

SPECIFICATION**TITLE OF THE INVENTION****METHOD FOR MANUFACTURING POLYSTYRENE TYPE BEADS
AND EXPANDABLE POLYSTYRENE TYPE BEADS**

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BACKGROUND OF THE INVENTION**1. Field of the Invention**

The present invention relates to a method for manufacturing polystyrene type beads and expandable polystyrene type beads. More particularly, the present invention relates to a method for manufacturing polystyrene type beads and expandable polystyrene type beads having a narrow bead size distribution.

15 **2. Description of the Related Arts**

One of the conventionally well-known methods for manufacturing polystyrene type beads employs suspension polymerization of a styrene type monomer in an aqueous medium under the presence of a suspension stabilizer.

20 Conventionally, as the above suspension stabilizer, slightly water-soluble inorganic salts such as tricalcium phosphate are usually used in view of heat stability, mechanical strength, transparency and others of the polymer beads to be obtained. These slightly water-soluble
25 inorganic salts do not have much affinity for styrene type

monomers, so that a small amount of a surfactant such as sodium dodecylbenzenesulfonate is usually admixed as an auxiliary suspension stabilizing agent.

However, by the above method of suspension
5 polymerization method employing a combination of a slightly water-soluble inorganic salt and a surfactant, it was difficult to arrange the bead sizes of the styrene type polymer beads to be obtained to a specific narrow range, yielding only polymer beads having a wide bead size
10 distribution.

Therefore, in an ordinary process for suspension polymerization, the obtained polymer beads are sieved and classified into several prescribed bead size ranges for various uses.

15 The polystyrene type beads obtained by the above suspension polymerization are made into expandable polystyrene type beads by impregnating them with a blowing agent such as butane and pentane. Expandable polystyrene type beads belonging to a bead size range of 0.25 to 2.0mm
20 are typically used depending on the needs. Expandable polystyrene type beads belonging to a bead size range of 0.25 to 0.5mm are made into cups for hot drinks, precooked foods and others, or for a lost foam applied to a casting process. Those belonging to a bead size range of 0.5 to
25 1.2mm are used for various packing materials and molded

articles such as a fish box. Those belonging to a bead size range of 0.7 to 2.0mm are made into large blocks used for lightweight embankment methods in civil engineering or heat insulating materials.

5 Consequently, there has been a strong industrial need for a polymerization method of producing polystyrene type beads having a narrow bead size distribution to effectively produce polymer beads having a desired bead size and to suppress generation of polymer beads of unwanted bead size
10 in view of promoting productivity, avoiding cumbersome stock management, and reducing the disposing process of polymer beads of unwanted grades.

A known method for suspension polymerization of a styrene type monomer employs polymerization for producing
15 polymer beads with approximately equal bead size under the presence of a slightly water-soluble phosphate and without using a surfactant (a method called soap-free polymerization) (See Japanese Examined Patent Publication No. Sho 46(1971)-15112 (which corresponds to British Patent No.
20 1188252) and U.S. Patent No. 2652392). With respect to such soap-free polymerization methods, a water-soluble sulfite is used in Japanese Examined Patent Publication No. Sho 46(1971)-15112, and a water-soluble persulfate is used in U.S. Patent No. 2652392 as an indispensable additive.

25 However, although the soap-free polymerization methods

disclosed in the above publications can make the bead size distribution width narrower than that by a general suspension polymerization method, the methods have not been satisfactory enough.

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SUMMARY OF THE INVENTION

Accordingly, a purpose of the present invention is to provide a method for manufacturing polystyrene type beads and expandable polystyrene type beads having an extremely
10 narrow bead size distribution to effectively produce polymer beads having a desired bead size and to suppress creation of polymer beads of unwanted bead size.

Another purpose of the present invention is to provide a method for controlling the bead size into a desired one
15 and manufacturing polystyrene type beads having a narrow bead size distribution width and to provide a method for manufacturing expandable polystyrene type beads which can yield an expanded molded article of excellent quality when the beads are subjected to expansion molding.

20 The present invention provides a method for manufacturing polystyrene type beads comprising the step of suspension polymerization of a styrene type monomer in an aqueous medium under agitation at an agitating blade tip speed of 2.3 to 5.5m/sec under the presence of a slightly
25 water-soluble phosphate and a water-soluble sulfite and/or

water soluble persulfate.

Also, the present invention provides a method for manufacturing polystyrene type beads according to the above method wherein the slightly water-soluble phosphate to be
5 used comprises amorphous calcium phosphate with the $\text{CaO}/\text{P}_2\text{O}_5$ ratio by weight being in the range of 0.90 to 1.45, and the amorphous calcium phosphate exhibits, when prepared as an aqueous slurry of 10% by weight, an electrical conductivity in the range of 150 to 10000 $\mu\text{S}/\text{cm}$, and exhibits, when
10 prepared as an aqueous slurry of 1.5% by weight, a half sedimentation time of 5 to 20 minutes.

Further, the present invention provides a method for manufacturing polystyrene type beads wherein the slightly water-soluble phosphate used in the method comprises
15 amorphous calcium phosphate with the $\text{CaO}/\text{P}_2\text{O}_5$ ratio by weight being in the range of 0.90 to 1.45 and, after the amorphous calcium phosphate is sintered at 800°C for three hours, the obtained sintered product contains β -TCP with the peak intensity ratio of 5 to 100% by calculation from
20 the strongest peaks of hydroxyapatite and β -TCP by X-ray diffraction.

Also, the present invention provides a method for manufacturing polystyrene type beads comprising the step of suspension polymerization of a styrene type monomer in an
25 aqueous medium under the presence of a slightly water-

soluble phosphate, and a combination of water-soluble sulfite and water-soluble persulfate.

Further, the present invention provides a method for manufacturing expandable polystyrene type beads according to
5 the above method wherein the styrene type beads are impregnated with a blowing agent during the polymerization.

Also, the present invention provides a method for manufacturing expandable polystyrene type beads wherein the styrene type beads produced by the above method are, after
10 or without isolation, subjected to impregnation with a blowing agent.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The styrene type monomer used for the present
15 invention is a styrene monomer or a mixture of monomers containing styrene as a major component, namely, a single styrene or a monomer mixture of styrene as a major component and other monomers. Examples of the other monomers include a styrene type monomer such as alpha-methylstyrene, p-
20 methylstyrene, t-butylstyrene or chlorostyrene, a methacrylate monomer such as methyl methacrylate, butyl methacrylate or isobutyl methacrylate, an acrylate monomer such as ethyl acrylate or 2-ethylhexyl acrylate, a vinyl cyanide type monomer such as acrylonitrile or
25 methacrylonitrile, and a multifunctional monomer such as

divinylbenzene or polyethylene glycol dimethacrylate.

Examples of the water-soluble sulfite to be used for the present invention include sodium hydrogensulfite, potassium hydrogensulfite, and ammonium hydrogensulfite.

- 5 Also, a substance which dissolves in and reacts with water in the polymerization system to yield a sulfite may be used. Examples of the sulfite precursor substance include water-soluble pyrosulfite, pyrosulfate, dithionite, thiosulfate, sulfoxylate, and sulfate. Among these, sodium
- 10 hydrogensulfite, sodium pyrosulfite, sodium dithionite or formaldehyde sodium sulfoxylate are preferably used.

- The amount of the water-soluble sulfite to be used is in the range of 1.5 to 100ppm, preferably 2 to 100ppm with respect to styrene type monomer when the water-soluble
- 15 sulfite is used singly with the styrene type monomer. When the amount is smaller than 1.5ppm, the effect of addition will not appear, or the expanded molded article obtained by expansion molding of expandable polymer beads impregnated with a blowing agent will not have a good quality, hence not
- 20 preferable. When the amount is larger than 100ppm, no quality problem occurs in particular, but the effect of the excess amount cannot be obtained.

Examples of the water-soluble persulfate include sodium persulfate, potassium persulfate, and ammonium persulfate.

- 25 Among these, potassium persulfate is preferably used.

The amount of the water-soluble persulfate to be used is in the range of 1.5 to 50ppm, preferably 2 to 10ppm with respect to styrene type monomer when the water-soluble persulfate is used singly with the styrene type monomer.

- 5 When the amount is smaller than 1.5ppm, the effect of addition will not appear, the bead size distribution of the polymer beads will be a little wider, and the obtained expanded molded article will have inferior quality, hence not preferable. On the other hand, when the amount is
- 10 larger than 50ppm, the expanded molded article will have inferior quality, hence not preferable.

- When a combination of the above water-soluble sulfite and the water-soluble persulfate is to be used, the amounts to be used are adapted so that the water-soluble sulfite is
- 15 used at 0.2 to 100ppm, preferably 2 to 50ppm with respect to styrene type monomer, the water-soluble persulfate is used at 0.1 to 10ppm, preferably 0.5 to 5ppm with respect to styrene type monomer, and the sum of the amounts is larger than 1.5ppm. When the amounts of water-soluble sulfite and
- 20 the water-soluble persulfate are outside of the above ranges, there will be problems such as described in the above explanation of usage outside the preferable range in a single use. Also, when the sum of the amounts of the two is less than 1.5ppm, dispersion insufficiency of polymer beads
- 25 will occur during the polymerization reaction, so that the

polymerization will not be completed, hence not preferable.

The above water-soluble sulfite and persulfate used in the present invention are reductive and oxidative, respectively and both are a little unstable. Therefore, they must be added to the reaction system with care. When the water-soluble sulfite is used mainly, the water-soluble persulfate may be added from the time of supplying to the time when the polymer conversion rate of the styrene type monomer becomes 40%, with little influence to the bead size distribution, but with some influence to the average diameter and reproducibility of polymer beads. In view of a good control over the average diameter and good reproducibility of polymer beads, it is particularly preferable that the water-soluble persulfate is added at the beginning of raising the temperature in polymerization. When the water-soluble persulfate is added at the time of supplying, it is supposed that the effective amount will vary due to the decomposition of the water-soluble sulfite and persulfate since the time required for the preparation changes. When the water-soluble persulfate is added after the raising of the temperature, the average diameter and reproducibility of polymer beads varies widely, which is supposed to be a result of variation in reactivity caused by the temperature change.

The above phenomena are true of the case where the

water-soluble persulfate is used mainly. Even if the water-soluble sulfite is added after the polymer conversion rate becomes over 40%, the effect of the additive cannot be obtained because the polymerization of monomers have
5 advanced too much.

In the present invention, a slightly water-soluble phosphate may be used mainly as a suspension stabilizer. The expression "slightly water-soluble" employed here includes also "difficulty water soluble" and "very slightly
10 soluble." Examples of the slightly water-soluble phosphate include calcium phosphate, hydroxyapatite and magnesium phosphate, and are used in powder or aqueous slurry. The slightly water-soluble phosphate is added at an amount of 0.03 to 1% by weight (calculated by conversion into solid
15 components) with respect to styrene type monomer. When the amount is less than 0.03% by weight, it is not possible to maintain the dispersion state of polymer beads. When the amount is more than 1% by weight, the effect of using the phosphate in such a large amount cannot be produced, hence
20 not economical, although the polymerization reaction of the monomer is possible.

An especially preferable slightly water-soluble phosphate is one comprising an amorphous calcium phosphate having the $\text{CaO}/\text{P}_2\text{O}_5$ ratio by weight in the range of 0.90 to
25 1.45, in which the amorphous calcium phosphate shows an

electrical conductivity of 150 to 10000 μ S/cm when prepared as an aqueous slurry of 10% by weight and shows a half sedimentation time of 5 to 20 minutes when prepared as an aqueous slurry of 1.5% by weight or, alternatively, when the
5 amorphous calcium phosphate is sintered at 800°C for three hours, the obtained sintered product contains 5 to 100% β -TCP in peak intensity ratio calculated from the intensities of the strongest peaks of hydroxyapatite and β -TCP by X-ray diffraction.

10 The slightly water-soluble phosphate comprising the above amorphous calcium phosphate preferably has the CaO/P₂O₅ ratio by weight of 0.90 to 1.45, more preferably 1.15 to 1.20. If the CaO/P₂O₅ ratio is less than 0.90, calcium hydrogenphosphate is formed, so that the function
15 thereof as a dispersion stabilizer becomes very low, hence inappropriate for use. If the ratio is more than 1.45, there will be a large amount of unreacted calcium, hence not economical and, moreover, there will be an adverse effect on the bead size distribution at the time of polymerization
20 reaction.

The above amorphous calcium phosphate preferably shows a half sedimentation time of 5 to 20 minutes, more preferably 5 to 15 minutes when prepared as an aqueous slurry of 1.5% by weight. If the half sedimentation time of
25 the aqueous slurry of 1.5% by weight is less than 5 minutes,

the beads will be large, so that it will have a poor effect as a dispersion agent and the polymerization reaction will not be completed. On the other hand, if the half sedimentation time is more than 20 minutes, the bead size distribution of polymer beads will be wide probably because the dispersion effect will be too good, hence not preferable.

Further, the above amorphous calcium phosphate preferably shows an electrical conductivity of 50 to 10000 μ S/cm, more preferably 300 to 8000 μ S/cm when prepared as an aqueous slurry of 10% by weight. If the electrical conductivity is less than 150 μ S/cm, the bead size distribution of polymer beads will be wide probably because the dispersion effect will be too good. If the electrical conductivity is more than 10000 μ S/cm, it sometimes happens that the polymerization will not be completed probably because the dispersion force will be weak, hence not preferable.

Here, the above amorphous calcium phosphate cannot be analyzed as it is by an X-ray diffraction apparatus because the obtained peak is too broad. Namely, it is an uncrystallized amorphous calcium phosphate. For analysis, the amorphous calcium phosphate is sintered at 800°C for three hours and the obtained sintered product is measured by an X-ray diffraction apparatus. An especially suitable suspension stabilizer for soap-free polymerization according

to the present invention is the amorphous calcium phosphate in which the peak intensity ratio of β -TCP calculated by the measured intensities of the strongest peaks of hydroxyapatite and β -TCP is 5 to 100%, preferably 25 to 100%. If the peak intensity ratio of β -TCP is less than 5%, the generated bead size distribution of polymer beads will be wide probably because the dispersion force increases, hence not preferable.

The polymerization initiator for use in suspension polymerization according to the present invention may be one generally used for radical polymerization of a styrene type monomer. Examples of the polymerization initiator include organic peroxides such as benzoylperoxide, t-butylperoxyacetate, t-butylperoxy-2-ethylhexanoate, t-butylperoxybenzoate and 2,2-bis-t-butylperoxybutane, and azo compounds such as azobisisobutyronitrile.

Also, a general additive may be used in the present invention. For example, a nucleating agent such as ethylenbisstearylamine or polyethylene wax, or a fire retardant such as hexabromocyclododecane may be used.

The agitating blade for agitation in the autoclave tank used for suspension polymerization according to the present invention may be one generally used for suspension polymerization, for example, a flat paddle wing, a pitched paddle wing, and an anchor wing. These agitating blades are

used in a single array or a multi-array, and are not specifically limited. In order to manufacture polystyrene type beads having a narrow bead size distribution, the agitation speed is adjusted so that the tip velocity of the
5 agitating blade is in the range of 2.3 to 5.5m/sec, more preferably 2.5 to 4.5m/sec.

If the tip velocity of the agitating blade is less than 2.3m/sec, it is not possible to manufacture polymer beads with equal sizes, hence not preferable. If the tip velocity
10 is more than 5.5m/sec, the obtained effect will be the same though requiring more driving power, hence not economical.

According to the present invention, it is possible to obtain expandable polystyrene type beads by impregnating the styrene type beads with a blowing agent during the
15 polymerization of the styrene type monomer. Also, it is possible to obtain expandable polystyrene type beads wherein the styrene type beads produced by suspension polymerization are, after or without isolation, subjected to impregnation with a blowing agent.

20 The blowing agent to be used for the present invention may be one selected from various known ones. Preferable examples include saturated C3-6 hydrocarbons such as propane, butane, pentane, hexane, cyclopentane and cyclohexane, and halogenated hydrocarbons such as methyl chloride,
25 dichlorodifluoromethane. The blowing agent may be used

singly or in a combination of two or more kinds.

The above blowing agent is added for impregnation preferably at an amount of 3 to 15% by weight with respect to polystyrene type beads. If the blowing agent is to be
5 added for impregnation during the polymerization, it is preferable to add the agent at the time when the polymerization conversion degree is more than 85%. If, on the other hand, the blowing agent is to be added after the polymerization, the obtained polymer beads may be
10 impregnated, without isolation, with a blowing agent in the same autoclave tank used for suspension polymerization or, alternatively, the obtained polymer beads may be taken out for isolation and introduced into a different autoclave for impregnation with a blowing agent. The impregnation
15 condition of the blowing agent may be suitably selected from the ordinary conditions generally used in the field of art.

The thus manufactured expandable polystyrene type beads are heated conventinally by steam to yield pre-expanded beads, and then subjected to expansion molding in a mold
20 having a cavity of prescribed shape to yield an expanded molded article.

The pre-expansion can be conducted, for example, by introducing steam into the above expandable polystyrene type beads at a vapor pressure of about 0.05kg/cm²G in a pre-
25 expansion apparatus. The time for introduction is generally

assumed to be 30 to 180 seconds. The obtained pre-expanded beads are preferably left to stand for maturing at an ordinary temperature for about a day for maturing and, thereafter, subjected to expansion molding.

5 The expansion molding can be conducted by filling, with the pre-expanded beads, a mold which can be closed but cannot be completely closed off and which has a cavity of a desired shape and, thereafter, by introducing, for example, steam having a vapor pressure of 0.5 to 1.5kg/cm²G into the
10 mold for heating expansion. The obtained expanded molded article is cooled and taken out of the mold.

EXAMPLES

The present invention will hereinafter be detailed by
15 way of preferred Examples and comparison Examples. However, these examples are not intended to limit the scope of the present invention.

In these examples, the "peak three meshes" represent the ratio occupied by three consecutive ranges (meshes)
20 having the largest weight including the range comprising the bead diameter D_{50} . Here, D_{50} means the average bead diameter (median diameter) at which the accumulated weight occupies 50% in the accumulated weight distribution curve of bead size when the beads are classified by JIS standard meshes
25 into opening 2.36mm (7.5 mesh), opening 2.00mm (8.6 mesh),

opening 1.70mm (10 mesh), opening 1.40mm (12 mesh), opening 1.18mm (14 mesh), opening 1.00mm (16 mesh), opening 0.85mm (18 mesh), opening 0.71mm (22 mesh), opening 0.60mm (26 mesh), opening 0.50mm (30 mesh), opening 0.425mm (36 mesh),
5 opening 0.355mm (42 mesh), opening 0.300mm (50 mesh), opening 0.250mm (60 mesh), opening 0.212mm (70 mesh) and opening 0.180mm (83 mesh).

In the examples, the following method was used for the measurement of $\text{CaO/P}_2\text{O}_5$ ratio by weight, electrical
10 conductivity, and half sedimentation time.

[$\text{CaO/P}_2\text{O}_5$ ratio by weight]

When the sample was a powder, it was used as it was and, when the sample was a slurry, it was filtered and dried at 140°C for three hours. The sample was then diluted in 1N
15 nitric acid. The calcium concentration and the phosphorus concentration were measured by using a sequential-type high frequency plasma emission spectral line analyzer (manufactured by Seiko Instruments, Ltd. in Japan), and the $\text{CaO/P}_2\text{O}_5$ ratio by weight was calculated.

20 [Electrical conductivity]

The sample was prepared as a 10% (by weight) aqueous slurry, and the electrical conductivity was measured by using a conductometer (manufactured by Horiba, Ltd. in Japan).

25 [Half sedimentation time]

A 1.5% aqueous slurry in which the sample was uniformly dispersed was prepared and kept quiet in a 100ml sedimentation tube at 25°C. The time until the volume of the sediments became 50ml was measured.

- 5 The peak intensity ratio (%) of β -TCP was calculated by using the following method.

[β -TCP peak intensity ratio]

- When the sample was a powder, it was used as it was and, when the sample was a slurry, it was filtered and dried at 10 140°C for three hours. The sample was then sintered at 800°C for three hours and the obtained sintered product was measured by an X-ray diffractometer (manufactured by Rigaku Electric Co., Ltd. in Japan). Peak intensities of the strongest peaks of hydroxyapatite (Miller index (211) 2θ 15 =31.7 deg.) and tricalcium phosphate (β -TCP) (Miller index (217) 2θ =31.0 deg.) were compared, and the peak intensity ratio (%) of β -TCP was calculated by the following equation.
- peak intensity ratio of β -TCP (%) = (peak intensity of β -TCP) / (peak intensity of hydroxyapatite + peak intensity of 20 β -TCP) X 100

Examples 1 to 14 and comparison examples 1 to 7

- Tricalcium phosphate 120g (manufactured by Taihei Chemical Co., Ltd. in Japan) and sodium hydrogensulfite and 25 potassium persulfate of amounts shown in Table 1 and Table 2

were introduced into a 100 liter autoclave and, further, benzoyl peroxide 140g (purity: 75%), t-butylperoxybenzoate 30g, demineralized water 40kg, and styrene monomer 40kg were supplied into the autoclave and mixed. The mixture was
5 dissolved and dispersed under agitation to form an aqueous suspension solution.

Next, the styrene monomer was polymerized at 90°C for six hours and then at 115°C for two hours under agitation condition shown in Table 1 and Table 2 with pitched paddle
10 (four wings, two-array structure) and flat paddle (three wings, one-array structure). After the polymerization reaction, the reaction product was cooled, taken out from the autoclave, subjected to centrifugation, and dried to yield polystyrene beads.

15 With respect to the average diameter (D_{50}) and the bead size distribution (peak three meshes) of the obtained polystyrene beads, Table 1 shows the result of suspension polymerization when sodium hydrogensulfite was used and, Table 2 shows the result of suspension polymerization when
20 potassium persulfate was used and the result of suspension polymerization when a combination of sodium hydrogensulfite and potassium persulfate was used.

Table 1

	Additive(amount)	Agitation blade	Agitation speed		Result of polymerization Peak three meshes (%)
			Agitation blade tip speed (m/sec)	Rotation speed (rpm)	
Comparison example 1	sodium hydrogensulfite (0.6g)	45° pitched paddle (diameter 236mm)	1.60	129	57
" 2			2.00	162	61
Example 1			2.80	186	77
" 2			2.60	210	81
" 3			3.50	238	88
" 4			4.50	364	81
" 5			5.10	418	80
Comparison example 3		flat paddle (diameter 290mm)	2.00	132	59
Example 6			2.80	152	78
" 7			3.00	198	83
" 8			4.50	297	81

Table 2

	Additive(amount)	Agitation blade	Agitation speed		Result of polymerization
			Agitation blade tip speed (m/sec)	Rotation speed (rpm)	Peak three meshes (%)
Comparison example 4	potassium persulfate (0.8g)	45° pitched paddle (diameter 236mm)	1.60	129	55
" 5			2.00	162	61
Example 9			2.80	186	80
" 10			4.50	364	81
Comparison example 6	sodium hydrogensulfite (0.17g) and potassium persulfate (0.17g)		1.60	129	55
" 7			2.00	162	62
Example 11			2.80	186	79
" 12			2.60	210	82
" 13			4.50	364	82
" 14			5.10	418	81

As shown in Table 1 and Table 2, it is found that polystyrene type beads having a narrow bead size distribution can be obtained by suspension polymerization of a styrene type monomer in an aqueous medium under agitation with the agitating blade tip velocity in the range of 2.3 to 5.5m/sec under the presence of a slightly water-soluble phosphate and a water-soluble sulfite and/or a water-soluble persulfate.

10 **Examples 15 to 27 and comparison examples 8 to 13**
(Method for synthesizing an amorphous calcium phosphate)

A five-liter vessel was supplied with 4075g of demineralized water and 355g of calcium hydroxide to form a dispersion solution. Continuously into this dispersion solution was added 436.5g of 75.1% aqueous phosphate solution under strong agitation for 30 minutes using a plunger pump. The temperature of the dispersion solution of calcium hydroxide at the beginning of adding the aqueous phosphate solution was 20°C, but the temperature at the end of adding was 40°C.

After the addition of aqueous phosphate solution, the dispersion solution was left to stand under agitation for 30 minutes, and then cooled under agitation to yield a slurry. The solid component of the slurry occupied 10.56% and the measured $\text{CaO/P}_2\text{O}_5$ ratio by weight was 1.11.

Also, a slurry was formed in the same manner as in the above except that the added amount of 75.1% aqueous solution was changed to be 407.7g. In this embodiment, the solid component of the slurry occupied 10.24% and the measured
5 CaO/P₂O₅ ratio by weight was 1.20.

An amorphous calcium phosphate weighing 120g when measured as a solid component and having a property shown in Table 3 was introduced as a suspension stabilizer into a 100 liter autoclave and, further, sodium hydrogensulfite 0.4g,
10 benzoyl peroxide 140g (purity: 75%), t-butylperoxybenzoate 30g, demineralized water 40kg and styrene monomer 40kg were mixed and supplied into the autoclave. The mixture was then dissolved and dispersed under agitation to form an aqueous suspension solution.

15 Next, the styrene monomer was subjected to polymerization reaction at 90°C for six hours and then at 115°C for two hours by using a flat paddle (diameter: 290mm, three wings, one array) as an agitating blade under an agitation condition of agitating blade tip velocity of
20 3.04m/sec and rotation speed of 200rpm. The reaction product was then cooled, taken out of the autoclave, subjected to centrifugation and dried to yield polystyrene beads.

The bead size distribution (peak three meshes) of the
25 obtained polystyrene beads is shown in Table 3.

Here, potassium persulfate was added in Examples 26 and 27 and Comparison Examples 12 and 13, as shown in Table 3.

Also, TCP-10 manufactured by Taihei Chemical Co., Ltd. and tricalcium phosphate C13-09 manufactured by Budenheim

5 Chemical Co., Ltd., which are known as a suspension stabilizer used in combination with a surfactant in conventional suspension polymerization methods, were used in Comparison Examples 10 to 13.

The employed suspension stabilizer was sintered at 800°C
10 for three hours, and the sintered product was measured by an X-ray diffraction apparatus. The peak intensity ratio (%) of β -TCP calculated from the intensities of the strongest peaks of hydroxyapatite and β -TCP is shown in Table 3. As shown in Table 3, the conventional suspension stabilizer
15 which was labeled "tricalcium phosphate" (TCP) proved to be hydroxyapatite. On the other hand, it was found out that the sintered product of the suspension stabilizer according to the present invention consisted of hydroxyapatite and tricalcium phosphate (β -TCP), or mostly tricalcium
20 phosphate (β -TCP).

Table 3

		Sulfite (g)	Persulfate (g)	CaO/P ₂ O ₅ ratio by weight	Half sedimentation time (minutes)	Electrical conductivity (μ S/cm)	β -TCP ratio (%) after baking	Result of polymerization
								Bead size yield (%) Peak three meshes
Examples	15	0.4	—	0.94	10	7560	6	95
	16	0.4	—	1.11	7	1400	100	92
	17	0.4	—	1.20	5	2540	53	93
	18	0.4	—	1.25	11	8850	29	91
	19	0.4	—	1.30	18	2140	44	94
	20	0.4	—	1.31	13	5000	35	95
	21	0.4	—	1.39	15	500	18	90
	22	0.4	—	1.19	26	160	38	91
	23	0.4	—	1.21	21	56	25	90
	24	0.4	—	1.26	15	35	18	90
	25	0.4	—	1.31	14	4750	0	92
	26	—	0.3	1.20	5	2540	53	94
	27	0.16	0.16	1.20	5	2540	53	96
Comparison examples	8	0.4	—	0.80	4	12900	4	poor dispersion during polymerization
	9	0.4	—	1.34	20	45	3	75
	10	0.4	—	1.36	over 60	76	0	82
	11	0.4	—	1.30	10	48	2	79
	12	—	0.4	1.36	over 60	76	0	81
	13	0.16	0.16	1.36	over 60	76	0	82

* Sulfite (sodium hydrogensulfite), persulfate (potassium persulfate) are used.

* Comparison example 10, 12, 13 The suspension stabilizer is TCP-10 (10% aqueous slurry) manufactured by Taihei Chemical Co., Ltd.

* Comparison example 11 The suspension stabilizer is tricalcium phosphate C18-09 (fine powder) manufactured by Budenheim Chemical Co., Ltd.

As shown in Table 3, it is understood that, by using the specific amorphous calcium phosphate according to the present invention as a suspension stabilizer, it is possible to obtain polystyrene type beads having a narrower bead size distribution than that of the case when a conventional slightly water-soluble phosphate is used.

It seems that, when a conventional suspension stabilizer is used (Comparison Examples 10 to 13), there will be a strong dispersion protection effect of styrene type monomer drops in the polymerization reaction system. However, the suspension stabilizer comprising the above specific amorphous calcium phosphate according to the present invention has a weak dispersion protection effect of monomer drops in the suspension polymerization method, thereby exhibiting an effect of narrowing the width of the bead size distribution of the obtained polymer beads.

Examples 28 to 34 and Comparison Examples 14 to 23

Tricalcium phosphate (manufactured by Taihei Chemical Co., Ltd.) 120g and sodium hydrogensulfite and potassium persulfate with amounts shown in Table 4 were introduced into a 100 liter autoclave and, further, benzoyl peroxide 140g (purity: 75%), t-butylperoxybenzoate 30g, demineralized water 40kg and styrene monomer 40kg were mixed and supplied into the autoclave. The mixture was then dissolved and

dispersed under agitation to form an aqueous suspension solution.

Next, the styrene monomer was subjected to polymerization reaction at 90°C for six hours and then at
5 115°C for two hours by using a flat paddle (diameter: 290mm, three wings, one array) as an agitating blade under an agitation condition of agitating blade tip velocity of 3.04m/sec (rotation speed of 200rpm). The reaction product was then cooled, taken out of the autoclave, subjected to
10 centrifugation and dried to yield polystyrene beads.

The average bead size (D_{50}) and the bead size distribution (peak three meshes) of the obtained polystyrene beads are shown in Table 4.

The obtained polystyrene beads were classified into
15 small beads of 0.3 to 0.4mm and large beads of 0.6 to 0.7mm and then impregnated with a blowing agent, as shown below, to yield expandable polystyrene beads, which were, after pre-expansion, subjected to expansion molding to produce an expanded molded article. In the case of Comparison Example
20 17, the average bead size was so large that beads of 0.3 to 0.4mm could not be collected, making it impossible to evaluate the obtained expanded molded article. The small beads were evaluated by making them into an expanded molded article having a cup-like shape. The large beads were
25 evaluated by making them into an expanded molded block

having a rectangular parallelepiped shape of 300 X 450 X 100mm.

(Impregnation with a blowing agent, pre-expansion, expansion molding of small beads)

5 A five-liter autoclave was supplied with 2000g of water, 12g of magnesium pyrophosphate and 0.3g of sodium dodecylbenzenesulfonate to form an aqueous medium, which was then supplied with 2000g of the above small polystyrene beads and agitated at 300rpm.

10 Next, the temperature was raised to 100°C and, while maintaining this temperature, the small beads were impregnated with 120g of pressingly added pentane for two hours and then cooled to yield expandable polystyrene beads.

15 The obtained expandable polystyrene beads were left to stand for maturing at 15°C for 24 hours for maturing and then subjected to pre-expansion process, which yielded pre-expanded beads having a bulk expansion ratio of 10. Further, the pre-expanded beads were left to stand at an ordinary temperature for 24 hours for maturing, and then loaded into
20 a mold having a cup-like cavity with an inner volume of 450ml and a thickness of 2mm. Afterwards, steam of 1.8kg/cm²G was introduced for 7 seconds for heat expansion molding and the obtained product was cooled and separated from the mold to complete an expanded polystyrene molded
25 article having a cup-like shape.

(Impregnation with a blowing agent, pre-expansion, expansion molding of large beads)

A five-liter autoclave was supplied with 2000g of water, 9g of magnesium pyrophosphate and 0.3g of sodium dodecylbenzenesulfonate to form an aqueous medium, which was then supplied with 2000g of the above large polystyrene beads and agitated at 300rpm.

Next, the temperature was raised to 90°C and, while maintaining this temperature, the large beads were impregnated with 180g of pressingly added butane for three hours and then cooled to yield expandable polystyrene beads.

The obtained expandable polystyrene beads were left to stand at 15°C for 4 days for maturing and then subjected to pre-expansion process, which yielded pre-expanded beads having a bulk expansion ratio of 60. Further, the pre-expanded beads were left to stand at an ordinary temperature for 24 hours for maturing, and then loaded into a mold having a cavity of 300 X 450 X 100mm rectangular parallelepiped shape. Afterwards, steam of 0.6kg/cm²G was introduced for 30 seconds for heat expansion molding and the obtained product was cooled by water for 20 seconds and separated from the mold to complete an expanded polystyrene form having a rectangular parallelepiped shape.

(Evaluation of expanded molded article)

The printing property and the curry soup leakage of the

thus obtained cup-like expanded molded article, and the irregularity degree of cells, the surface extension and the fusion degree of the expanded molded block having a rectangular parallelepiped shape were evaluated and the results are shown in Table 4. The standard for each item of measurement is as follows.

[Printing Property]

◎: very good, ○: good, △: a little inferior, X: inferior

The printing property is one of the qualities required of a cup-like container for precooked foods. The factors having an influence on the printing property are the cell size, the cell condition and the surface smoothness of the molded article.

[Curry soup leakage]

Curry soup powder was loaded into a cup-like expanded molded article to fill 80% of its inner volume and left to stand at 60°C in a thermostatic chamber for 24 hours. The ratio of surface area where the curry caused a surface color change from white to yellow was measured to evaluate the oozing (leakage) of fat and oil components of the curry. yellow change, ○: 0 to 5%, △: 5 to 20%, X: over 20%

[Cell size irregularity]

○: uniform cells with no irregularities

△: with a few irregularities

X: with irregularities

[Appearance]

○: good, △: a little inferior, X: inferior

When the surface appearance is improved, the gap between the expanded beads on the surface of the expanded
5 molded article will be smaller. This improves the smoothness and, therefore, the appearance of the expanded molded article.

[Fusion]

fusion ratio, ○: over 80%, △: 60 to 80%, X: less than 60%

10 The fusion ratio is the percentage of the internally broken beads with respect to the total expanded beads in the ruptured surface when the expanded molded article is fractured.

Table 4

		Sodium hydrogensulfite (ppm/Sm)	Potassium persulfate (ppm/Sm)	Result of polymerization		Evaluation of expanded molded cup		Evaluation of expanded molded block		
				D ₅₀ (mm)	Peak three meshes(%)	Printing property	Curry soup leakage	Cell irregularity	Appearance	Fusion
Comparison example	14	120	—	0.41	68	×	×	△	△	△
"	15	40	—	0.49	71	×	△	○	○	△
"	16	20	—	0.60	76	△	△	○	○	○
"	17	10	—	0.75	80	NT	NT	○	○	○
"	18	—	6.0	0.49	80	⊙	○	○	△	△
"	19	—	12	0.44	81	○	○	○	×	△
"	20	0.1	6.0	0.48	79	○	○	○	△	△
"	21	40	0.01	0.47	72	×	△	○	○	△
"	22	40	1.5	0.43	78	○	○	×	△	△
"	23	0.5	0.5	poor dispersion	(reaction was not possible)	NT	NT	NT	NT	NT
"	24	—	—	0.50	64	○	○	○	○	○
Example	28	50	0.8	0.48	77	△	○	○	○	○
"	29	40	0.5	0.46	76	○	○	○	○	○
"	30	30	1.0	0.47	79	⊙	○	○	○	○
"	31	20	2.0	0.52	82	⊙	○	○	○	○
"	32	10	4.0	0.49	81	⊙	○	○	○	△
"	33	5.0	8.0	0.48	80	○	○	○	○	△
"	34	1.0	8.0	0.51	81	⊙	○	○	○	△

*NT: no evaluation

*Sm: Styrene monomer

As shown in Table 4, it is understood that, when polystyrene beads are manufactured with a combination of water-soluble sulfite and water-soluble persulfate, the bead size can be easily controlled to a desired size, so that
5 polystyrene beads having a narrow bead size distribution can be obtained.

Also, it is found that the expanded molded article obtained by expansion molding after impregnating the above polystyrene beads with a blowing agent shows excellent
10 quality.

The methods for manufacturing polystyrene type beads by employing a conventional soap-free suspension polymerization and impregnating the beads with a blowing agent to produce expanded polystyrene type beads required two different
15 processes to obtain a satisfactory quality of the expanded molded article, namely, the suspension polymerization method using a water-soluble persulfate for small beads of 0.25 to 0.5mm and the suspension polymerization method using a water-soluble sulfite for large beads of 0.5 to 2.0mm.
20 Accordingly, there were industrial problems such as cumbersomeness of production and stock management and disposal process of unnecessary (off-grade) polymer beads, so that it was not possible to make the best use of the merits of the polymerization method for obtaining polymer
25 beads having a narrow bead size distribution.

On the other hand, the method for manufacturing polystyrene type beads using a combination of water-soluble sulfite and water-soluble persulfate of the present invention provides excellent effects that a single
5 polymerization method can be widely applied to production of beads of various size with the average diameter in the range of 0.20 to 2.0mm, and that it is possible to produce polystyrene type beads and expandable polystyrene type beads which are fully satisfactory with respect to bead size
10 distribution and quality of the expanded molded article.

Comparison example 24

Tricalcium phosphate (manufactured by Taihei Chemical Co., Ltd.) 60g, a surfactant alpha-olefinsulfonate 2.2g as
15 an auxiliary suspension stabilizer, benzoyl peroxide 140g (purity: 75%), t-butylperoxybenzoate 30g, demineralized water 40kg and styrene monomer 40kg were mixed and supplied into a 100 liter autoclave. The mixture was then dissolved and dispersed under agitation to form an aqueous suspension
20 solution.

Next, the styrene monomer was subjected to polymerization reaction at 90°C for six hours and then at 115°C for two hours by using a flat paddle (diameter: 290mm, three wings, one array) as an agitating blade under an
25 agitation condition of agitating blade tip velocity of

1.75m/sec (rotation speed of 115rpm).

Tricalcium phosphate (manufactured by Taihei Chemical Co., Ltd.) 6g was added each time after two hours and after three hours during the above reaction at 90°C.

5 After the polymerization, the reaction products were subjected to processes similar to those in Examples 28 to 34. The result of the polymerization and the evaluation of the obtained expanded molded article are shown in Table 4.

10 This result shows that, if water-soluble sulfite and water-soluble persulfate are not used, the yield of polymer beads in a narrow bead size range is bad, though the quality of the obtained expanded molded article has no problem.

Examples 35 to 41 and Comparison example 25

15 Polystyrene beads were manufactured in the same manner as in the Examples 28 to 34 except that sodium hydrogensulfite 20ppm and potassium persulfate 2ppm were used with respect to styrene monomer and the time of adding each of the above compounds was changed as in the Table 5.

20 The same polymerization reaction was repeated three times to evaluate the reproducibility.

 The average diameter (D_{50}) and the bead size distribution (peak three meshes) of the obtained polystyrene beads are shown in Table 5.

Table 5

		Time of addition of sodium hydrogensulfite	Time of addition of potassium persulfate	First time		Second time		Third time	
				D ₅₀ (mm)	Peak three meshes (%)	D ₅₀ (mm)	Peak three meshes (%)	D ₅₀ (mm)	Peak three meshes (%)
Example	35	at the time of supplying	at the time of supplying	0.52	88	0.55	82	0.60	83
"	36	at the time of supplying	at the beginning of raising the temperature (15~80°C)	0.52	81	0.52	82	0.53	82
"	37	at the time of supplying	during the raising of temperature (60°C)	0.46	79	0.47	81	0.51	80
"	38	at the time of supplying	at the end of raising the temperature (90°C)	0.40	78	0.49	80	0.52	81
"	39	at the time of supplying	after two hours at 90°C polymer conversion rate 37%	0.39	78	0.45	79	0.47	79
"	40	during the raising of temperature (60°C)	at the time of supplying	0.47	80	0.50	81	0.55	82
"	41	after two hours at 90°C polymer conversion rate 37%	at the time of supplying	0.40	79	0.45	80	0.46	78
Comparison examples	25	at the time of supplying	after three hours at 90°C polymer conversion rate 46%	0.58	76	0.60	74	0.61	77

It shows that, if a combination of water-soluble sulfite and water-soluble persulfate is used and the water-soluble sulfite is used as a base, bead diameter control and reproducibility will be excellent when the water-soluble

5 persulfate is added at the beginning of raising the temperature for the polymerization reaction.

WHAT WE CLAIM IS:

1. A method for manufacturing polystyrene type beads comprising the step of suspension polymerization of a styrene type monomer in an aqueous medium under agitation at an agitating blade tip speed of 2.3 to 5.5m/sec under the presence of a slightly water-soluble phosphate and a water-soluble sulfite and/or water soluble persulfate.
2. A method for manufacturing polystyrene type beads according to claim 1, wherein the slightly water-soluble phosphate is tricalcium phosphate.
3. A method for manufacturing polystyrene type beads according to claim 1 or 2, wherein the slightly water-soluble phosphate comprises amorphous calcium phosphate with the $\text{CaO}/\text{P}_2\text{O}_5$ ratio by weight being in the range of 0.90 to 1.45, and the amorphous calcium phosphate exhibits, when prepared as an aqueous slurry of 10% by weight, an electrical conductivity in the range of 150 to 10000 $\mu\text{S}/\text{cm}$, and exhibits, when prepared as an aqueous slurry of 1.5% by weight, a half sedimentation time of 5 to 20 minutes.
4. A method for manufacturing polystyrene type beads according to claim 1 or 2, wherein the slightly water-soluble phosphate comprises amorphous calcium phosphate with



the $\text{CaO/P}_2\text{O}_5$ ratio by weight being in the range of 0.90 to 1.45, and, after the amorphous calcium phosphate is sintered at 800°C for three hours, the obtained sintered product contains β -TCP with the peak intensity ratio of 5 to 100% by calculation from the strongest peaks of hydroxyapatite and β -TCP by X-ray diffraction.

5 5. A method for manufacturing polystyrene type beads according to any one of claims 1 to 4, wherein the slightly
10 water-soluble phosphate is added in an amount of 0.03 to 1% by weight.

6. A method for manufacturing polystyrene type beads according to any one of claims 1 to 5, wherein the water-
15 soluble sulfite is at least one selected from the group consisting of sodium hydrogensulfite, sodium pyrosulfite, sodium dithionite and formaldehyde sodium sulfoxylate.

7. A method for manufacturing polystyrene type beads
20 according to any one of claims 1 to 6, wherein the water-soluble sulfite is added in an amount of 1.5 to 100ppm with respect to styrene type monomer.

8. A method for manufacturing polystyrene type beads
25 according to any one of claims 1 to 7, wherein the water-



* C L M S *

soluble persulfate is at least one selected from the group consisting of sodium persulfate, potassium persulfate and ammonium persulfate.

- 5 9. A method for manufacturing polystyrene type beads according to any one of claims 1 to 8, wherein the water-soluble persulfate is added in an amount of 1.5 to 50ppm with respect to styrene type monomer.
- 10 10. A method for manufacturing polystyrene type beads according to any one of claims 1 to 9, wherein the water-soluble sulfite and the water-soluble persulfate are used in a combination.
- 15 11. A method for manufacturing polystyrene type beads according to claim 10, wherein either the water-soluble sulfite or the water-soluble persulfate is added beforehand into a reaction system for the suspension polymerization, and the other one is added into the reaction system at the
20 beginning of raising the temperature for the suspension polymerization.
12. A method for manufacturing polystyrene type beads according to claim 10 or 11, wherein the water-soluble
25 sulfite is added in an amount of 0.2 to 100ppm with respect



* C L M S *

to styrene type monomer and the water-soluble persulfate is added in an amount of 0.1 to 10ppm with respect to styrene type monomer, and the sum of the amounts of the added water-soluble sulfite and persulfate is more than 1.5ppm with
5 respect to styrene type monomer.

13. A method for manufacturing polystyrene type beads according to any one of claims 1 to 12, wherein the average diameter of the polystyrene type beads to be obtained is
10 adjusted to be within the range of 0.2 to 2.0mm.

14. A method for manufacturing expandable polystyrene type beads according to any one of claims 1 to 13, further comprising the step of impregnation with a blowing agent
15 during the polymerization to produce expandable polystyrene type beads.

15. A method for manufacturing expandable polystyrene type beads, wherein the polystyrene type beads produced according
20 to any one of claims 1 to 13 are, after or without isolation, subjected to impregnation with a blowing agent to produce expandable polystyrene type beads.

