polypropyleneglycol, glycerin, polyglycerin, 2-butene-1,4-diol, 1,3-butandiol, 1,4-butandiol, 1,5-pentandiol, 1,6-hexanediol, 1,2-cyclohexanedimethanol, 1,2-cyclohexanol, trimethylolpropane, diethanolamine, triethanolamine, polyoxypropylene, oxyethylene-oxypropylene block copolymer, pentaerythritol, and sorbitol; epoxy compounds such as ethyleneglycol diglycidyl ether, polyethyleneglycol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, propyleneglycol diglycidyl ether, polypropyleneglycol
diglycidyl ether, and glycidol; multivalent amine compounds such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and polyethyleneimine, and inorganic salts or organic salts thereof (for example, aziridinium salt and the like); multivalent isocyanate compounds such as 2,4-tolylenediisocyanate, and hexamethylenediisocyanate; multivalent oxazoline compounds such as 1,2-ethylenebisoxazoline; carbonic acid derivatives such as urea, thiourea, guanidine, dicyandiamide, and 2-oxazolidinone; alkylene carbonate compounds such as 1,3-dioxolane-2-one, 4-methyl-1,3-dioxolane-2-one, 4,5-dimethyl-1,3-dioxolane-2-one, 4,4-dimethyl-1,3-dioxolane-2-one, 4-ethyl-1,3-dioxolane-2-one, 4-hydroxymethyl-1,3-dioxolane-2-one, 1,3-dioxane-2-one, 4-methyl-1,3-dioxane-2-one, 4,6-dimethyl-1,3-dioxane-2-one, and 1,3-dioxisopane-2-one; haloepoxy compounds such as epichlorohydrin, epibromohydrin, and α-methylepichlorohydrin, and multivalent amine addition products thereof (for example, Kymene produced by Hercules: registered trademark); silane coupling agents such as γ-glycidoxypropyltrimethoxysilane and γ-aminopropyltriethoxysilane; and oxethane compounds such as 3-methyl-3-oxethane methanol, 3-ethyl-3-oxethane methanol, 3-butyl-3-oxethane methanol, 3-methyl-3-oxethane
ethanol, 3-ethyl-3-oxethane ethanol, 3-butyl-3-oxethane ethanol, 3-chloromethyl-3-methylloxethane, 3-chloromethyl-3-ethylloxethane, and a multivalent oxethane compound; and the like. These surface cross-linking agents may be used either independently or in a suitable combination of two or more kinds. Among the cross-linking agents, the polyhydric alcohol is preferable since it is superior in terms of safety and it improves the hydrophilic property of the surfaces of the water-absorbent resin particles.

In the surface cross-linking treatment, when the surface cross-linking agent which can react with a carboxyl group is obtained by mixing a first surface cross-linking agent and a second surface cross-linking agent different from each other in terms of a solubility parameter (SP value) as proposed by USP No. 5422405, it is possible to obtain an absorbing agent whose absorbency against pressure is further improved. The first surface cross-linking agent is preferably a compound which is reactive with a carboxyl group and has a solubility parameter of not less than 12.5 (cal/cm³)¹/², more preferably a compound which is reactive with a carboxyl group and has a solubility parameter of not less than 13.0 (cal/cm³)¹/² (its upper limit is 23.4 (cal/cm³)¹/²). The second surface cross-linking agent is preferably a compound which is reactive with a carboxyl group and has a solubility parameter
of less than 12.5 (cal/cm³)¹/², more preferably a compound which is reactive with a carboxyl group and has a solubility parameter of not less than 9.5 (cal/cm³)¹/² and not more than 12.0 (cal/cm³)¹/²).

It is preferable that an amount of the surface cross-linking agent used is 0.001 part by weight or more and 5 parts by weight or less with respect to 100 parts by weight of the solid content of the water-absorbent resin particles.

In mixing the water-absorbent resin particles with the surface cross-linking agent, it is preferable to use water as solvent of the surface cross-linking agent. An amount of water used is preferably more than 0 and 20 parts by weight or more, more preferably 0.5 parts by weight or more and 10 parts by weight or less, with respect to 100 parts by weight of the water-absorbent resin particles.

In mixing the water-absorbent resin particles with the surface cross-linking agent, a hydrophilic organic solvent (aqueous liquid) may be used together as required. Examples of the hydrophilic organic solvent include: monovalent alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, and isopropyl alcohol; ketones such as acetone; ethers such as dioxane and tetrahydrofuran; and the like. With respect to 100 parts by weight of the water-absorbent resin particles, an amount of the hydrophilic organic solvent is preferably 20 parts by weight or less, more preferably 0
part by weight or more and 10 parts by weight or less.

In order to improve the mixing property and the reactivity, 0 part by weight or more and 5 parts by weight or less of a basic compound such as surfactant, inert inorganic powder, organic acid (salt), inorganic acid (salt), caustic soda, and the like may be used together.

It is preferable to spray or drop/mix the thus obtained aqueous solution to a water-absorbent resin obtained by mixing the water-absorbent resin particles with the surface cross-linking agent, and it is more preferable to spray the aqueous solution. As to a size of a droplet sprayed, an average particle diameter thereof preferably ranges from 0.1 μm to 300 μm, more preferably from 0.1 μm to 200 μm. In case of mixing the water-absorbent resin particles with the surface cross-linking agent, water-insoluble fine powder and surfactant may coexist as long as the effect of the present invention is not impaired.

After the water-absorbent resin particles and the surface cross-linking agent are mixed with each other, the mixture is heated, thereby cross-linking surfaces of the water-absorbent resin particles. That is, in order to react the cross-linking agent in the vicinity of the surfaces of the water-absorbent resin particles, it is preferable to carry out the heating treatment in consideration for the simplicity and the productivity of the production device. A temperature at
which the heating treatment is carried out depends on a type of the surface cross-linking agent used, but it is preferable that the heating treatment is carried out at a temperature ranging from 80°C to 250°C, more preferably from 100°C to 200°C. The heating treatment can be carried out by using a general dryer or a general heating oven. Examples of the dryer include a groove type mixing dryer, a rotary dryer, a disk dryer, a fluidized-bed dryer, an flash dryer, an infrared dryer, and the like.

The "aqueous liquid" is water, aqueous solution or slurry which includes water-soluble metallic salt, or hydrophilic organic solvent, water-soluble polymer, surfactant, and water-insoluble organic particles.

The aqueous liquid is not particularly limited, but a slight amount of cross-linking agent (for example, the aforementioned cross-linking agent) or surfactant may be included so that a rate of water included in the aqueous liquid ranges from 70 wt% or more and 100 wt% or less, preferably from 80 wt% or more and 100 wt% or less, more preferably from 90 wt% or more and 100 wt% or less. In order to achieve the object of the present invention, a temperature of the aqueous liquid is not particularly limited, but the temperature is generally 5°C or higher and the boiling point or lower, preferably 20°C or higher. There is no change when the temperature exceeds 100°C, so that the temperature is
generally set to 100°C or lower.

With respect to 100 parts by weight of the water-absorbent resin particles, an amount of the aqueous liquid used is generally within 1 part by weight to 150 parts by weight, preferably within 5 parts by weight to 100 parts by weight, more preferably within 5 parts by weight to 50 parts by weight, still more preferably within 5 parts by weight to 30 parts by weight, most preferably within 5 parts by weight to 20 parts by weight. When the amount of the aqueous liquid exceeds 150 parts by weight, a aggregate is likely to occur, so that it is difficult to treat the resultant as agglomerates. Moreover, this is disadvantageous in terms of the drying cost, the property, and the like. While, in case where the amount of the aqueous liquid used is less than 1 part by weight, the granulation strength is insufficient, so that the final product may be incapable of exhibiting the granulation property. Further, the components are unevenly mixed, so that it may be impossible to obtain the agglomerates.

The mixture of the water-absorbent resin particles and the aqueous liquid can be carried out by using a conventional known mixer. The mixer used is not particularly limited, but it is preferable to use a vessel fixing mixer, particularly, it is preferable to use a mechanical stirring mixer. Examples thereof include a cylindrical mixer, a screw mixer, a screw extruder, a turbulizer, a nauta mixer, a V-shaped mixer, a
ribbon blender, a double-arm kneader, a flow mixer, an air current mixer, a rotary disc mixer, a roll mixer, a convolution mixer, a paddle mixer, and a Loedige mixer. Further, the mixer may be a batch-type mixer or a sequential-type mixer. It may be preferable to use the batch-type mixer since it is possible to achieve the stable performance.

A method for adding the aqueous liquid to the water-absorbent resin particles is not particularly limited. However, in order to efficiently carry out the granulation, it is preferable to adopt: a method in which it is possible to evenly disperse the aqueous liquid into the water-absorbent resin particles; a method in which the aqueous liquid is sprayed into the mixer; or the like.

In this specification, the "hydrated water-absorbent resin" is a resultant in which at least the water-absorbent resin particles and the aqueous liquid are mixed with each other and at least a part of the aqueous liquid is absorbed in the water-absorbent resin particles. A temperature of the hydrated water-absorbent resin is within 30°C to 100°C, preferably within 40°C to 100°C, more preferably within 50°C to 100°C. Other component which can be mixed therewith is not particularly limited as long as the component does not prevent the aqueous liquid from granulating the water-absorbent resin. For example, it is possible to mix (i) aqueous multivalent metal salt or the cross-linking agent
which enhances liquid permeation in the water-absorbent resin, (ii) color protection agent, (iii) and the like.

Examples of the aqueous multivalent metal salt include aluminum chloride, aluminum polychloride, aluminum sulfate, aluminum nitrate, aluminum potassium bis sulfate, sodium aluminum bis sulfate, potassium alum, ammonium alum, sodium alum, sodium aluminate, calcium chloride, calcium nitrate, magnesium chloride, magnesium sulfate, magnesium nitrate, zinc chloride, zinc sulfate, zinc nitrate, zirconium chloride, zirconium sulfate, and zirconium nitrate.

Examples of the color protection agent include: sulfuric reducer; chelating agent such as amino multivalent carboxylic acid or salt thereof and organic phosphoric compound or salt thereof; hydrogen peroxide; and the like.

The hydrated water-absorbent resin may be obtained by mixing second water-absorbent resin particles with a system obtained by mixing first water-absorbent resin particles and the aqueous liquid. The wording of “first water-absorbent resin particles” and “second water-absorbent resin particles” means that the water-absorbent resin particles are mixed with the aqueous solution in two steps. As each of the first and second water-absorbent resin particles, it is possible to use water-absorbent resin particles which are similar to the water-absorbent resin particles described above. Types of the first and second water-absorbent resin particles may be
identical with each other or may be different from each other.

Particle diameters of the first and second water-absorbent resin particles may be equal to each other or may be different from each other. For example, the first water-absorbent resin particles may be in the fine powder phase and the second water-absorbent resin particles may be in a coarse particle phase. A method for mixing the water-absorbent resin particles with the aqueous liquid in two steps will be described later.

According to the thus described process of adding aqueous solution, the mixture of the water-absorbent resin particles and the aqueous solution brings about adhesiveness, so that granulation is carried out, thereby obtaining the hydrated water-absorbent resin.

<Process of adding fine particles>

The process of adding fine particles is a process in which at least the hydrated water-absorbent resin and fine particles so as to obtain a hydrated water-absorbent resin composite. According to the process, the hydrated water-absorbent resin is disaggregated into agglomerate particles (hydrated water-absorbent resin composition) having a relatively even particle diameter, so that it is possible to give the hydrated water-absorbent resin the fluidity in a short time. Further, since the hydrated water-absorbent resin is disaggregated, a surface area for each particle volume
increases, so that a gap between the agglomerate particles increases. Thus, it is possible to cure the hydrated water-absorbent resin at a lower temperature and in a shorter time.

Examples of the fine particles favorably used in the present invention include silicon dioxide, aluminum oxide, titanium dioxide, calcium phosphate, calcium carbonate, diatom earth, bentonite, zeolite, other metal oxide, and the like. The fine particles mixed with the hydrated water-absorbent resin in the process of adding fine particles include no water-absorbent resin fine particles. Examples of the fine particles include organic fine particles such as chitin, chitosan, cellulose, pulp, soluble starch, and the like. It is preferable that both the inorganic fine particles and the organic fine particles are water-insoluble or hardly soluble in water. Particularly, it is preferable to use water-insoluble inorganic fine particles which exhibit any effect when even a slight amount of the water-insoluble inorganic fine particles is added. A substance which is hardly soluble in water means a substance whose solubility in water at 23°C is less than 5 wt% or 1 wt% or more.

A particle diameter of the fine particles is preferably 100 μm or less, more preferably 50 μm or less, still more preferably 10 μm or less. It is particularly preferable that a lower limit thereof is about 1 nm. When the particle diameter
exceeds 100 μm, it is impossible to obtain sufficient granulation strength and it is impossible to sufficiently disaggregate the hydrated water-absorbent resin. Such condition is not preferable. Note that, the particle diameter can be measured by a Coulter counter or the like.

The fine particles have to be added to the hydrated water-absorbent resin. That is, it is necessary to add the fine particles to a reaction system after mixing the water-absorbent resin particles with the aqueous liquid. If the aqueous liquid is added after mixing the water-absorbent resin particles with the fine particles, a aggregate whose length is several mm may be formed. Such condition is not preferable.

A method for adding the fine particles to the hydrated water-absorbent resin is not particularly limited. Examples of the method include: a method in which the fine particles are added directly to the hydrated water-absorbent resin; a method in which solution obtained by dispersing the fine particles into various kinds of organic solvent or the like is sprayed or dropped to the water-absorbent resin; and the like. As described above, the hydrated water-absorbent resin may be obtained by further mixing water-absorbent resin particles to a system obtained by mixing those water-absorbent resin particles with the aqueous liquid. In this case, the fine particles may be mixed with the further added
water-absorbent resin particles in advance.

Note that, the mixture of the water-absorbent resin particles and the fine particles can be carried out by using a conventional known mixer described in [Process of adding aqueous solution].

In this specification, the "hydrated water-absorbent resin composite" is a mixture of at least the hydrated water-absorbent resin and the fine particles. The hydrated water-absorbent resin and the fine particles may be coupled to each other. Examples of other mixable components include aqueous liquid in which the fine particles are to be dispersed, various kinds of organic solvent, and the like.

The hydrated water-absorbent resin composite solely has fluidity. This results from the following condition: the fine particles are further mixed with the mixture of the water-absorbent resin particles and the aqueous liquid, so that the hydrated water-absorbent resin is disaggregated, thereby preventing the resultant from changing into the aggregate. Thus, it is possible to smoothly carry out a process of curing and/or a process of drying that will be described later. The fluidity is not particularly limited, but it is preferable that a flowing rate (based on a measurement method recited in Examples described later) measured within 10 minutes after finishing the process of adding fine particles is within 30 seconds.
An amount of the fine particles is not particularly limited. However, with respect to 100 parts by weight of the hydrated water-absorbent resin, the amount of the fine particles is preferably 0.01 parts by weight or more and 10 parts by weight or less, more preferably 0.05 parts by weight and 10 parts by weight or less, particularly preferably 0.1 part by weight or more and 10 parts by weight or less.

When the amount of the fine particles is less than 0.01 part by weight, the amount of the fine particles is too small, so that the fine particles cannot sufficiently intervene between the water-absorbent resin particles. As a result, it is impossible to sufficiently disaggregate the excessively growing hydrated water-absorbent resin. Such condition is not preferable. While, when the amount of the fine particles exceeds 10 parts by weight, performances (absorbency against pressure: described later) of the water-absorbent resin may drop. Such condition is not preferable.

According to the process of adding fine particles, the fine particles such as silicon dioxide act so as to disaggregate the excessively growing hydrated water-absorbent resin, so that the fine particles change into agglomerates (hydrated water-absorbent resin composite) having a relatively even particle diameter. As a result, it is possible to give the hydrated water-absorbent resin the fluidity in a short time. Further, since the hydrated water-absorbent resin is
disaggregated, a surface area for each particle volume increases, so that a gap between the agglomerates increases. Thus, it is possible to smoothly carry out the process of curing which will be described later.

Fig. 1 is a schematic illustrating the process of adding aqueous solution and the process of adding fine particles. As illustrated in Fig. 1, the mixture of the water-absorbent resin particles and the aqueous liquid promotes the granulation, thereby obtaining the hydrated water-absorbent resin. Subsequently, the mixture of the hydrated water-absorbent resin and/or an agglomeration thereof and the fine particles dis aggregate the hydrated water-absorbent resin, thereby generating the hydrated water-absorbent resin composite without generating any aggregate.

<Process of curing>

The process of curing is a process in which the hydrated water-absorbent resin composite is kept warm or is heated so that the hydrated water-absorbent resin composite is cured. The “curing” is such a phenomenon that: moisture (aqueous liquid) included in the hydrated water-absorbent resin composite is absorbed in the water-absorbent resin, so that the surface of the water-absorbent resin seems to be dry. Note that, whether the curing is finished or not can be determined by the hardness and the fluidity of the surfaces of the agglomerate particles.
<Process of drying>

The process of drying is a process in which the hydrated water-absorbent resin composite is kept warm and is heated so that the hydrated water-absorbent resin composite is dried. In this specification, the "drying" means such condition that: moisture (aqueous liquid) included in the hydrated water-absorbent resin composite externally flies in all directions (this also means evaporation).

The process of curing and the process of drying can be simultaneously carried out since the hydrated water-absorbent resin composite is heated or is kept warm in both the processes. While, only the process of curing or only the process of drying may be carried out.

A method for keeping the hydrated water-absorbent resin composite warm or heating the hydrated water-absorbent resin composite is not particularly limited. For example, it is possible to favorably adopt a conventional method in which a single heater or two or more heaters such as a doldrums dryer, a band dryer, a stirring dryer, and a fluidized bed dryer are used. The hydrated water-absorbent resin composite may be kept warm or may be heated while being stirred. Alternatively, the hydrated water-absorbent resin composite may be kept warm or may be heated while being left still. A moisture content of the water-absorbent resin agglomerates obtained by carrying out the process of
curing and/or the process of drying preferably ranges from 0.5 wt% to 50 wt%, more preferably from 2 wt% to 30 wt%, particularly preferably from 5 wt% to 20 wt%.

A temperature at which the hydrated water-absorbent resin composite is heated or is kept warm preferably ranges from 30°C to 250°C, more preferably from 40°C to 200°C, further preferably from 50°C to 150°C. A time for which the hydrated water-absorbent resin composite is heated or is kept warm ranges from one minute to two hours, preferably from one minute to one hour. The “temperature at which the hydrated water-absorbent resin composite is heated or is kept warm” is a temperature of a heat medium. In case where it is impossible to define the heat medium temperature as in drying with a microwave, the temperature is defined by a material temperature.

In the production method according to the present invention, the hydrated water-absorbent resin composite obtained by mixing the hydrated water-absorbent resin with the fine particles has the fluidity and can be sufficiently cured and/or dried at a low temperature and in a short time. This new finding is based on the following condition: the hydrated water-absorbent resin is disaggregated by the fine particles mixed with the hydrated water-absorbent resin so as to increase a surface area for each particle volume, so that a gap between the agglomerate particles increases, which makes
it easier for thermal energy to spread among the agglomerate particles.

While, Patent Document 19 discloses the following condition: when fine powdery sirica was mixed with a mixture of high water-absorbent resin powder and oil-in-water type emulsion of an ethylene-and-acrylic-acid copolymer, a large number of aggregates occurred. That is, it is the present invention that first found the following condition: By adding and mixing the fine particles after obtaining the hydrated water-absorbent resin through mixture of the water-absorbent resin particles and the aqueous liquid, it is possible to obtain a hydrated water-absorbent resin composite which has the fluidity and can be efficiently heated.

Note that, the object of the invention disclosed in Patent Document 19 is to enhance the granulation strength (adhesiveness between particles) by adding an ethylene-and-acrylic-acid copolymer. Let us assume that the object in adding the fine powdery sirica is the same as the object of the present invention (reduction of adhesiveness due to an inorganic substance intervening between particles). Based on this assumption, the invention of Patent Document 19 can be regarded as follows: High granulation strength (excessively high granulation strength) caused by adding the ethylene-and-acrylic-acid copolymer makes it difficult for the fine powdery sirica added to the mixture of high
water-absorbent resin powder and oil-in-water type emulsion of an ethylene-and-acrylic-acid copolymer to intervene between the agglomerate particles, so that a large number of aggregates occurred.

That is, the technique of Patent Document 19 is completely different from the present invention in terms of the technical concept. Thus, it is the present invention that first found the following condition: By adding and mixing the fine particles after obtaining the hydrated water-absorbent resin through mixture of the water-absorbent resin particles and the aqueous liquid, it is possible to obtain a hydrated water-absorbent resin composite which has the fluidity and can be efficiently cured and/or heated.

<Leaving the hydrated water-absorbent resin composite still/ventilating>

In the present invention, the process of curing and/or the process of drying may include at least either "leaving the hydrated water-absorbent resin composite still" or "ventilating". That is, the process of curing and/or the process of drying may be carried out under such condition that the hydrated water-absorbent resin composite is left still and ventilation is carried out. The "leaving the hydrated water-absorbent resin composite still" means to leave the hydrated water-absorbent resin composite unstirred or not-flowed.
The hydrated water-absorbent resin composite is left still in the process of curing and/or the process of drying, so that the process of curing and/or the process of drying is carried out under such condition that the hydrated water-absorbent resin composite is not stirred and not flowed, thereby preventing the excessive particle breakage of the water-absorbent resin agglomerates. As a result, it is possible to suppress deterioration of properties of the resultant water-absorbent resin agglomerates. Further, any special device is not required in leaving the hydrated water-absorbent resin composite still, so that it is possible to carry out the process of curing and/or the process of drying, whereby the foregoing effect is exhibited, with low energy.

Further, the present invention may be arranged so that ventilation is carried out in the process of curing and/or the process of drying. The ventilation allows moisture evaporated from the water-absorbent resin composite to move to the outside of the system. Thus, it is possible to highly efficiently carry out the process of curing and/or the process of drying. A method for the ventilation is not particularly limited. As to a wind force at the time of the ventilation, its linear velocity preferably ranges from 0.01m/second to 10m/second, more preferably from 0.5m/second to 3m/second.

In the process of curing and/or the process of drying, at least either "leaving the hydrated water-absorbent resin
composite still” or “ventilating” may be carried out, so that both the operations may be simultaneously carried out or either of the operations may be carried out.

Further, “heating” may be carried out in these operations. The “heating” means to heat the aforementioned heater in the process of curing and/or the process of drying. The “heating” is carried out, so that the process of curing and/or the process of drying is carried out while being heated, thereby further improving the efficiency in these processes.

According to the present invention, it is possible to much more efficiently carry out the “curing” and/or the “drying” than the conventional arrangement, so that even a small-size dryer whose heat quantity is small can carry out the “curing” and/or the “drying” in a short time. Therefore, this arrangement is extremely useful in terms of the shorter production time, the production cost reduction, the energy saving, and the like. For example, Patent Document 19 discloses an arrangement in which the drying is carried out at a temperature preferably ranging from 100°C to 150°C. However, in Examples of the present invention which are described later, the inventors of the present invention succeeded in curing the hydrated water-absorbent resin composite by leaving the hydrated water-absorbent resin composite still (not stirred and not flowed) in a well-closed container at 60°C for one hour.
Due to the process of curing and/or the process of drying, it is possible to obtain the water-absorbent resin agglomerates in which the fluidity of the hydrated water-absorbent resin composite is further enhanced and the particle diameters are relatively even. In this specification, the "water-absorbent resin agglomerates" means a resultant obtained by curing and/or drying the hydrated water-absorbent resin composite. The water-absorbent resin agglomerates may be pulverized and classified as required. A particle diameter of the water-absorbent resin agglomerates having been granulated is not particularly limited. However, a difference between a mass average particle diameter of the agglomerates which have not been granulated and a mass average particle diameter of the agglomerates which have been granulated preferably ranges from 10 μm to 1000 μm, more preferably from 20 μm to 500 μm, still more preferably from 30 μm to 300 μm.

A method for pulverization is not particularly limited, and a conventional known method can be adopted. For example, it is possible to carry out the pulverization by using a pulverizer such as a roll mill, a knife mill, a hammer mill, a pin mill, a jet mill, and the like. It is preferable that the pulverizer includes means for heating an internal wall surface of the pulverizer itself.

A method for classification is not particularly limited,
but it is preferable to carry out sieve classification (metal sieve, stainless sieve). It is preferable to simultaneously use plural sieves in the classification so as to obtain desired properties and particle sizes.

<Plural-step granulation>

Another embodiment may be arranged so that: in the process of adding aqueous solution, second water-absorbent resin particles are mixed with a system obtained by mixing first water-absorbent resin particles with the aqueous liquid, thereby obtaining a hydrated water-absorbent resin. Hereinafter, the production method according to the present embodiment is referred to as “plural-step granulation” in convenience of description. According to the plural-step granulation, by adding the water-absorbent resin particles in plural steps, it is possible to intentionally unevenly add the aqueous solution to the water-absorbent resin particles which require the aqueous liquid.

In the plural-step granulation, it is preferable that: the first water-absorbent resin particles are water-absorbent resin particles including as main components particles whose particle diameter is less than 200 µm (hereinafter, the water-absorbent resin particles are referred to as fine powder), and the second water-absorbent resin particles including as main components particles whose particle diameter is 200 µm or more and 850 µm or less (hereinafter, the second
water-absorbent resin particles are referred to as coarse particles) are mixed with hydrated fine powder obtained by mixing the fine powder with the aqueous liquid, thereby obtaining the hydrated water-absorbent resin. The "hydrated fine powder" is hydrated mixture of at least the fine powder and the aqueous solution.

The "water-absorbent resin particles whose particle diameter is less than 200 μm" are water-absorbent resin particles whose particle diameter is less than 200 μm defined in classification using a standard sieve. In other words, water-absorbent resin particles having passed through a JIS standard sieve whose mesh size is 200 μm are regarded as the foregoing water-absorbent resin particles.

As described above, it is hard for the aqueous solution to be distributed in the water-absorbent resin particles (fine powder), so that a rate of the fine powder remaining without being granulated increases in the water-absorbent resin particles having the fine powder. Thus, it is difficult to obtain the agglomerate particles whose particle diameters are even. When a large amount of the fine powder remains, powder dusts or the like deteriorate the working environment and the absorption properties of the water-absorbent resin particles.

The inventors of the present invention divided the water-absorbent resin particles into the fine powder and other particles in advance. They first granulated the fine powder,
and then mixed other particles, and further mixed the fine particles, thereby efficiently granulating the fine powder and efficiently producing the agglomerate particles having less amount of remaining fine powder and having even particle diameters. On this account, it is possible to effectively use also the fine powder as a material of the water-absorbent resin agglomerates, so that it is possible to improve the yield of the water-absorbent resin agglomerates and it is possible to reduce occurrence or the like of the dusts, thereby improving also a working efficiency. In the resultant water-absorbent resin agglomerates, a residual ratio of the fine powder is low, so that properties such as absorption properties are favorable.

As a method for separating the fine powder from the water-absorbent resin particles, a conventional known method can be adopted. An example thereof is a method in which the water-absorbent resin particles including the fine powder are classified by using JIS standard sieves whose mesh sizes are 200 µm through 150 µm in consideration for a classification efficiency.

It is preferable that a mass average particle diameter of the fine powder is less than 200 µm. The fine powder is water-absorbent resin particles including as main components particles whose particle diameter is less than 200 µm, and a ratio of the water-absorbent resin powder whose particle
diameter is 150 μm or less is preferably 50 wt% or more (upper limit is 100 wt%), more preferably 70 wt% or more, still more preferably 90 wt% or more.

A mass average particle diameter of the coarse particles is 200 μm or more and 800 μm or less, more preferably 230 μm or more and 600 μm or less, still more preferably 260 μm or more and 500 μm or less. It is preferable that the coarse particles are in a dry state. In the present invention, the dry state means a state in which a moisture content of the water-absorbent resin powder is not necessarily 0% but generally 0% or more and 15% or less, preferably 0% or more and 10% or less. Note that, the coarse particles are water-absorbent resin particles including as main components particles whose particle diameter is 200 μm or more and less than 850 μm, and the water-absorbent resin particles include 80% or more, preferably, 90% or more (upper limit is 100%) of water-absorbent resin particles whose particle diameter is 200 μm or more and less than 850 μm defined in classification using a standard sieve.

A ratio of the fine powder and the coarse particles is not particularly limited, but a weight ratio of the fine powder and the coarse particles is generally 1/99 or more and 50/50 or less, preferably, 2/98 or more and 40/60 or less, still more preferably 3/97 or more and 30/70 or less.

In the process of mixing aqueous liquid, a method
similar to the aforementioned method for mixing the water-absorbent resin particles with the aqueous liquid can be used as a method for adding the fine powder to the aqueous liquid. As other mixable components in this specification, components similar to those described in “Hydrated water-absorbent resin” can be used.

The “process of adding coarse particles” is a process in which the hydrated fine powder is added to the water-absorbent resin particles including as main components particles whose particle diameter is 200 μm or more and less than 850 μm (hereinafter, the water-absorbent resin particles are referred to also as “coarse particles”) so as to obtain hydrated coarse particles. It is preferable that the coarse particles include 80% or more (upper limit is 100%) of water-absorbent resin particles whose particle diameter is 200 μm or more and less than 850 μm defined in classification using a standard sieve, and it is more preferable that the coarse particles include 90% or more of the water-absorbent resin particles whose particle diameter is 200 μm or more and less than 850 μm defined in classification using a standard sieve.

A method for adding the hydrated fine powder to the coarse particles is not particularly limited, and it is possible to carry out the mixture by using the aforementioned conventional known mixer. In the hydrated water-absorbent
resin obtained by mixing the hydrated fine powder with the coarse particles, the hydrated fine powder and the coarse particles may be coupled to each other. Examples of other mixable components include aqueous solution, various kinds of organic solvent, and the like, in which the fine particles added in the process of adding fine particles are dispersed.

A method for adding the fine particles to the hydrated water-absorbent resin, a mixing method, a type of the fine particles, a particle diameter, and an amount of the fine particles are the same as those described in <Process of adding fine particles>. Note that, also in the plural-step granulation, the amount of the fine particles is preferably 0.05 parts by weight or more and 20 parts by weight or less with respect to 100 parts by weight of the water-absorbent resin particles. In the plural-step granulation method, “100 parts by weight of the water-absorbent resin particles” means “100 parts by weight of a mixture obtained by mixing the fine powder and the coarse particles”.

The process of curing and/or the process of drying are carried out in the same manner as described above.

In the plural-step granulation, an amount of the aqueous solution generally ranges from 1 part by weight to 150 part by weight, preferably from 5 parts by weight to 100 parts by weight, more preferably from 5 parts by weight to 50 parts by weight, still more preferably from 5 parts by weight
to 30 parts by weight, most preferably from 5 parts by weight to 15 parts by weight.

A moisture content (defined on a measurement method recited in Examples described later) of the hydrated fine powder (referred to also as hydrated gel) generally ranges from 20 wt% to 99 wt%, preferably from 30 wt% to 95 wt%, more preferably from 40 wt% to 90 wt%.

Fig. 2 is a schematic illustrating how the process of adding aqueous solution and the process of adding fine powder are carried out in the plural-step granulation described above. As illustrated in Fig. 2, the fine powder and the aqueous solution are mixed with each other in the process of adding aqueous solution, so that the granulation is promoted, thereby obtaining the hydrated fine powder. Subsequently, by adding the hydrated fine powder and/or an agglomeration thereof with the coarse particles, it is possible to obtain the hydrated water-absorbent resin. Further, the mixture of the hydrated water-absorbent resin and the fine powder results in disaggregation, so that the hydrated water-absorbent resin composite without generating any aggregate.

<Properties of the water-absorbent resin agglomerates obtained on the basis of the production method according to the present invention>

An absorbency under no pressure (CRC) at which the
water-absorbent resin agglomerates obtained on the basis of the production method according to the present invention absorb physiological saline is 27 g/g or more, preferably 30 g/g or more, 33 g/g or more, and 36 g/g or more. In case where the absorbency under no pressure is less than 20 g/g, the water-absorbent resin agglomerates may fail to exhibit excellent properties in being used in a diaper. Further, an upper limit of the absorbency under no pressure is not particularly limited, but about 50 g/g is sufficient as the upper limit. In case of realizing 50 g/g or more absorbency under no pressure, it is difficult to produce the water-absorbent resin agglomerates having such property, with the result that the cost increases.

In the water-absorbent resin agglomerates obtained on the basis of the production method according to the present invention, an absorbency against pressure of 1.9 kPa (AAP 1.9 kPa) is 20 g/g or more, more preferably 22 g/g or more, still more preferably 24 g/g or more, particularly preferably 26 g/g or more. In case where the absorbency against pressure is less than 20 g/g, the water-absorbent resin agglomerates may fail to exhibit excellent properties in being used in a diaper. Further, an upper limit of the absorbency against pressure is not particularly limited, but about 40 g/g is sufficient as the upper limit. In case of realizing 40 g/g or more absorbency against pressure, it is difficult to produce the
water-absorbent resin agglomerates having such property, with the result that the cost increases.

In the water-absorbent resin agglomerates obtained on the basis of the production method according to the present invention, an absorbency against pressure of 4.8 kPa (AAP 4.8 kPa) is 10 g/g or more, more preferably 15 g/g or more, still more preferably 20 g/g or more. In case where the absorbency against pressure is less than 10 g/g, the water-absorbent resin agglomerates may fail to exhibit excellent properties in being used in a diaper. Further, an upper limit of the absorbency against pressure is not particularly limited, but about 30 g/g is sufficient as the upper limit. In case of realizing 30 g/g or more absorbency against pressure, it is difficult to produce the water-absorbent resin agglomerates having such property, with the result that the cost increases.

A mass average particle diameter (D50) of the water-absorbent resin agglomerates obtained on the basis of the production method according to the present invention is 200 μm or more and 800 μm or less, more preferably 250 μm or more and 600 μm or less, still more preferably 300 μm or more and 500 μm or less. Before the process damage, an amount of the fine powder whose mass average particle diameter is less than 150 μm is 0% or more and 5% or less, more preferably 3% or less, particularly preferably 1% or less. After the process damage, the amount is 0% or more and 5%
or less, more preferably 3% or less. In this manner, it is preferable that the amount of the fine powder whose mass average particle diameter is less than 150 μm is extremely small. A logarithmic standard deviation (σξ) is set to 0.25 or more and 0.50 or less, preferably 0.30 or more and 0.45 or less.

An absorption rate (Vortex) of the water-absorbent resin agglomerates obtained on the basis of the production method according to the present invention is 20 seconds or more and 50 seconds or less, more preferably 20 seconds or more and 40 seconds or less, still more preferably 20 seconds or more and 30 seconds or less.

If the absorption rate exceeds 50 seconds, leakage or increase of the rewet may be brought about in being used in a diaper. If the absorption rate is higher than 20 seconds, in being used in a diaper, a high absorption rate causes a gel block to occur in an absorbent core of a diaper, with the result that leakage may occur.

With respect to the amount of the water-absorbent resin particles, a moisture content of the water-absorbent resin agglomerates obtained on the basis of the production method according to the present invention ranges from 1 wt% to 150 wt%, preferably from 5 wt% to 100 wt%, more preferably from 5 wt% to 50 wt%, still more preferably from 5 wt% to 30 wt%, further still more preferably from 5 wt% to 20 wt%,
particularly preferably from 5 wt% to 15 wt%. In case where the moisture content is less than 1 wt%, the granulation is insufficiently carried out, so that fine powder is likely to occur. In case where such water-absorbent resin particles are provided in a final product such as a diaper, clogging is likely to occur, which may cause leakage or the like. This condition is not preferable.

While, in case where the moisture content is more than 150 wt%, the water-absorbent resin agglomerates are likely to change into a aggregate due to excessively high granulation strength. In sizing (pulverizing) the agglomerates, the water-absorbent resin particles are damaged, so that properties such as an absorbency deteriorate, which may cause leakage in case where the water-absorbent resin agglomerates are provided in a final product such as a diaper.

With respect to the amount of the water-absorbent resin particles, an amount of the fine particles (amount of inorganic fine particles) included in the water-absorbent resin agglomerates obtained on the basis of the production method according to the present invention ranges from 0.01 wt% to 20 wt%, preferably from 0.01 wt% to 15 wt%, more preferably from 0.1 wt% to 10 wt%. In case where the amount of the fine particles is less than 0.01 wt%, it may be impossible to obtain sufficient fluidity. In case where the amount of the fine particles ranges from 0.01 wt% to 10 wt%, it is possible to
obtain sufficient fluidity. In case where the amount of the fine particles exceeds 20 wt%, performances (absorbency against pressure and other properties) of the water-absorbent resin may deteriorate. This condition is not preferable.

In the water-absorbent resin agglomerates obtained on the basis of the production method according to the present invention, it is preferable that an amount of particles passing through a JIS standard sieve whose mesh size is 150 μm is 0 part by weight or more and 5 parts by weight or less with respect to 100 parts by weight with respect to 100 parts by weight of the water-absorbent resin agglomerates. On this account, in case where the water-absorbent resin agglomerates are used in a diaper or the like, the fine powder hardly clog a mesh of a final product. Thus, it is possible to suppress drop of the permeability in a product such as a diaper.

As described, in the water-absorbent resin agglomerates obtained on the basis of the production method according to the present invention, it is more preferable that the amount of the particles passing through a JIS standard sieve whose mesh size is 150 μm is smaller, so that the amount may be 0 part by weight.

In the water-absorbent resin agglomerates according to the present invention, an amount of moisture is 5 parts by weight or more and 15 parts by weight or less with respect to
100 parts by weight of the water-absorbent resin agglomerates, and an amount of inorganic fine particles is 0.01 part by weight or more and 10 parts by weight or less with respect to 100 parts by weight of the water-absorbent resin agglomerates, and the water-absorbent resin agglomerates have the following properties: (1) an absorbency under no pressure in absorbing 0.90 wt% of sodium chloride aqueous solution is 27 g/g or more; (2) an absorbency against pressure of 1.9 kPa in absorbing 0.90 wt% of sodium chloride aqueous solution is 20 g/g or more; (3) an absorbency against pressure of 4.8 kPa in absorbing 0.90 wt% of sodium chloride aqueous solution is 10 g/g or more; (4) an absorption rate in absorbing 0.90 wt% of sodium chloride aqueous solution is 20 seconds or more and 50 second or less; and (5) an amount of particles passing through a JIS standard sieve whose mesh size is 150 μm is 0 part by weight or more and 5 parts by weight or less with respect to 100 parts by weight of the water-absorbent resin agglomerates.

The water-absorbent resin agglomerates can be produced on the basis of the aforementioned method according to the present invention for producing the water-absorbent resin agglomerates. That is, in the production method, single-step granulation or plural-step granulation may be carried out. The properties recited in the items (1) to (5) are as described above.
Note that, in case of producing the water-absorbent resin agglomerates according to the present invention on the basis of the plural-step granulation, 5 parts by weight or more and 20 parts by weight or less of the aqueous solution is used with respect to 100 parts by weight which is a total of the first water-absorbent resin particles and the second water-absorbent resin particles. In case of producing the water-absorbent resin agglomerates according to the present invention, it is preferable to suitably adjust an amount of the aqueous solution and an amount of the inorganic fine particles so that an amount of moisture included in the water-absorbent resin agglomerates and the amount of the inorganic fine particles included in the water-absorbent resin agglomerates are equal to an amount of moisture included in the water-absorbent resin particles and the amount of the inorganic fine particles included in the water-absorbent resin particles.

<Use of the water-absorbent resin agglomerates produced on the basis of the production method according to the present invention>

To the water-absorbent resin agglomerates produced on the basis of the production method according to the present invention, 0 wt% or more and 30 wt% or less, preferably, 0 wt% or more and 5 wt% or less of disinfectant, antibacterial agent, perfumery, foaming agent, colorant, dye, hydrophilic
short fiber, fertilizer, oxidizer, reducer, water, saline, and the like are added, thereby giving various functions. The water-absorbent resin agglomerates produced on the basis of the production method according to the present invention is applicable in the same manner as various conventional known water-absorbent resins. However, the water-absorbent resin agglomerates produced on the basis of the production method according to the present invention have less fine powder and are superior in an absorbency against pressure and an absorption rate, so that the water-absorbent resin agglomerates can be favorably used in absorbing articles such as (i) a sanitary material, which includes an absorbent core, e.g., a disposable diaper, a sanitary napkin, and an incontinence pad, (ii) a waste fluid solidification agent, and (iii) a water block agent.

The present invention is not limited to the description of the embodiments above, but may be altered by a skilled person within the scope of the claims. An embodiment based on a proper combination of technical means disclosed in different embodiments is encompassed in the technical scope of the present invention.

[Examples]

The present invention is more specifically described below with some enforcement examples. The present invention is however not limited to those examples. Note
that, in this specification, the term "mass" or "mass %" has the same meaning as "weight", "weight %", or "parts by weight. Further, for ease of explanation, the "parts by mass" may be expressed simply as "parts", and "litter" may be expressed simply as "L". Similarly, "mass %" may be expressed as "wt %".

The various properties of water-absorbent resin particles, water-absorbent resin hydrate composite, water-absorbent resin agglomerates (hereinafter referred to as "sample" as appropriate) are measured by the following methods. Unless otherwise specified, the following measurements are carried out under a temperature of 25±2°C, and a humidity of 50RH%.

Experiment Method

(1) Mass average particle diameter (D50) and fine powder content (fine powder content after 150μm sieving)

The water-absorbent resin particles or the particle water absorbing agent was sieved by using JIS standard sieves respectively having mesh sizes of 850 μm, 710 μm, 600 μm, 500 μm, 425 μm, 300 μm, 212 μm, 150 μm, 106 μm, 75μm, 45 μm, and the like, and a residual percentage was plotted on a logarithmic probability paper. Then, the mass average particle diameter (D50) and fine powder content (pass 150μm sieve rate) were found.

The sieving was performed as follows. 10.00g of the
water-absorbent resin powder or the particle water absorbing agent was put through a JIS standard sieve (The IIDA TESTING SIEVE; internal diameter: 80 mm), and was classified for 5 minutes by using a row-tap-type sieve shaking apparatus (ES-65 sieve shaking apparatus, product of Iida Seisakusho, Ltd.). Note that, the mass average particle diameter (D50) is a particle diameter of a standard sieve, having a certain mesh size, which corresponds to 50 wt % of the whole particles (see U.S. Patent No. 5051259 for example).

At this time, the fine powder content (mass %) was found by the following formula, based on the total mass amount of water-absorbent resin or the particle water absorbing agent obtained through the sieving using the 150μm JIS standard sieve.

The fine powder content (mass %) = the total mass amount of water-absorbent resin or the particle water absorbing agent obtained through the sieving using the 150μm JIS standard sieve/the total mass amount (g) of water-absorbent resin or the particle water absorbing agent × 100.

(2) Centrifuge Retention Capacity (CRC) with respect to 0.90 mass % of sodium chloride aqueous solution (physiological saline)

0.20 g of a particle water absorbing agent resin or a particle water absorbing agent was evenly contained in a bag
(60 mm × 85 mm) made of a nonwoven fabric. Then, the bag was soaked in 0.90 wt % sodium chloride aqueous solution (physiological saline) whose temperature had been adjusted to 25±2°C, and was withdrawn 30 minutes later. By using a centrifugal separator, the bag was drained for three minutes at 250G, and a weight W1 (g) of the bag was measured. Next, the same operation was performed without using the water-absorbent resin (or the particle water absorbing agent), and a weight W0 (g) was measured. Then, from the weights W0 and W1, an absorbency under no pressure (g/g) was calculated according to the following equation.

Absorbency under no pressure (g/g) with respect to 0.90 mass % of sodium chloride aqueous solution (physiological saline) = \( \frac{(\text{weight W1 (g)} - \text{weight W0 (g)})}{\text{weight of water-absorbent resin (particle water absorbing agent) (g)}} - 1 \)

(3) Moisture Content

The “Moisture Content” is defined by the amount of water contained in the water-absorbent resin (or the particle water absorbing agent, or hydrated gel). The following equation denotes the relationship between the moisture content and the solid content.

\[ \text{Moisture content (mass %)} = 100 - \text{Solid content (mass %)} \]
The moisture content was found as follows.

1 g (weight W1) of the water-absorbent resin (or the particle water absorbing agent, or hydrated gel) or the hydrated component (weight W1) were taken into an aluminum cup (weight W0) 5cm in bottom diameter and dried for 3 hours (16 hours for measurement of hydrated gel) in a windless oven at 180°C. The weight (W2) of the dried aluminum cup + the water-absorbent resin (or the particle water absorbing agent, or hydrated gel) was measured, and the moisture content was found by the following equation.

\[
\text{Moisture content (mass %)} = (1 - (W2 - W0)/W1) \times 100
\]

(4) Absorbency under no pressure modified by moisture content

The absorbency under no pressure modified by moisture content is defined by an absorbency under no pressure with an assumption that the moisture content of the water-absorbent resin (or the particle water absorbing agent) is 0 mass %, and is found by the following equation.

\[
\text{Absorbency under no pressure modified by moisture content (g/g)} = \frac{(\text{absorbency under no pressure (g/g)} + \text{moisture content (mass %)}) / 100}{(1 - \text{moisture content})}
\]
(5) Absorbency against pressure (AAP) of 1.9kPa with respect to 0.90 mass % sodium chloride aqueous solution (physiological saline)

On a bottom of a plastic supporting cylinder 60 mm in internal diameter, a metal gauze of stainless-steel (mesh size of 38 μm) was fusion-bonded. Then, 0.90 g of water-absorbent resin particles (or water absorbing agent) were evenly spread on the mesh. Subsequently, a piston (cover plate) was placed on the water-absorbent resin particles (or the particle water absorbing agent), and the weight W3: the total weight of the supporting cylinder, water-absorbent resin (or particle water absorbing agent), and the piston was measured. The piston was slightly smaller than 60 mm in external diameter which was the internal diameter of the supporting cylinder, so that there was no gap between the piston and the supporting cylinder, and upward and downward movements of the piston was not hampered.

Further, a load to evenly apply, together with the piston, 1.9kPa to the water-absorbent resin (or the particle water absorbing agent) was placed thereon, thereby completing a measurement apparatus system. Inside a petri dish 150 mm in diameter, a glass filter 90 mm in diameter and 5mm in thickness was placed. Thereafter, a 0.90 mass % of sodium
chloride aqueous solution (physiological saline) whose temperature had been adjusted to 25±°C was added until the liquid surface reached a level of an upper surface of the glass filter. Then, a piece of filter paper (product of Advantec Toyo Kaisha, Ltd.; No. 2) 9 cm in diameter was placed thereon, so that an entire surface of the filter paper was wetted. An excess of the liquid was then removed.

The measurement apparatus system was then placed on the wet filter paper, and the solution was absorbed by the paper against pressure. Extra liquid was supplied when the liquid surface came below the upper surface of the glass filter so that the liquid surface is kept at a certain level. After 1 hour, the measurement apparatus was lifted and a weight \( W_4 \) (g) of the measuring apparatus was measured after the load was removed (i.e. the weight of supporting cylinder + swollen water-absorbent resin (particle water absorbing agent) + piston). From the values of \( W_3 \) and \( W_4 \) so measured, an absorbency against pressure of 1.9 kPa (g/g) with respect to a 0.90 mass % sodium chloride aqueous solution (physiological saline) was calculated using the following formula.

\[
\text{Absorbency Against pressure of 1.9kPa (g/g) with respect to a 0.90 mass % sodium chloride aqueous solution (physiological saline) = } \frac{\text{weight } W_4 \text{ (g) - weight } W_3 \text{ (g)}}{\text{water-absorbent resin (particle water absorbing agent)}}
\]
(6) Absorbency Against Pressure modified by moisture content (g/g)

The absorbency against pressure (g/g) modified by moisture content (g/g) is defined by an absorbency against pressure with an assumption that the moisture content of the water absorbent resin (or the particle water absorbing agent) is 0 mass %, and is found by the following equation.

Absorbency Against pressure (g/g) modified by moisture content (g/g) = \( \frac{\text{Absorbency Against pressure (g/g)} \times \text{moisture content (mass %)} + \text{moisture content (mass %)} \times 100}{100} \)

(7) Shock Resistance Test

A shock resistant test of the water-absorbent resin (or the water absorbing agent) was performed as follows. 30g of water-absorbent resin (or the particle water absorbing agent) was taken to a 250ml mayonnaise bottle (55mmØ x 110mm) containing 10g of glass balls (6-7mmØ). Four of these mayonnaise bottles are prepared. After the lids are placed, the bottles are set in a paint shaker (product of Advantec Toyo Kaisha, Ltd.), and were shaken for 10 minutes. The water-absorbent resin (or the particle water absorbing agent) was then taken out from each mayonnaise bottle.

[Soluble amount (amount of water-soluble component)]
184.3 g of a 0.90 mass % sodium chloride aqueous solution (physiological saline) was taken into a 250 ml plastic container having a lid. Into the solution, 1.00 g of the sample was added, and the solution was stirred by a fluoroplastic-coated column-shaped stirrer chip 7 mm in diameter (8 mm in the center) and 30 mm in length at 300 rpm ± 30 rpm for 16 hours, thereby extracting a soluble content from the sample. The extract solution was filtered through a piece of filter paper, thereby obtaining a filtrate. 50.0 g of the filtrate was measured so as to be used as a measurement solution.

First, only the physiological saline was titrated by using a 0.1 N NaOH solution, until pH of the physiological saline reached 10. Thereafter, the physiological saline was titrated by using a 0.1 N HCl solution, until pH of the physiological saline reached 2.7. In this way, blank titration amounts ([bNaOH]ml and [bHCl]ml) were measured. The same operation was performed with respect to the measurement solution, thereby measuring titration amounts ([NaOH]ml and [HCl]ml).

For example, in the case of a water-absorbent resin including a known amount of acrylic acid and its sodium salt, an amount of soluble content in the water-absorbent resin was calculated, in accordance with the following equation, from an average molecular mass of the monomer and the titration amounts obtained by the foregoing operation. Note that, in the case where the content is unknown, the average molecular mass of the monomer can be found in accordance
with a neutralization ratio which is found by titration.

\[
\text{Amount of soluble content (wt \%) = 0.1 \times \left(\frac{\text{average molecular mass}}{184.3 \times 100 \times \frac{[	ext{HCl}]-[	ext{bHCl}]}{1000/1.0/50.0}}\right)}
\]

Neutralization ratio (mol \%) = \left(1-\frac{[	ext{NaOH}]-[	ext{bNaOH}]}{[	ext{HCl}]-[	ext{bHCl}]}\right) \times 100

[Absorbency Against pressure of 1.9kPa with respect to a 0.90 mass % sodium chloride aqueous solution (physiological saline) (AAP1.9kPa)]

A stainless-steel mesh (mesh size = 38 \, \mu m) was fused on the bottom of a plastic support cylinder 60 mm in inner diameter, and 0.90 g of a sample was uniformly sprinkled on the sieve. The cylinder had a piston (cover plate) slightly smaller than 60 mm in external diameter which was the internal diameter of the supporting cylinder, so that there was no gap between the piston and the cylinder, and upward and downward movements of the piston was not hampered. Then, a total weight W3 (g) = supporting cylinder + sample + piston was measured.

A load was added to the piston so that a load of 1.9 kPa was uniformly applied on the sample. The measurement apparatus system was thus completed. Then, a glass filter 90 mm in diameter 5mm in thickness was placed inside a
Petri dish 150 mm in diameter, and 0.90 mass % sodium chloride aqueous solution (physiological saline) adjusted to 25±2°C was added to the level of the upper surface of the glass filter. On the glass filter, a piece of filter paper 9 cm in diameter (product of Toyo Roshi, No. 2) was placed to completely wet the filter paper, and an excess solution was removed.

The measurement apparatus system was then placed on the wet filter paper, and the solution was absorbed by the paper against pressure. Extra liquid was supplied when the liquid surface came below the upper surface of the glass filter so that the liquid surface is kept at a certain level. After 1 hour, the measurement apparatus was lifted and a weight W4 (g) of the measuring apparatus was measured after the load was removed (i.e. the weight of supporting cylinder + swollen sample + piston). From the values of W3 and W4 so measured, an absorbency against pressure (g/g) of 1.9 kPa with respect to a 0.90 mass % sodium chloride aqueous solution (physiological saline) was calculated using the following formula.

\[AAP_{1.9\text{kPa}} (\text{g/g}) = \frac{\text{weight W4 (g) - weight W3 (g)}}{\text{weight of sample (g)}}\]

[Absorbency Against pressure of 4.8kPa with respect to a
0.90 mass % sodium chloride aqueous solution (physiological saline) (AAP4.8kPa)]

An absorbency against pressure of 4.8kPa with respect to a 0.90 mass % sodium chloride aqueous solution (physiological saline) was calculated in the same method used for measuring the absorbency against pressure (g/g) of 1.9 kPa with respect to a 0.90 mass % sodium chloride aqueous solution (physiological saline) except that the load of piston was changed to 4.8kPa.

The absorbency against pressure of 4.8kPa with respect to a 0.90 mass % sodium chloride aqueous solution (physiological saline) (AAP4.8kPa)] was calculated as follows.

\[ \text{AAP 4.8kPa (g/g)} = \frac{(\text{weight W4 (g)} - \text{weight W3 (g)})}{\text{weight of sample (g)}} \]

[Bulk specific gravity, Speed of flow]

The bulk specific gravity of the sample was measured in accordance with JIS K 3362 using a bulk specific gravity measurement apparatus (Zouji Kagaku Kiki Co. Ltd.). 100g of sample (water-absorbent resin agglomerates), which had been well-mixed until the particle size becomes uniform, was supplied to a funnel with the damper closed, and then the damper was immediately opened to drop the sample onto a receiver. The time period (seconds) from the start to the end
of dropping was counted as a speed of flow. Excessive powder on the surface was removed by flattening the surface by a glass bar. Then the weight of the receiver containing the sample was accurately measured in unit of 0.1g, and the bulk specific gravity was calculated according to the following formula.

\[
\text{Bulk specific gravity (g/ml)} = \frac{\text{(weight of receiver containing the sample (g))} - \text{weight of receiver (g))}}{\text{internal volume of receiver (100ml)}}
\]

Note that, the measurements were carried out under a temperature of 25±2°C, and a humidity of not less than 30RH% but not more than 50RH%.

[Paint Shaker Test (Process Damage)]

An examination called “Paint Shaker Test (PS)” was carried out. In this examination, 10g of glass beads each 6mm in diameter and 30g of sample were supplied to a glass container 6cm in diameter and 11cm in height, and the container is attached to a paint shaker (product of Toyo Seiki Seisakusho Co. Ltd.; No. 488), and shaken at 800 cycle/min (CPM). The details of the apparatus were disclosed in Japanese Unexamined Patent Publication Tokukaihei 09-235378. The shaking time was 10 minutes in both
Examples of the present invention and Comparative Examples.

After the shaking, glass beads were removed by a JIS standard sieve (mesh size = 2mm), and the sample gone through process damage was obtained.

[Determination of agglomeration amount]

10.00g of water-absorbent resin agglomerates having been through a curing process, or the water-absorbent resin agglomerates gone through process damage were supplied to a JIS standard sieve (The IIDA TESTING SIEVE; internal diameter: 80 mm) 850μm in mesh size, and was classified for 5 minutes by using a row-tap-type sieve shaking apparatus (ES-65 sieve shaking apparatus, product of Iida Seisakusho, Ltd.).

After the 5-minutes classification, the amount of residue water-absorbent resin agglomerates on the 850μm mesh with respect to the whole water-absorbent resin (10.00g) supplied to the sieve was calculated as an agglomeration amount. The agglomeration amount can be found by the following formula.

\[
\text{Agglomeration amount (mass %) = (an amount of residue water-absorbent resin agglomerates on the 850μm)/ the whole water-absorbent resin (10.00g) supplied to the sieve} \times 100
\]

[Mass average particle diameter (D50) and logarithmic
standard deviation ($\sigma \xi$)]

The sample was sieved by using JIS standard sieves respectively having mesh sizes of 850 $\mu$m, 710 $\mu$m, 600 $\mu$m, 500 $\mu$m, 425 $\mu$m, 300 $\mu$m, 212 $\mu$m, 150 $\mu$m, 106 $\mu$m, 75$\mu$m, and 45 $\mu$m, and a residual percentage was plotted on a logarithmic probability paper. Note that a different sieve may be added according to the particle size of sample. In this way, the particle diameter corresponding to $R = 50$ mass % was calculated as a mass average particle diameter (D50). Further, the logarithmic standard deviation ($\sigma \xi$) of particle size distribution was calculated as follows, in which a small $\sigma \xi$ means a small particle size distribution.

$$\sigma \xi = 0.5 \times \ln \left( \frac{X2}{X1} \right)$$

($X1$, and $X2$ are particle diameters in the cases where $R = 84.1\%$ and $R = 15.9\%$, respectively)

The sieving was performed as follows. 10.00g of the sample was put through a JIS standard sieve (The IIDA TESTING SIEVE; internal diameter: 80 mm) respectively having mesh sizes of 850 $\mu$m, 710 $\mu$m, 600 $\mu$m, 500 $\mu$m, 425 $\mu$m, 300 $\mu$m, 212 $\mu$m, 150 $\mu$m, 106 $\mu$m, 75$\mu$m, 45 $\mu$m and the like, and was classified for 5 minutes by using a row-tap-type sieve shaking apparatus (ES-65 sieve shaking apparatus, product of Iida Seisakusho, Ltd.).

Note that, the mass average particle diameter (D50) is a particle diameter of a standard sieve, having a certain mesh size, which corresponds to 50 wt % of the whole particles (see
U.S. Patent No. 5051259 for example).

[Vortex]

The test was performed according to JIS K7224-1996, using a stirrer chip 40mm in length. The test liquid (0.90 mass % sodium chloride aqueous solution (physiological saline)) was kept at 30±1°C.

[Pass 150μm Ratio]

According to the foregoing measurement of mass average particle diameter (D50), the respective masses of (i) the amount of sample passed through the 150 μm JIS standard sieve and (ii) the whole amount of the agglomerates supplied to the 150 μm sieve were used to figure out a “Pass 150μm Ratio”.

\[
\text{Pass 150μm Ratio (\%) = a mass (g) of sample passed through the 150 μm JIS standard sieve/the whole mass (g) of the agglomerates supplied to the 150 μm sieve } \times 100
\]

[Inorganic fine particle content]

The inorganic fine particle content designates a ratio of inorganic fine particle in 100 parts by mass of the water-absorbent resin agglomerates.

To determine the content of inorganic fine particles in the water-absorbent resin agglomerates, a qualitative elemental analysis was performed for the element of the inorganic fine particles contained in the water-absorbing
resin agglomerates through EPMA (Electron Probe Micro-Analysis), SEM-EDS (Scanning Electron Microscopy/Energy Dispersion X-ray Spectrometry) or the like.

Then, the ratio of element of the inorganic fine particles to the whole water-absorbing resin agglomerates was determined through fluorescent X-ray analysis. In this way, the inorganic fine particle content in the water-absorbing resin agglomerates was figured out.

(Production Example 1): Productions of water-absorbent resin concoction (C) and water-absorbent resin fraction (D)

5.30 g of polyethylene glycol diacrylate (n = 9) were dissolved in 6600 g of sodium acrylate aqueous solution having been neutralized to 75 mol % (unsaturated monomer concentration = 37.7 mass %), in a reactor that had been prepared by placing a lid on a 10 L stainless-steel double-arm kneader equipped with two sigma blades and a jacket, thereby obtaining a reaction solution. Then, the reaction solution was deaerated for 20 minutes in an atmosphere of nitrogen gas. Subsequently, 39.6 g of 10 mass % sodium persulfate aqueous solution and 1.39 g of 1 mass % L-ascorbic acid aqueous solution were added to the reaction solution, while the reaction solution was stirred. Approximately 30 seconds later, polymerization was initiated. During the polymerization, the reaction solution was kept at 20°C to 95°C while the generated gel was being pulverized.
After 45 minutes from the initiation of the polymerization, the cross-linked hydrogel polymer was removed from the reactor. Thus obtained cross-linked hydrogel polymer had been fragmented so that its diameter was approximately 5 mm. The cross-linked hydrogel polymer fragmented was spread out on a wire mesh of 850μm JIS standard mesh sieve, and was dried by hot air at 180°C for 35 minutes. As a result, a water-absorbent resin (A) was obtained. The produced resin was pulverized by using a roll mill (WML-type: product of Inoguchi Giken), and then classified by using a JIS standard sieve whose mesh size was 850 μm, thereby obtaining a water-absorbent resin which passes through 850μm mesh.

3.93 parts by mass of cross-linking agent solution, constituted of 0.03 parts by mass of ethylene glycol diglycidyl ether, 0.9 parts by mass of propylene glycol, and 3 parts by mass of water, was mixed with 100 parts by mass of the water-absorbent resin, and the mixture was supplied to a mortar-type mixer to be heated for 45 minutes at 190°C. The product of this thermal process was classified by 850μm JIS standard sieve, thereby obtaining a water-absorbent resin (B) which passes through the 850μm mesh. The mass average particle diameter of the water-absorbent resin (B) was 275μm, and 9.5 mass % of them were fine powders which pass through 150μm mesh. In this water-absorbent
resin (B), the absorbency under no pressure was 32.2g/g, the absorbency against pressure was 30.7g/g, and the moisture content was 4.0 mass %. The water-absorbent resin (B) was classified by cylinder screens of 500μm, 425μm, 300μm, 212μm and 150μm, respectively, by using a turbo-screener (Turbo Kogyo Co. Ltd.). The resulting plural sizes of water-absorbent resin particles, more specifically, the particles passed through the 500μm but caught by 425μm, particles passed through 425μm mesh but caught by 300μm mesh, the particles passed through 300μm mesh but caught by 212μm mesh, and the particles passed through 212μm mesh but caught by 150μm mesh are mixed together, to be a water-absorbent resin concoction (C) which passes through 500μm mesh but will be caught by 150μm mesh; and the particles passed through 150μm mesh was separated as a water-absorbent resin fraction (D). The mass average particle diameter of the water-absorbent resin concoction (C) was 288μm, and the average particle diameter of the water-absorbent resin fraction (D) was 125μm.

(Production Example 2) : Productions of water-absorbent resin fractions (F) and (G)

The water-absorbent resin (A) obtained by Reference Example 1 was pulverized by a roll mill (WML-type: product of Inoguchi Giken), and the particles were then classified by 850μm JIS standard sieve. 100 parts by mass of this
water-absorbent resin which passes through 850µm mesh was
mixed with 4.03 parts by mass of cross-linking agent solution,
constituted of 0.03 parts by mass of ethyleneglycol diglycidyl
ether, 1.0 parts by mass of propylene glycol, and 3 parts by
mass of water, and then the mixture was supplied to a
mortar-type mixer to be heated for 40 minutes at 190°C. The
product of this thermal process was classified by 850µm JIS
standard sieve, thereby obtaining a water-absorbent resin (E)
which passes through the 850µm mesh. The mass average
particle diameter of the water-absorbent resin (E) was 297µm,
and 9.4 mass % of them were fine powders which pass
through 150µm mesh. In this water-absorbent resin (E), the
absorbency under no pressure was 32.4g/g, the absorbency
against pressure was 30.9g/g, and the moisture content was
3.9 mass %. The water-absorbent resin (E) was classified by
a sieve of 150µm mesh, by using a Sanitary MINOX shifter
(Product of Nishimura Machine Works Co. Ltd.). The
particles are thus classified into a water-absorbent resin
fraction (F) which passes through 500µm mesh but will be
cought by 150µm mesh; and a water-absorbent resin fraction
(G) which passes through 150µm mesh. The mass average
particle diameter of the water-absorbent resin fraction (F) was
293µm, and the mass average particle diameter of the
water-absorbent resin fraction (G) was 120µm.

(Production Example 3) : Productions of water-absorbent
resin fractions (I) and (J)

The water-absorbent resin (A) obtained by Reference Example 1 was pulverized by a roll mill (WML-type: product of Inoguchi Giken), and the particles were then classified by 850μm JIS standard sieve. 100 parts by mass of this water-absorbent resin which passes through 850μm mesh was mixed with 4.03 parts by mass of cross-linking agent solution, constituted of 0.029 parts by mass of ethyleneglycol diglycidyl ether, 1.0 parts by mass of propylene glycol, and 3 parts by mass of water, and then the mixture was supplied to a mortar-type mixer to be heated for 40 minutes at 190°C. The product of this thermal process was classified by 850μm JIS standard sieve, thereby obtaining a water-absorbent resin (H) which passes through the 850μm mesh. The mass average particle diameter of the water-absorbent resin (H) was 263μm, and 8.7 mass % of them were fine powders which pass through 150μm mesh, and 0.0 mass % of them passed through 45μm mesh. In this water-absorbent resin (H), the absorbency under no pressure was 32.7g/g, the absorbency against pressure was 31.2g/g, and the moisture content was 4.2 mass %. The water-absorbent resin (H) was further classified into a water-absorbent resin fraction (I) which passes through 500μm mesh but was caught by 150μm mesh; and a water-absorbent resin fraction (J) which passes through 150μm mesh. The mass average particle diameter of the
water-absorbent resin fraction (I) was 293μm, and the average particle diameter of the water-absorbent resin fraction (J) was 118μm.

[Production Example 4; Production of water-absorbent resin particles (K) through neutralization polymerization]

5.45 g of polyethyleneglycoldiacrylate (n = 9) were dissolved in 6600 g of sodium acrylate aqueous solution having been neutralized to 75 mol % (unsaturated monomer density = 40.0 mass %), in a reactor that had been prepared by placing a lid on a 10 L stainless-steel double-arm kneader equipped with two sigma blades and a jacket, thereby obtaining a reaction solution. Then, the reaction solution was deaerated for 20 minutes in an atmosphere of nitrogen gas. Subsequently, 35.8 g of 10 mass % sodium persulfate aqueous solution and 1.49 g of 1 mass % L-ascorbic acid aqueous solution were added to the reaction solution, while the reaction solution was stirred. Approximately 20 seconds later, polymerization was initiated.

During the polymerization, the reaction solution was kept at 20°C (start of polymerization) to 95°C (peak of polymerization) while the generated gel was being pulverized. After 42 minutes from the initiation of the polymerization, the cross-linked hydrogel polymer was removed from the reactor. Thus obtained cross-linked hydrogel polymer had been fragmented so that its diameter was approximately 5
mm. The cross-linked hydrogel polymer fragmented was spread out on a 20 wire meshes (mesh size = 850µm) JIS standard sieve, and was dried by hot air at 180°C for 40 minutes.

The produced resin was pulverized by using a roll mill (WML-type: product of Inoguchi Giken), and then classified by using a JIS standard sieve whose mesh size was 850 µm, thereby obtaining an arbitrarily pulverized water-absorbent resin particles (K) whose mass average particle diameter was 366µm. 3.2 mass % of particles has a particle diameter ranging from 600µm to less than 850µm, and 3.3 mass % of particles were 150 µm or less in particle diameter. In the water-absorbent fine particles, the logarithmic standard deviation (σŋ) was 0.377, and the moisture content was 6 mass %.

The properties of the produced water-absorbent resin particles (K) were examined. CRC (Absorbency under no pressure with respect to 0.90 mass % sodium chloride aqueous solution (physiological saline)) was 47.0(g/g), and the soluble content was 15.0 mass %.

500g of the water-absorbent resin particles (K) was supplied to a 5L Loedige mixer (M-5R type: product of Loedige Co. Ltd.), and the stirring wing of Loedige mixer was driven at 330rpm for 1 minute, while spraying 17.9g of mixed solution containing 0.03 mass % of Denacol (Product of
Nagase Chemtex Corp.), 0.32 mass % of 1,4-butandiol, 0.5 mass % of propylene glycol, and 2.73 mass % of water into the mixer. Thereafter the stirring was stopped, and the mixture was immediately taken out of the mixer.

The mixture taken out was then supplied to a mortar-type mixer (product of Nishi-Nihon Shiken-ki Seisakusho), which had been heated to 210°C in oil bath, and are stirred well until the mixture was evenly heated. After 30 minutes, the mixture was taken out from the mortar mixer, and the whole mixture was classified by 850μm JIS standard sieve, thereby obtaining a water-absorbent resin particles (K) having a processed surface. Table 3 shows the properties of this surface-processed water-absorbent resin particles (K).

[Production Example 5; Production of water-absorbent resin particles (L) through neutralization polymerization]

5.45 g of polyethylene glycol diacrylate (n = 9) were dissolved in 6600 g of sodium acrylate aqueous solution having been neutralized to 75 mol % (unsaturated monomer density = 40.0 mass %), in a reactor that had been prepared by placing a lid on a 10 L stainless-steel double-arm kneader equipped with two sigma blades and a jacket, thereby obtaining a reaction solution. Then, the reaction solution was deaerated for 20 minutes in an atmosphere of nitrogen gas. Subsequently, 35.8 g of 10 mass % sodium persulfate
aqueous solution and 1.49 g of 1 mass % L-ascorbic acid aqueous solution were added to the reaction solution, while the reaction solution was stirred. Approximately 20 seconds later, polymerization was initiated.

During the polymerization, the reaction solution was kept at 20°C (start of polymerization) to 95°C (peak of polymerization) while the generated gel was being pulverized. After 42 minutes from the initiation of the polymerization, the cross-linked hydrogel polymer was removed from the reactor. Thus obtained cross-linked hydrogel polymer had been fragmented so that its diameter was approximately 5 mm. The cross-linked hydrogel polymer fragmented was spread out on a 20 wire meshes (mesh size = 850 μm) JIS standard sieve, and was dried by hot air at 180°C for 40 minutes. The produced resin was pulverized by using a roll mill (WML-type: product of Inoguchi Giken), and then classified by using a JIS standard sieve whose mesh size was 600 μm, thereby obtaining an arbitrarily pulverized water-absorbent resin particles (L) whose mass average particle diameter was 270 μm. 0.2 mass % of particles had a particle diameter ranging from 500 μm to less than 600 μm, and 9.0 mass % of particles were 150 μm or less in particle diameter. In the water-absorbent resin particles (L), the logarithmic standard deviation (σ) was 0.365, and the moisture content was 6 mass %.
The properties of the produced water-absorbent resin particles (L) were examined. CRC was 45.0(g/g), and the soluble content was 13.0 mass %.

500g of the water-absorbent resin particles (L) was supplied to a 5L Loedige mixer (M-5R type: product of Loedige Co. Ltd.), and the stirring wing of Loedige mixer was driven at 330rpm for 1 minute, while spraying 17.9g of mixed solution which containing 0.03 mass % of Denacol (product of Nagase ChemteX Corp.), 0.32 mass % of 1,4-butanediol, 0.5 mass % of propylene glycol, and 2.73 mass % of water into the mixer. Thereafter the stirring was stopped, and the mixture was immediately taken out of the mixer.

The mixture taken out was then supplied to a mortar-type mixer (product of Nishi-Nihon Shiken-ki Seisakusho), which had been heated to 210°C in oil bath, and are stirred well until the mixture was evenly heated. After 30 minutes, the mixture was taken out from the mortar mixer, and the whole mixture was classified by 850μm JIS standard sieve, thereby obtaining a water-absorbent resin particles (L) having a processed surface.

Table 3 shows the properties of this surface-processed water-absorbent resin particles (L). After the surface processing, the water-absorbent resin particles (L) was classified by a 150 μm JIS standard sieve, so that the particles are classified into a group (coarse particles (o)) 150
μm or greater in particle diameter, and a group (fine particles (β)) less than 150 μm in particle diameter.

[Example 1]

4.8g of the water-absorbent resin fraction (D) passed through 150μm mesh was supplied to a 600ml-capacity plastic container (85mmφ x 119mm), and 7.5g of deionized water was added thereto. They were mixed by a spatula for 30 seconds, and the resulting mixture (mixture of water-absorbent resin fraction (D) passed through 150μm mesh and deionized water) was mixed with 45.2g of the water-absorbent resin concoction (C) which was passed through 850μm mesh but caught by 150μm mesh, and was again stirred by a spatula for 30 seconds. Then the resulting mixture was immediately spread on a petri dish (145 mmφ), dried in a windless oven for 60 minutes at 80°C, and then was classified by a 850μm sieve, thereby obtaining particle water absorbing agent (1) passed through 850μm mesh.

[Example 2]

4.8g of the water-absorbent resin fraction (D) passed through 150μm mesh was supplied to a 600ml-capacity plastic container (85mmφ x 119mm), and 15g of deionized water was added thereto. They were mixed by a spatula for 30 seconds, and the resulting mixture (mixture of water-absorbent resin fraction (D) passed through 150μm mesh and deionized water) was mixed with 45.2g of the
water-absorbent resin concoction (C) which was passed through 850μm mesh but caught by 150μm mesh, and was again stirred by a spatula for 30 seconds. Then the mixture was immediately spread on a petri dish (145 mmϕ), dried in a windless oven for 90 minutes at 80°C, and then was classified by a 850μm sieve, thereby obtaining a particle water absorbing agent (2) which passes through 850μm mesh.

[Example 3]

4.8g of the water-absorbent resin fraction (D) passed through 150μm mesh was supplied to a 600ml-capacity plastic container (85mmϕ × 119mm), and 2.5g of deionized water was added thereto. They were mixed by a spatula for 30 seconds, and the resulting mixture (mixture of water-absorbent resin fraction (D) passed through 150μm mesh and deionized water) was mixed with 45.2g of the water-absorbent resin concoction (C) which was passed through 850μm mesh but caught by 150μm mesh, and was again stirred by a spatula for 30 seconds. Then the mixture was immediately spread on a petri dish (145 mmϕ), dried in a windless oven for 30 minutes at 80°C, and then was classified by a 850μm sieve, thereby obtaining a particle water absorbing agent (3) which passes through 850μm mesh.

[Example 4]

15.0g of the water-absorbent resin fraction (D) passed through 150μm mesh was supplied to a 600ml-capacity
plastic container (85mmϕ x 119mm), and 22.5g of deionized water was added thereto. They were mixed by a spatula for 30 seconds, and the resulting mixture (mixture of water-absorbent resin fraction (D) passed through 150μm mesh and deionized water) was mixed with 35.0g of the water-absorbent resin concoction (C) which was sieved through 850μm mesh but caught by 150μm mesh, and was again stirred by a spatula for 30 seconds. Then the mixture was immediately spread on a petri dish (145 mmϕ), dried in a windless oven for 150 minutes at 80°C, and then was classified by a 850μm sieve, thereby obtaining a particle water absorbing agent (4) which passes through 850μm mesh.

[Example 5]

28.5g of the water-absorbent resin fraction (G) passed through 150μm mesh was supplied to a 600ml-capacity plastic container (85mmϕ x 119mm), and 45g of deionized water was added thereto. They were stirred for 60 seconds. The whole resulting mixture (mixture of water-absorbent resin fraction (G) passed through 150μm mesh and deionized water) was then supplied at once to a 5L Loedige mixer (M-5R type: product of Loedige Co. Ltd.) in which 271.5g of water-absorbent resin fraction (F) passed through 850μm mesh but caught by 150μm mesh was supplied in advance. The stirring wing of Loedige mixer was driven at 330rpm to mix them together for 10 minutes. Then the mixture was
immediately spread on a petri dish (145 mmϕ), dried in a windless oven for 60 minutes at 80°C, and then was classified by a 850μm sieve, thereby obtaining particle water absorbing agent (5) passed through 850μm mesh.

[Example 6]

27.0g of the water-absorbent resin fraction (J) passed through 150μm mesh was supplied to a 5L Ploughshare Mixer (WB-5 type, product of Pacific Machinery & Engineering Co. Ltd.), and 135g of deionized water was added thereto. The stirring wing of the mixer was driven at 330rpm to stir them for 1 minute. During the stirring, 273.0g of water-absorbent resin fraction (I) passed through 850μm mesh but caught by 150μm mesh was added thereto at once, and the operation of stirring wing was kept at 330rpm to mix them together for another minute. Then the mixture was immediately spread on a 38μm mesh, dried by a hot-air drier for 25 minutes at 80°C, and then was classified by a 850μm sieve, thereby obtaining particle water absorbing agent (6) passed through 850μm mesh.

[Example 7]

27.0g of the water-absorbent resin fraction (J) passed through 150μm mesh was supplied to a 5L Ploughshare Mixer (WB-5 type, product of Pacific Machinery & Engineering Co. Ltd.), and 45g of deionized water was added thereto. The stirring wing of the mixer was driven at 330rpm to stir them
for 10 minute. During the stirring, 273.0g of water-absorbent resin fraction (I) passed through 850µm mesh but caught by 150µm mesh was added thereto at once, and the operation of the stirring wing was kept at 330rpm to mix them for 5 more minutes. Then the mixture was immediately spread on a 38µm mesh, dried by a hot-air drier for 10 minutes at 80°C, and then was classified by a 850µm sieve, thereby obtaining particle water absorbing agent (7) passed through 850µm mesh.

[Example 8]

27.0g of the water-absorbent resin fraction (J) passed through 150µm mesh was supplied to a 5L Ploughshare Mixer (WB-5 type, product of Pacific Machinery & Engineering Co. Ltd.), and 30g of deionized water was added thereto. The stirring wing of the mixer was driven at 330rpm to stir them for 10 minute. During the stirring, 273.0g of water-absorbent resin fraction (I) passed through 850µm mesh but caught by 150µm mesh was added thereto at once, and the operation of the stirring wing was kept at 330rpm to mix them for another 10 minutes. Then the mixture was immediately spread on a 38µm mesh, dried by a hot-air drier for 10 minutes at 80°C, and then was classified by a 850µm sieve, thereby obtaining particle water absorbing agent (8) which passes through 850µm mesh.

[Example 9]
500g of the surface-processed water absorbent resin (K) obtained through the method of Production Example 1 was supplied to a 5L Loedige mixer (M-5R type: product of Loedige Co. Ltd.), and the main wing (plow-like wing) of Loedige mixer was driven at 330rpm for 1 minute, while spraying 50g of water into the mixer. As a result, hydrated water absorbent resin particles were obtained (a process of adding aqueous solution).

As soon as the hydrated water-absorbent resin were obtained, 1.5g of non-soluble inorganic fine particles (Aerosil 200: Product of Aerosil Co. Ltd.) were added to the rotating Loedige mixer. Then the mixing carried on another 30 seconds until all the agglomerations were dispersed (a process of mixing fine particles). As a result, a hydrate water-absorbent resin composite (9) was obtained.

The produced hydrate water-absorbent resin composite (9) was a fluid, the speed of flow was 21 seconds/100g (measured by a JIS K3362 measurement apparatus). The produced hydrate water-absorbent resin composite (9) was then put into a sealed container, placed still for an hour in a windless oven at 60°C. As a result, the resin was cured (the added aqueous solution was absorbed to water-absorbent resin component). After the 1-hour heating, the cured water-absorbent resin agglomerates (IX) were taken out of the oven. The cured water-absorbent resin agglomerates (IX)
were also a fluid, the speed of flow was 18 seconds/100g.

The water-absorbent resin agglomerates (IX) were then subjected to process damage (Paint Shaker: (P/S): SAP, Glass Beads/Shaking Time = 30g/10g/10 minutes). After that, the water-absorbent resin agglomerates (I) were measured for various properties: particle size distribution, CRC, AAP1.9kPa, AAP4.8kPa, Vortex, Speed of Flow, Bulk Specific Gravity, Moisture Content, and Content of Inorganic fine particles. Table 3 shows the results.

[Example 10]

The same method as that of Example 9 was carried out except that 250g of water was added into the mixer. The water-absorbent resin agglomerates (X) were measured for the same factors as those of Example 9. Table 3 shows the result.

[Example 11]

45g of surface-processed fine particles (β) obtained through the method of Production Example 5 were supplied to a 5L Loedige mixer (M-5R type: product of Loedige Co. Ltd.), and the main wing (plow-like wing) of Loedige mixer was driven at 330rpm for 1 minute, while supplying 25g of water at once into the mixer. As a result, hydrated fine particle gel was obtained (a process of adding aqueous solution).

As soon as the hydrated fine particle gel was obtained, 455g of surface-processed coarse particles (α) were added to
the hydrated fine particle gel in the Loedige mixer and was mixed for another minute (a process of adding aqueous solution). Further, after the coarse particles were mixed, 1.5g of inorganic fine particles (Aerosil 200: Product of Aerosil Co. Ltd.) were added to the rotating Loedige mixer. Then the mixing carried on another 30 seconds until all the agglomerations were dispersed (a process of mixing fine particles). As a result, a hydrate water-absorbent resin composite (11) was obtained.

The produced hydrate water-absorbent resin composite (11) was a fluid, the speed of flow was 20 seconds/100g (measured by a JIS K3362 measurement apparatus). The produced hydrate water-absorbent resin composite (11) was then put into a sealed container, placed still for an hour in a windless oven at 60°C. As a result, the resin was cured (the added aqueous solution was absorbed to water-absorbent resin component). After the 1-hour heating, the cured water-absorbent resin agglomerates (XI) were taken out of the oven. The cured resin agglomerates (XI) were also a fluid, the speed of flow was 12 seconds/100g. The water-absorbent resin agglomerates (XI) were then subjected to process damage (Paint Shaker: (P/S): SAP, Glass Beads/Shaking Time = 30g/10g/10 minutes). After that, the water-absorbent resin agglomerates (XI) were measured for various properties: particle size distribution, CRC, AAP1.9kPa,
AAP4.8kPa, Vortex, Speed of Flow, Bulk Specific Gravity, Moisture Content, and Content of Inorganic fine particles. Table 3 shows the results.

[Example 12]

The same method as that of Example 11 was carried out except that 50g of water was added into the mixer. The water-absorbent resin agglomerates (XII) were measured for the same factors as those of Example 11. Table 3 shows the result.

[Example 13]

The same method as that of Example 11 was carried out except that 75g of water, and 5g of Aerosil 200 were added into the mixer. The water-absorbent resin agglomerates (XIII) were measured for the same factors as those of Example 3. Table 4 shows the result.

[Example 14]

The same method as that of Example 13 was carried out except that the produced hydrate water-absorbent resin composite was cured/dried in an opened container (a SUS container (296mm × 231mm × 49mm in outer dimension, 250mm × 185mm in bottom dimension)), placed still for 60 minutes in a windless oven at 80°C. The water-absorbent resin agglomerates (XIV) were measured for the same factors as those of Example 13. Table 4 shows the result.

[Example 15]
The same method as that of Example 13 was carried out except that the produced hydrate water-absorbent resin composite was cured/dried in an opened container (a SUS container (296mm × 231mm × 49mm in outer dimension, 250mm × 185mm in bottom dimension)), placed still for 60 minutes in a windless oven at 150°C. The water-absorbent resin agglomerates (XV) were measured for the same factors as those of Example 11. Table 4 shows the result.

[Example 16]

The same method as that of Example 11 was carried out except that the amount of water added was 50g, and 2.5g of bamboo skin powder less than 45 μm in diameter (measured by a JIS standard sieve) was added together with Aerosil 200. The water-absorbent resin agglomerates (XVI) were measured for the same factors as those of Example 11. Table 4 shows the result.

[Example 17]

The same method as that of Example 11 was carried out except that the amount of water added was 50g, and 5g of soluble starch was added instead of Aerosil 200. The water-absorbent resin agglomerates (XVII) were measured for the same factors as those of Example 11. Table 4 shows the result.

[Example 18]

The same method as that of Example 11 was carried out
except that the amount of water added was 50g, and 1.5g of CARPLEX22S (Sionogi pharmaceutical Co. Ltd.) was added instead of Aerosil 200. The water-absorbent resin agglomerates (XVIII) were measured for the same factors as those of Example 11. Table 5 shows the result.

[Example 19]

The same method as that of Example 9 was carried out except that the amounts of the water-absorbent resin particles (K), water, and Aerosil 200 added were 200g, 400g, and 20g, respectively. However, the resulting hydrated water-absorbent resin composite was not sufficiently cured, and therefore needed to be dried. The hydrated water-absorbent resin composite was placed still for 30 minutes in a windless oven at 150°C. The resulting water-absorbent resin agglomerates (XIX) were measured for the same factors as those of Example 9. Table 5 shows the result. In this example, the resulting water-absorbent resin agglomerates had fluidity, but they needed to go through a drying process. In view of this, the amount of water added is preferably reduced to avoid increase in energy cost.

[Example 20]

The same method as that of Example 11 was carried out except that 3 mass % aqueous solution colloidal silica (HS-30 (Product of Aldrich): pure liquid was diluted \times 10) was added instead of water, and no Aerosil 200 was added. The
water-absorbent resin agglomerates (XX) were measured for the same factors as those of Example 11. Table 5 shows the result.

[Example 21]

The same method as that of Example 11 was carried out except that no Aerosil 200 was added. The water-absorbent resin agglomerates (XXI) were measured for the same factors as those of Example 10. Table 5 shows the result.

[Example 22]

The same method as that of Example 12 was carried out except that no Aerosil 200 was added. The water-absorbent resin agglomerates (XXII) were measured for the same factors as those of Example 10. Table 6 shows the result.

[Example 23]

The same method as that of Example 13 was carried out except that no Aerosil 200 was added. The resulting water-absorbent resin agglomerates (XXIII) were not sufficiently cured, and therefore needed to be dried. Then, the hydrate water-absorbent resin composite was placed still for 30 minutes in a windless oven at 150°C. The resulting water-absorbent resin agglomerates (XXIII) were measured for the same factors as those of Example 10. Table 6 shows the result.

[Example 24]

The same method as that of Example 12 was carried out
except that the Aerosil 200 (1.5g) was added to the hydrated fine particle gel. Then the product was mixed with coarse particles. The water-absorbent resin agglomerates (XXIV) were measured for the same factors as those of Example 2. Table 6 shows the result.

[Comparative Example 1]

45.2g of water-absorbent resin concoction (C) passed through 850μm mesh but caught by 150μm mesh and 4.8g of the water-absorbent resin fraction (D) passed through 150μm mesh were mixed in a 600ml-capacity plastic container (85mmφ × 119mm), and 7.5g of deionized water was added thereto. They were mixed by a spatula for 30 seconds, and the resulting mixture was then immediately spread on a petri dish (145 mmφ), dried in a windless oven for 60 minutes at 80°C, and then was classified by a 850μm sieve, thereby obtaining a comparative particle water absorbing agent (1) which passes through 850μm mesh.

[Comparative Example 2]

45.2g of water-absorbent resin concoction (C) which passed through 850μm mesh but caught by 150μm mesh and 4.8g of the water-absorbent resin fraction (D) passed through 150μm mesh were mixed in a 600ml-capacity plastic container (85mmφ × 119mm), and 2.5g of deionized water was added thereto. They were mixed by a spatula for 30 seconds, and the resulting mixture was then immediately spread on a
petri dish (145 mmϕ), dried in a windless oven for 30 minutes at 80°C, and then was classified by a 850μm sieve, thereby obtaining a comparative particle water absorbing agent (2) which passes through 850μm mesh.

[Comparative Example 3]

28.5g of the water-absorbent resin fraction (G) passed through 150μm mesh and 271.5g of water-absorbent resin fraction (F) which passed through 850μm mesh but caught by 150μm mesh were simultaneously supplied to a 5L Loedige mixer (M-5R type: product of Loedige Co. Ltd.). The stirring wing of Loedige mixer was driven at 330rpm while adding 45g of deionized water, and they are stirred for 10 minutes. Then the mixture was immediately spread on a petri dish (145 mmϕ), dried in a windless oven for 60 minutes at 80°C, and then was classified by a 850μm sieve, thereby obtaining comparative particle water absorbing agent (3) which passes through 850μm mesh.

[Comparative Example 4]

28.5g of the water-absorbent resin fraction (G) passed through 150μm mesh and 271.5g of water-absorbent resin fraction (F) which was passed through 850μm mesh but caught by 150μm mesh were simultaneously supplied to a 5L Loedige mixer (M-5R type: product of Loedige Co. Ltd.). The stirring wing of Loedige mixer was driven at 330rpm while adding 90g of deionized water, and they are stirred for 10
minutes. This mixture contained a large number of aggregates, each of which was 1cm or greater in diameter. Then the mixture was immediately spread on a petri dish (145 mm$\phi$), dried in a windless oven for 60 minutes at 80°C. The dry product contained a large number of hard aggregates, each of which was 1cm or greater in diameter. The sieving was performed with 850μm mesh, but comparative particle water absorbing agent (4) passed through 850μm mesh were hardly obtained. The particles of this experiment were not desirable in quality.

[Comparative Example 5]

The same method as that of Example 9 was carried out except that no Aerosil 200 was added. The comparative water-absorbent resin agglomerates (5) were measured for the same factors as those of Example 9.

The present invention is not limited to the description of the embodiments above, but may be altered by a skilled person within the scope of the claims. An embodiment based on a proper combination of technical means disclosed in different embodiments is encompassed in the technical scope of the present invention.

[Experiment Example]

The particle water absorbing agents (1) through (8) and comparative particle water absorbing agents (1) through (4) were measured in terms of mass average particle diameter,
fine particle ratio, absorbency under no pressure, absorbency against pressure, and moisture content. Also, the shock resistant test was carried out for each of those agents. Tables 1 to 7 show the results.
<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AMOUNT OF WATER ADDED</strong> (MASS %)</td>
</tr>
<tr>
<td>THE WAY OF AGGLOMERATION</td>
</tr>
<tr>
<td>TYPE OF FINE PARTICLES</td>
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<tr>
<td>PROPERTIES</td>
</tr>
<tr>
<td><strong>CRC</strong> (g/g)</td>
</tr>
<tr>
<td><strong>AAP1.9kPa</strong> (g/g)</td>
</tr>
<tr>
<td><strong>AAP4.8kPa</strong> (g/g)</td>
</tr>
<tr>
<td><strong>VORTEX (SECOND)</strong></td>
</tr>
<tr>
<td><strong>MOISTURE CONTENT</strong> (MASS %)</td>
</tr>
<tr>
<td><strong>D50</strong> (um)</td>
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<tr>
<td><strong>PASS 150um RATE CONTENT</strong> (MASS %)</td>
</tr>
<tr>
<td><strong>INORGANIC FINE PARTICLE (MASS %)</strong></td>
</tr>
</tbody>
</table>

* 1) SINGLE-STEP : SINGLE-STEP GRANULATION
* 2) PLURAL-STEP : PLURAL-STEP GRANULATION
* 3) AGGLOMERATION : PARTICLES AT OR GREATER THAN 850um IN DIAMETER AFTER 5 MINUTES ROW TAP CLASSIFICATION
* 4) IN EXAMPLE AND COMPARATIVE EXAMPLE, THE VALUES OF PROPERTIES ARE MEASURED AFTER PS
| Table 2 |
|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                        | EXAMPLE 4       | EXAMPLE 5       | EXAMPLE 6       | EXAMPLE 7       | EXAMPLE 8       |
| AMOUNT OF WATER ADDED  | (MASS %)        | 45              | 15              | 45              | 15              | 10              |
| THE WAY OF AGGLOMERATION| PLURAL-STEP     | PLURAL-STEP     | PLURAL-STEP     | PLURAL-STEP     | PLURAL-STEP     |
| TYPE OF FINE PARTICLES |                 |                 |                 |                 |                 |
| PROPERTIES              |                 |                 |                 |                 |                 |
| CRC (g/g)               | 28.0            | 31.1            | 31.5            | 33.0            | 33.0            |
| AAP1.9kPa (g/g)         | 27.3            | 29.3            | 29.2            | 25.0            | 25.0            |
| AAP4.8kPa (g/g)         | 22.7            | 24.2            | 24.2            | 25.0            | 25.0            |
| VORTEX (SECOND)        | 29              | 32              | 31              | 33              | 35              |
| MOISTURE CONTENT (MASS %) | 13.4            | 7.4             | 7.5             | 4.2             | 4.0             |
| D50 (μm)               | 346             | 351             | 369             | 338             | 286             |
| PASS 150μm RATE        |                 |                 |                 |                 |                 |
| CONTENT OF INORGANIC FINE PARTICLE (MASS %) | 3.6 | 1.5 | 2.2 | 2.0 | 2.2 |

* 1) SINGLE-STEP : SINGLE-STEP GRANULATION
* 2) PLURAL-STEP : PLURAL-STEP GRANULATION
* 3) AGGLOMERATION : PARTICLES AT OR GREATER THAN 850μm IN DIAMETER AFTER 5 MINUTES ROW TAP CLASSIFICATION
* 4) IN EXAMPLE AND COMPARATIVE EXAMPLE, THE VALUES OF PROPERTIES ARE MEASURED AFTER PS
Table 3

<table>
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<tr>
<th></th>
<th>P. EX 4</th>
<th>P. EX 5</th>
<th>EXAMPLE 9</th>
<th>EXAMPLE 10</th>
<th>EXAMPLE 11</th>
<th>EXAMPLE 12</th>
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*1) SINGLE-STEP : SINGLE-STEP GRANULATION
*2) PLURAL-STEP : PLURAL-STEP GRANULATION
*3) AGGLOMERATION : PARTICLES AT OR GREATER THAN 850µm IN DIAMETER AFTER 5 MINUTES ROW TAP CLASSIFICATION
*4) IN EXAMPLE AND COMPARATIVE EXAMPLE, THE VALUES OF PROPERTIES ARE MEASURED AFTER PS
*5) P. EX means COMPARATIVE EXAMPLE
# Table 4

<table>
<thead>
<tr>
<th></th>
<th>EXAMPLE 13</th>
<th>EXAMPLE 14</th>
<th>EXAMPLE 15</th>
<th>EXAMPLE 16</th>
<th>EXAMPLE 17</th>
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<tbody>
<tr>
<td><strong>AMOUNT OF WATER ADDED</strong> (MASS %)</td>
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<td>296</td>
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<td><strong>CONTENT OF INORGANIC FINE PARTICLES</strong> (MASS %)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.3</td>
<td>-</td>
</tr>
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</table>

\* 1) SINGLE-STEP : SINGLE-STEP GRANULATION
\* 2) PLURAL-STEP : PLURAL-STEP GRANULATION
\* 3) AGGLOMERATION : PARTICLES AT OR GREATER THAN 850µm IN DIAMETER AFTER 5 MINUTES ROW TAP CLASSIFICATION
\* 4) IN EXAMPLE AND COMPARATIVE EXAMPLE, THE VALUES OF PROPERTIES ARE MEASURED AFTER PS
<table>
<thead>
<tr>
<th></th>
<th>Example 18</th>
<th>Example 19</th>
<th>Example 20</th>
<th>Example 21</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amount of Water Added</strong></td>
<td>(Mass %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Way of Agglomeration</td>
<td>Plural-Step</td>
<td>Single-Step</td>
<td>Plural-Step</td>
<td>Plural-Step</td>
</tr>
<tr>
<td>Type of Fine Particles</td>
<td>Carplex</td>
<td>Inorganic</td>
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<tr>
<td><strong>Amount of Particles Added</strong></td>
<td>(Mass %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluidity of Particle</td>
<td></td>
<td></td>
<td>(Content of Solid Part)</td>
<td></td>
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<tr>
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<tr>
<td>Speed of Flow After Curing/Drying</td>
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<td></td>
<td></td>
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<td>Large Agglomeration Amount After PS</td>
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<td>(1) *c</td>
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<tr>
<td>Properties</td>
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<tr>
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<td>27</td>
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<td>14</td>
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<tr>
<td>DS0</td>
<td>[µm]</td>
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<td>(450) *b</td>
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<td>(9.1) *b</td>
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*1) Single-Step : Single-Step Granulation
*2) Plural-Step : Plural-Step Granulation
*3) Agglomeration : Particles at or greater than 850µm in diameter after 5 minutes row tap classification
*4) In Example and Comparative Example, the values of properties are measured after PS
*5) The value within () is measured after drying and PS
Table 6

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<th>EXAMPLE 24</th>
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<td>15</td>
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<td>PLURAL-STEP *2)</td>
<td>PLURAL-STEP *2)</td>
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<td><strong>TYPE OF FINE PARTICLES</strong></td>
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<td>0</td>
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<td>(ADDITION TO GEL)</td>
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<td>0.3+0.5</td>
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<tr>
<td><strong>FLUIDITY OF PARTICLE</strong></td>
<td>×</td>
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<td>UNDETECTABLE</td>
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<td><strong>AGGLOMERATION AMOUNT AFTER PS</strong>*3) (MASS %)</td>
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<td>17.0</td>
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<td>Vortex (SECOND)</td>
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<td>(24.1) *3)</td>
<td>27</td>
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<td><strong>SPEED OF FLOW</strong> (SECOND)</td>
<td>10</td>
<td>—</td>
<td>11</td>
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<tr>
<td><strong>BULK SPECIFIC GRAVITY</strong> (g/cm³)</td>
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<td>—</td>
<td>0.65</td>
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<td><strong>MOISTURE CONTENT</strong> (MASS %)</td>
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<td>(7.7) *3)</td>
<td>14.0</td>
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<td>D50 (µm)</td>
<td>31.9</td>
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<td><strong>PASS 150µm RATE</strong> (MASS %)</td>
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<td><strong>CONTENT OF INORGANIC FINE PARTICLES</strong> (MASS %)</td>
<td>—</td>
<td>—</td>
<td>0.3</td>
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</tbody>
</table>

*1) SINGLE-STEP : SINGLE-STEP GRANULATION

*2) PLURAL-STEP : PLURAL-STEP GRANULATION

*3) AGGLOMERATION : PARTICLES AT OR GREATER THAN 850µm IN DIAMETER AFTER 5 MINUTES ROW TAP CLASSIFICATION

*4) IN EXAMPLE AND COMPARATIVE EXAMPLE, THE VALUES OF PROPERTIES ARE MEASURED AFTER PS

*5) THE VALUE WITHIN () IS MEASURED AFTER DRYING AND PS
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<td>COMPARATIVE EXAMPLE 4</td>
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<td>COMPARATIVE EXAMPLE 3</td>
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<td>SINGLE-STEP*1</td>
<td>( \text{OF WHICH IS 1cm OR GREATER IN} )</td>
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<td>COMPARATIVE EXAMPLE 2</td>
<td>5</td>
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<td>( \text{DIAMETERS, AND WERE NOT DESIRABLE} )</td>
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<td>COMPARATIVE EXAMPLE 1</td>
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<td>( \text{PARTICLES} )</td>
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<table>
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<tr>
<th>AMOUNT OF WATER ADDED</th>
<th>THE WAY OF AGGLOMERATION</th>
<th>TYPE OF FINE PARTICLES</th>
<th>PROPERTIES</th>
<th>MOISTURE CONTENT</th>
<th>PASS 150µm RATE</th>
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</thead>
<tbody>
<tr>
<td>(M ASS %)</td>
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<td></td>
<td>CRC (g/g)</td>
<td>(M ASS %)</td>
<td>(µm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AAP1 89.9 Pa (g/g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AAP4 89.9 Pa (g/g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>VORTEX (SECOND)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>D50 (µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>CONTENT (%)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CONTENT (%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7

* 1) SINGLE-STEP : SINGLE-STEP GRANULATION
* 2) PLURAL-STEP : PLURAL-STEP GRANULATION
* 3) AGGLOMERATION : PARTICLES AT OR GREATER THAN 850 µm IN DIAMETER AFTER 5 MINUTES ROW TAP CLASSIFICATION
* 4) IN EXAMPLE AND COMPARATIVE EXAMPLE, THE VALUES OF PROPERTIES ARE MEASURES AFTER PS
The particle water absorbing agent 1 of the present invention and the comparative particle water absorbing agent 1 were compared with each other under the same addition amount of aqueous liquid. The fine powder content of the particle water absorbing agent 1 of the present invention was 3.6 mass %, which was superior than the fine powder content (= 6.0 mass %) of the comparative particle water absorbing agent 1, which was prepared by adding an aqueous liquid to a mixture of the first water-absorbent resin powder (water-absorbent resin fraction (D)) and the second water-absorbent resin powder (water-absorbent resin concoction (C)) (single-step granulation). Further, the fine powder content of the particle water absorbing agent 3 of the present invention was far superior (= 7.3 mass %) than the fine powder content (= 9.6 mass %) of the comparative particle water absorbing agent 2 manufactured through mass production. In the particle water absorbing agents 1 through 3 of the present invention, the fine powder content improves as the amount of aqueous liquid increases. The amount of fine powder greatly decreased even in the particle water absorbing agent 4 of the present invention which contains the largest amount of water (45 parts by mass), and in the agent containing a larger amount of fine powder, specifically, the first water-absorbent resin powder and the second water-absorbent resin powder were mixed by a ratio of 30:70.
The particle water absorbing agent 5 of the present invention and the comparative particle water absorbing agent 3 were compared with each other under the same addition amount of aqueous liquid (15 parts by mass). The fine powder content of the particle water absorbing agent 5 of the present invention was superior in fine powder content (fine powder content: 0.5 mass % before the shock resistance test, 1.5 mass % after the shock resistant test) than the comparative particle water absorbing agent 3 (fine powder content: 1.9 mass % before the shock resistance test, 4.9 mass % after the shock resistant test). In the case of comparative particle water absorbing agent 4 which contains a large amount of aqueous liquid (30 parts by mass), the products contained a number of hard aggregates, each of which is 1cm or greater in diameter, that is the particle production was not successfully carried out. On the other hand, in the case of particle water absorbing agent 6 of the present invention, a large amount of aqueous liquid (45 parts by mass) were evenly added, and therefore the resulting agglomerates have higher strength.

The embodiments and concrete examples of implementation discussed in the foregoing detailed explanation serve solely to illustrate the technical details of the present invention, which should not be narrowly interpreted within the limits of such embodiments and
concrete examples, but rather may be applied in many variations within the spirit of the present invention, provided such variations do not exceed the scope of the patent claims set forth below.

INDUSTRIAL APPLICABILITY

As described above, the method of the present invention mixes at least water-absorbent resin particles and an aqueous solution, and the resulting hydrated water-absorbent resin is further mixed with water-absorbent resin particles or fine particles. In this manner, the resulting agglomerates have high strength and their physicalities are not decreased by the granulation process. Also, the content of fine particles is significantly reduced.

Besides, the method of the present invention prevents the particles to be agglomerated, and therefore the resulting hydrated water-absorbent resin composite can be processed (curing etc.) in a short time at a low temperature. Because of this, it is possible to produce agglomerates with high moisture content (5 mass % to 20 mass %), and durability to process damage.

The present invention is therefore useful for a field of products using water-absorbent resin agglomerates, such as sanitary products, diapers, ameliorants etc.
CLAIMS

1. A method of producing water-absorbent resin agglomerates, comprising the steps of:

(a) mixing first water-absorbent resin particles and an aqueous solution so as to produce a hydrated water-absorbent resin; and

(b) mixing the hydrated water-absorbent resin with second water-absorbent resin particles or fine particles other than water-absorbent resin particles.

2. The method as set forth in claim 1, wherein:

in the step (b), the hydrated water-absorbent resin is mixed with the second water-absorbent resin particles, and a moisture content of the hydrated water-absorbent resin is not less than 20 mass % but not more than 99 mass %.

3. The method as set forth in claim 1 or 2, wherein:

the first water-absorbent resin particles containing the aqueous solution is a hydrated gel.

4. The method as set forth in any one of claims 1 through 3, wherein:

the first water-absorbent resin particles have a smaller mass average particle diameter than a mass average particle
diameter of the second water-absorbent resin particles.

5. The method as set forth in any one of claims 1 through 4, wherein:

the first water-absorbent resin particles each have a cross-linked surface.

6. The method as set forth in any one of claims 1 through 5, further comprising the step of:

(c) heating and drying a mixture of (i) the first water-absorbent resin particles containing the aqueous solution and (ii) the second water-absorbent resin particles.

7. The method as set forth in any one of claims 1 through 6, wherein:

a mass ratio of the first water-absorbent resin particles to the second water-absorbent resin particles is in a range of 1/99 to 50/50.

8. The method as set forth in any one of claims 1 through 7, further comprising the step of:

(d) classifying the mixture of (i) the first water-absorbent resin particles containing the aqueous solution and (ii) the second water-absorbent resin particles, or a product resulting from the step (c).
9. The method as set forth in any one of claims 1 through 8, wherein:

the water-absorbent resin agglomerates are constituted of the first water-absorbent resin particles and the second water-absorbent resin particles.

10. The method as set forth in any one of claims 1 through 9, wherein:

each of the first water-absorbent resin particles and the second water-absorbent resin particles is a polyacrylic acid based water-absorbent resin.

11. The method as set forth in claim 1 through 10, wherein:

in the step (b), the hydrated water-absorbent resin is mixed with fine particles so as to produce a hydrated water-absorbent resin composite,

the method further comprises the step of:

(i) curing the hydrated water-absorbent resin composite, and/or

(ii) drying the hydrated water-absorbent resin composite.

12. The method as set forth in claim 11, wherein:

in the step (i), the second water-absorbent resin
particles are mixed with a system created by mixing the first water-absorbent resin particles and an aqueous solution so as to produce a hydrated water-absorbent resin.

13. The method as set forth in claim 11 or 12, wherein:

in the step (a), an amount of the aqueous solution is not less than 1 part by mass and not more than 150 parts by mass with respect to 100 parts by mass of the first water-absorbent resin particles.

14. The method as set forth in any one of claims 11 through 13, wherein:

the first water-absorbent resin particles mainly contain particles less than 200\(\mu\)m in diameter (hereinafter referred to as fine powder), and the second water-absorbent resin particles mainly contain particles not less than 200\(\mu\)m and less than 850\(\mu\)m in diameter (hereinafter referred to as coarse particles), and

the hydrated water-absorbent resin is obtained by mixing the coarse particles with a hydrated fine powder which is produced by mixing the fine powder and an aqueous solution.

15. The method as set forth in any one of claims 11 through 14, wherein:
the first water-absorbent resin particles each have a cross-linked surface.

16. The method as set forth in any one of claims 1 through 15, wherein:

the amount of the fine particles is not less than 1 part by mass and not more than 150 parts by mass with respect to 100 parts by mass of the water-absorbent resin particles.

17. The method as set forth in any one of claims 1 through 16, wherein:

the fine particles are water-insoluble inorganic fine particles.

18. The method as set forth in any one of claims 11 through 17, wherein:

in the steps (i) and/or (ii), the hydrated water-absorbent resin composite is kept at a same temperature or heated up under a temperature range of 30°C to 250°C.

19. The method as set forth in any one of claims 11 through 18, wherein:

the steps (i) and/or (ii) are carried out by way of either or both of still-placement and aeration.
20. Water-absorbent resin agglomerates produced by the method as set forth in any one of claims 1 through 19, wherein:

the water-absorbent resin agglomerates contain moisture in an amount of not less than 5 parts by mass and not more than 20 parts by mass, and contain inorganic fine particles in an amount of not less than 0.01 parts by mass and not more than 10 parts by mass when a total amount of the water-absorbent resin agglomerates is 100 parts by mass,

(1) a centrifuge retention capacity of the water-absorbent resin agglomerates with respect to a 0.90 mass % of sodium chloride aqueous solution is 27g/g;

(2) an absorption against pressure of 1.9kPa of the water-absorbent resin agglomerates with respect to a 0.90 mass % of sodium chloride aqueous solution is 20g/g;

(3) an absorption against pressure of 4.8kPa of the water-absorbent resin agglomerates with respect to a 0.90 mass % of sodium chloride aqueous solution is 10g/g;

(4) an absorption speed of the water-absorbent resin agglomerates with respect to a 0.90 mass % of sodium chloride aqueous solution is not less than 20 seconds and not more than 50 seconds;

(5) the water-absorbent resin agglomerates contains particles which pass through a JIS standard sieve 150 μm in mesh size in an amount of not less than 0 parts by mass and
not more than 5 parts by mass.

21. The method as set forth in claim 20, wherein:
the inorganic fine particles are water-insoluble inorganic fine particles.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C08J3/12 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C08J3/00-3/28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Published examined utility model applications of Japan 1992-1996
Published unexamined utility model applications of Japan 1971-2006
Registered utility model specifications of Japan 1996-2006
Published registered utility model applications of Japan 1994-2006

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>X</td>
<td>JP 8-253597 A (NIPPON SYNTHETIC CHEM IND CO) 1996.10.01, claims, [0011], [0017], [0022], [0029], example 1-3 (Family: none)</td>
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<td>X</td>
<td>JP 2000-093792 A (NIPPON SHOKUBAI CO LTD) 2000.04.04, claims, [0018],[0046]-[0050], example 1, 2 (Family: none)</td>
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* 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
  “I” 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

Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search: 28.04.2006
Date of mailing of the international search report: 16.05.2006

Name and mailing address of the ISA/JP
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan

Authorized officer
ASHIHARA YURIKA
Telephone No. +81-3-3581-1101 Ext. 3457

Form PCT/ISA/210 (second sheet) (April 2005)
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<td>A</td>
<td>JP 57-117551 A (SEITETSU CHEM IND CO LTD) 1982.07.22, whole document (Family: none)</td>
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<td>JP 8-113653 A (MITSUBISHI PETROCHEMICAL CO LTD) 1996.05.07, comparative example 8 (Family: none)</td>
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<td>A</td>
<td>JP 2001-79829 A (NIPPON SHOKUBAI CO LTD) 2001.03.27, whole document (Family: none)</td>
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