

FLAME RETARDANT EXPANDABLE POLYSTYRENE BEADS

FIELD OF THE INVENTION

[0001] The present invention relates to flame retardant expandable polystyrene beads. More specifically, the present invention relates to flame retardant expandable polystyrene beads using tetrabromocyclooctane as a flame retardant.

BACKGROUND OF THE INVENTION

[0002] Expandable polystyrene beads have been used for a wide range of use applications such as in the fields of agricultural and fishing, home electronics, architectural and civil engineering and the like. Particularly, polystyrene expansion molded articles used as heat-insulating materials for walls or floors in the architectural field have been highly required to have excellent heat-insulation property from the aspect of energy conservation and further demanded for flame retardant property.

[0003] As a production method of the above expandable polystyrene beads, a method of adding a flame retardant together with a styrene monomer during polymerization, a method of adding a flame retardant to polystyrene resin particles when impregnated with a blowing agent and the like have been employed. As the method of the former, there are the methods described in JP 2003-335891 (Patent document 1) and

JP 2002-194130 (Patent document 2) and as the method of the latter, there is the method described in JP 2007-246606 (Patent document 3).

[Patent document 1] Japanese Published Unexamined Patent Application No. 2003-335891

[Patent document 2] Japanese Published Unexamined Patent Application No. 2002-194130

[Patent document 3] Japanese Published Unexamined Patent Application No. 2007-246606

DISCLOSURE OF INVENTION

PROBLEMS TO BE SOLVED BY INVENTION

[0004] In the former methods, hexabromocyclododecane (HBCD) mainly has been used as a flame retardant. HBCD, which is the material of concern about bioaccumulation, has been expected to eliminate its use. In the latter method, tetrabromocyclooctane (TBCO) mainly has been used, but there has been such a problem that TBCO is blocked with each other to become like a lump depending on a state of preservation although an elementary substance of TBCO is in powder form. Because TBCO becomes like a lump, the flame retardant is non-uniformly dispersed, and as a result, the powdery flame retardant is non-uniformly absorbed into resin particles and there has been a problem that a part of the resin particles absorbs a large amount of the flame retardant. In addition, since the flame retardant becomes like a

lump, there has been also a problem of bad handling property in the production process.

- [0005]** The object of the present invention is to provide flame retardant expandable polystyrene beads which, even though tetrabromocyclooctane (TBCO) in powder form is used as a flame retardant, TBCO can be prevented from non-uniform absorption into resin particles and also inhibited from becoming like a lump, thereby having good handling property in the production process.

MEANS TO SOLVE THE PROBLEM

- [0006]** Inventors of the present invention found it possible to provide expandable polystyrene beads which, by using a certain amount of a flame retardant having no bioaccumulation and good handling property in the production process, have excellent heat fusion property of particles to each other when expanded as well as an expansion molded article having excellent flame retardancy can be obtained, and reached to the invention.
- [0007]** The present invention is directed to flame retardant expandable polystyrene beads, wherein polystyrene resin particles dispersed in an aqueous suspension are impregnated with a powdery flame retardant of tetrabromocyclooctane dispersed by silica fine powders before or during impregnation of the polystyrene resin particles with a blowing agent and the flame retardant expandable polystyrene beads are taken out from the aqueous suspension. It is characterized in that the tetrabromocyclooctane is added in an amount of 0.45 to 2.0 parts by

weight relative to 100 parts by weight of the polystyrene resin and the flame retardant contains 0.3 to 1.5 parts by weight of the silica fine powders relative to 98.5 to 99.7 parts by weight of the tetrabromocyclooctane.

[0008] The present invention is also directed to a method of producing flame retardant expandable polystyrene beads comprising steps of

impregnating polystyrene resin particles dispersed in an aqueous suspension with 0.45 to 2.0 parts by weight of a powdery flame retardant of tetrabromocyclooctane dispersed by silica fine powders before or during impregnation of the polystyrene resin particles with a blowing agent and

taking out the flame retardant expandable polystyrene beads from the aqueous suspension.

It is characterized in that the powdery flame retardant contains 0.3 to 1.5 parts by weight of the silica fine powders relative to 98.5 to 99.7 parts by weight of the tetrabromocyclooctane.

EFFECT OF INVENTION

[0009] As described above, the flame retardant expandable polystyrene beads of the present invention are characterized in that a flame retardant is uniformly absorbed into expandable polystyrene particles. As the flame retardant, silica fine powders are added to tetrabromocyclooctane. By adding the silica fine powders, the dispersibility of the tetrabromocyclooctane is remarkably improved.

Therefore, flame retardant expandable polystyrene beads having very good handling property in manufacturing, capable of uniformly absorbing a flame retardant into expandable polystyrene resin particles and having good heat fusion property in the molding process can be provided.

- [0010]** Furthermore, since the tetrabromocyclooctane is dispersed uniformly and stably by the silica fine powders, secondary aggregation or settling of the tetrabromocyclooctane does not occur, nor do problems such as blocking a pipe line by the tetrabromocyclooctane and the like occur.
- [0011]** In addition, since all of the silica fine powders to be added to the flame retardant flow out into drainage water in the production process, only flame retardant is absorbed into the obtained expandable polystyrene beads. Then, flame retardancy of expanded articles obtained from the flame retardant expandable polystyrene beads is never lowered even though silica fine powders are not absorbed.
- [0012]** Additionally, the expanded articles are obtained from flame retardant expandable polystyrene beads not containing a flame retardant of HBCD, and therefore expandable polystyrene beads which can become molded articles having no bioaccumulation, excellent heat insulating property and flame retardancy can be obtained.

BEST MODE FOR CARRYING OUT THE INVENTION

- [0013]** The flame retardant expandable polystyrene beads of the present invention can be obtained by the method of producing flame retardant expandable polystyrene beads comprising steps of impregnating polystyrene resin particles dispersed in an aqueous suspension with

0.45 to 2.0 parts by weight of a powdery flame retardant, tetrabromocyclooctane before or during impregnation of the polystyrene resin particles with a blowing agent. It is characterized in that the flame retardant contains 0.3 to 1.5 parts by weight of silica fine powders relative to 98.5 to 99.7 parts by weight of the tetrabromocyclooctane. Here, when the tetrabromocyclooctane is added after impregnation with the blowing agent, there has been a problem that the obtained flame retardant expandable polystyrene beads are cured.

[0014] Hereinafter, embodiments of the present invention are described in more detail.

As the polystyrene resin particles in the present invention, polystyrene resin particles produced by the known methods can be used.

Examples of the known methods include the followings:

(1) a suspension polymerization method of producing polystyrene resin particles, which comprises steps of supplying with an aqueous medium, a styrene monomer and a polymerization initiator into an autoclave and carrying out suspension polymerization of the styrene monomer while heating and stirring inside the autoclave;

(2) a seed polymerization method of producing polystyrene resin particles, which comprises steps of supplying with an aqueous medium and polystyrene seed particles into an autoclave, dispersing the polystyrene seed particles into the aqueous medium, followed by supplying with a styrene monomer continuously or intermittently while heating and stirring inside the autoclave, polymerizing the polystyrene

seed particles in the presence of a polymerization initiator while absorbing the styrene monomer; and the like. It is noted that the polystyrene seed particles may be produced by the above (1) suspension polymerization method and classified.

- [0015]** Here, examples of the polystyrene resin in the present invention include homopolymer(s) of a styrene monomer such as styrene, α -methyl styrene, vinyl toluene, chlorostyrene, ethyl styrene, isopropyl styrene, dimethyl styrene, bromo styrene or the like or copolymer(s) thereof.
- [0016]** Furthermore, the polystyrene resin may be copolymer(s) of styrene monomer(s) of which the main component is the above styrene monomer and vinyl monomer(s) capable of copolymerization with this styrene monomer. Examples of such vinyl monomer(s) include alkyl (metha)acrylates such as methyl (metha)acrylate, ethyl (metha)acrylate, butyl (metha)acrylate, cetyl (metha)acrylate and the like, (metha)acrylonitrile, dimethyl maleate, dimethyl fumarate, diethyl fumarate, ethyl fumarate, as well as difunctional monomers such as divinyl benzene, alkylene glycol dimethacrylate and the like.
- [0017]** When cast molding is performed using the flame retardant expandable polystyrene beads, the average particle diameter of the polystyrene resin particles is preferably 0.3 to 2.0 mm, more preferably 0.6 to 1.4 mm from the aspect of fillability of pre-expanded particles obtained by pre-expansion of the flame retardant expandable polystyrene beads into a cavity.
- [0018]** When the weight average molecular weight of polystyrene resins

composed of the polystyrene resin particles in terms of styrene is small, mechanical strength of flame retardant polystyrene resin expansion molded articles obtained by expanding the flame retardant expandable polystyrene beads is reduced. On the other hand, when the weight average molecular weight is large, expandability of the flame retardant expandable polystyrene beads is lowered and flame retardant polystyrene resin expansion molded articles having a high expansion ratio possibly could not be obtained. Therefore, the weight average molecular weight is preferably 200,000 to 500,000, more preferably 240,000 to 400,000.

[0019] Examples of the polymerization initiator used in the above suspension polymerization method and the seed polymerization method include organic peroxides such as benzoyl peroxide, lauryl peroxide, t-butyl peroxybenzoate, t-butyl peroxide, t-butyl peroxy-pivalate, t-butyl peroxyisopropyl carbonate, t-butyl peroxy-2-ethylhexyl monocarbonate, isopropyl carbonate, t-butyl peroxyacetate, 2,2-bis(t-butyl peroxy)butane, t-butyl peroxy-3, 3, 5 trimethyl hexanoate, di-t-butyl peroxyhexahydro terephthalate and the like, azo compounds such as azobisisobutyronitrile, azobis dimethyl valero nitrile and the like, or the like, but are not particularly limited to these. These may be used alone or used in combination of two or more kinds.

[0020] As the aqueous suspension in which polystyrene resin particles are dispersed in an aqueous medium, a reaction solution after polymerization by the suspension polymerization method or the seed polymerization method may be used, or an aqueous suspension may be formed by separating the polystyrene resin particles obtained by

the suspension polymerization method or the seed polymerization method from a reaction solution and suspending these polystyrene resin particles in an aqueous medium prepared separately. It is noted that examples of the aqueous medium include water, alcohol and the like, but are not particularly limited to these and water is preferable.

- [0021]** In addition, in the suspension polymerization method or the seed polymerization method, when the styrene monomer is polymerized, a suspension stabilizer may be used in order to stabilize droplets of the styrene monomer or dispersibility of the polystyrene seed particles. Examples of such a suspension stabilizer include water-soluble polymers such as polyvinyl alcohol, methyl cellulose, polyacrylamide, polyvinyl pyrrolidone and the like or poor water-soluble inorganic salts such as Tribasic Calcium Phosphate, magnesium pyrophosphate and the like. When the poor water-soluble inorganic salts are used, an anion surfactant is generally used together.
- [0022]** Examples of the anion surfactant include alkyl sulfates such as sodium lauryl sulfate and the like, alkylbenzene sulfonates such as sodium dodecylbenzene sulfonate and the like, higher fatty acid salts such as sodium oleate and the like, β - tetrahydroxynaphthalene sulfonate and the like and alkylbenzene sulfonates are preferable.
- [0023]** In the method of producing the flame retardant expandable polystyrene beads of the present invention, the polystyrene resin particles dispersed in the aqueous suspension is impregnated with a blowing agent in the known procedure. As such a blowing agent, an organic compound which has a boiling point not greater than the

softening point of the polystyrene resin and is in a gas or liquid form at normal pressure is suitable. Examples of the blowing agent include carbon hydrides such as propane, n-butane, iso-butane, n-pentane, iso-pentane, neopentane, cyclopentane, cyclopentadiene, n-hexane, petroleum ether and the like, ketones such as acetone, methyl ethyl ketone and the like, alcohols such as methanol, ethanol, isopropyl alcohol and the like, ether compounds having a low boiling point such as dimethyl ether, diethyl ether, dipropyl ether, methyl ethyl ether and the like, inorganic gas(es) such as carbon gas, nitrogen, ammonia and the like. The carbon hydride having a boiling point of from -45 to 40 °C is preferable and particularly, propane, n-butane, iso-butane, n-pentane and iso-pentane are more preferable. It is noted that the blowing agent may be used alone or in combination of two or more kinds.

[0024] Furthermore, in the method of producing the flame retardant expandable polystyrene beads of the present invention, a powdery flame retardant of tetrabromocyclooctane is supplied into the aqueous suspension before or during impregnation of the polystyrene resin particles dispersed in the aqueous suspension with the blowing agent. The polystyrene resin particles are then impregnated with the powdery flame retardant under pressure. It is noted that the aqueous medium is not particularly limited as long as the aqueous medium has compatibility with the aqueous suspension in which the polystyrene resin particles are dispersed. Examples of the aqueous medium include water, alcohol and the like and water is preferable.

[0025] Silica fine powders are added to the powdery flame retardant of

tetrabromocyclooctane in order to improve the dispersibility. As a method of adding the silica fine powders to the tetrabromocyclooctane, they are preferably mixed in a mixture such as a Henschel mixer or the like for a certain period of time.

[0026] The silica fine powders to be added to the powdery flame retardant of tetrabromocyclooctane may be either hydrophilic or hydrophobic as long as they have specific surface area of 170 to 330 m²/g and the specific surface area is most preferably 200 m²/g. It is noted that when the specific surface area is less than 170 m²/g, the dispersibility of the tetrabromocyclooctane can not be improved and as a result, the tetrabromocyclooctane is secondarily aggregated. Also, when the specific surface area is larger than 330 m²/g, the scattering amount of the silica fine powders is increased, thereby causing a problem in deteriorating handling property in manufacturing.

[0027] The amount of adding the silica fine powders to the tetrabromocyclooctane is preferably 0.3 to 1.5 parts by weight relative to 98.5 to 99.7 parts by weight of the tetrabromocyclooctane and further most preferably 0.5 parts by weight as a lower limit. When the additive amount is less than 0.3 parts by weight, the dispersibility of the tetrabromocyclooctane can not be improved and as a result, the tetrabromocyclooctane is secondarily aggregated. Also, when the additive amount is more than 1.5 parts by weight, the scattering amount of the silica fine powders are increased, thereby causing a problem in deteriorating handling property in manufacturing.

[0028] The tetrabromocyclooctane content to the polystyrene resin particles is preferably adjusted so as to be preferably 0.45 to 2.0 parts by weight,

more preferably 0.6 to 1.5 parts by weight, particularly preferably 0.7 to 1.0 parts by weight relative to 100 parts by weight of the polystyrene resin particles. When the content is less than 0.45 parts by weight, the flame retardancy of the obtained flame retardant expanded polystyrene resin molded articles may be reduced. Also, when the content is more than 2.00 parts by weight, manufacturing cost is expensive, while a large amount of blocking caused during pre-expansion occurs, thereby deteriorating the fillability of the pre-expanded particles into a mold of a molding machine.

[0029] After the flame retardant expandable polystyrene beads are produced by impregnating polystyrene resin particles dispersed in an aqueous suspension with a blowing agent and a powdery flame retardant, these flame retardant expandable polystyrene beads are taken out from the aqueous suspension and the flame retardant expandable polystyrene beads may be subject to washing and drying as required.

[0030] In addition, when cast molding is performed, the average particle diameter of the flame retardant expandable polystyrene beads is preferably 0.3 to 2.0 mm, more preferably 0.6 to 1.4 mm from the aspect of the fillability of the pre-expanded particles obtained by preliminarily expanding the flame retardant expandable polystyrene beads into a cavity.

[0031] It is noted that additive agents such as a foam adjusting agent, a filling agent, a flame retardant assistant agent, a lubricant, a colorant, a solvent and the like can be added to the flame retardant expandable polystyrene beads as required besides the powdery flame retardant to the extent that the physical properties are not impaired. When these

additive agents are added to the flame retardant expandable polystyrene beads, the additive agents may be added to the aqueous suspension in which the polystyrene resin particles are dispersed.

[0032] Next, a procedure of producing the flame retardant polystyrene resin expansion molded articles is explained by using the flame retardant expandable polystyrene beads. As the procedure of producing the flame retardant polystyrene resin expansion molded articles using the flame retardant expandable polystyrene beads, known methods can be adopted. Specifically, the flame retardant expandable polystyrene beads are heated and preliminarily expanded to prepare polystyrene resin pre-expanded particles having a bulk density of around 0.01 to 0.05 g/cm³. These polystyrene resin pre-expanded particles are filled into a cavity of a mold, heated and expanded, thereby enabling to obtain the flame retardant polystyrene resin expansion molded articles.

[0033] When the density of the flame retardant polystyrene resin expansion molded articles is low, the closed-cell ratio of the flame retardant polystyrene resin expansion molded articles is lowered and heat insulating properties or mechanical strength of the flame retardant polystyrene resin expansion molded articles can be reduced. On the other hand, when the density is high, time required for one cycle in the cast molding gets longer and the production efficiency of the flame retardant polystyrene resin expansion molded articles may be decreased. Therefore, the density is preferably 0.01 to 0.05 g/cm³.

EXAMPLE

[0034] Hereinafter, the present invention is illustrated by Examples and Comparative Examples, but the present invention is not limited to these.

[0035]

(Example 1)

(Example for production) An aqueous suspension was formed by supplying an autoclave equipped with a stirrer having an internal volume of 100 liters with 120 g of Tribasic Calcium Phosphate (manufactured by Taihei Chemical Industrial Co. Ltd.), 2.4 g of sodium dodecylbenzenesulfonate, 140 g of benzoyl peroxide (having a 75 % by weight purity), 30 g of t-butylperoxy-2-ethylhexyl monocarbonate, 40 kg of ion-exchange water and 40 kg of styrene monomer and stirring them by rotating stir blades at a rotation rate of 100 rpm.

[0036] Next, while stirring the aqueous suspension by rotating the stir blades at a rotation rate of 100 rpm, the temperature inside the autoclave was raised up to 90°C and maintained at 90°C for six hours and further, the temperature inside the autoclave was raised up to 120°C and maintained at 120°C for two hours, thereby carrying out suspension polymerization of styrene monomer.

[0037] After that, the temperature inside the autoclave was cooled down to 25 °C. The polystyrene particles were taken out from the inside of the autoclave, repeatedly washed and dehydrated multiple times. After undergoing a drying process, the polystyrene particles were classified,

thereby obtaining polystyrene particles having a particle diameter of 0.6 to 0.85 mm and a weight average molecular weight of 300,000.

[0038] Next, another autoclave with a stirrer having an internal volume of 100 liters was supplied with 30 kg of ion-exchange water, 4 g of sodium dodecylbenzenesulfonate and 100 g of magnesium pyrophosphate, followed by supplying with 11 kg of the polystyrene particles as seed particles into the autoclave and stirring them to be uniformly dispersed in water.

[0039] In addition, a dispersion in which 2g of sodium dodecylbenzenesulfonate and 20 g of magnesium pyrophosphate are dispersed in 6kg of ion-exchange water was prepared, while a styrene monomer solution in which, as polymerization initiators, 88 g of benzoyl peroxide (having a 75% purity) and 50 g of t-butylperoxy-2-ethylhexyl monocarbonate are dissolved into 5 kg of styrene monomer was prepared. This styrene monomer solution was added to the dispersion and stirred with a homomixer, and the mixture was then emulsified, thereby obtaining an emulsion.

[0040] After the inside of the autoclave was heated and maintained at 75°C, the emulsion was added to the inside of the autoclave and it was maintained for 30 minutes so as to absorb the styrene monomer and benzoyl peroxide smoothly into polystyrene seed particles. After that, while raising the temperature inside the autoclave from 75°C to 108°C at a rate of temperature increase of 0.2°C per minute, 28 kg of the styrene monomer was continuously dropped into the autoclave for 160 minutes. Next, 20 minutes after completing the dropping of the

styrene monomer, the temperature was raised up to 120°C at a rate of temperature increase of 1°C per minute and maintained for 90 minutes, thereby obtaining polystyrene particles by seed polymerization. All of the styrene monomer was used for polymerization.

[0041]

(Example 1)

A flame retardant A was prepared by adding silica (under the trade name "AEROSIL 200" manufactured by AEROSIL Japan Inc.) as a fluidizer to 440 g of a flame retardant, tetrabromocyclooctane (under the trade name "Pyroguard FR-200" manufactured by DAI-ICHI KOGYO SEIYAKU CO.,LTD.) and undergoing dry blending (for example, with a Henschel mixer).

[0042] Next, after cooling down to 90°C inside the autoclave at a rate of temperature decrease of 1°C per minute, 132 g of dicumyl peroxide was supplied as a flame retardant assistant agent into the autoclave, followed by supplying the flame retardant A into the autoclave.

[0043] Then, after 30 minutes has passed since the flame retardant A was supplied into the autoclave, the autoclave was sealed. After that, as blowing agents, 2640 g of butane (having an iso-butane/n-butane (weight ratio)=30/70) and 1100 g of pentane (having an iso-pentane/n-pentane (weight ratio) =20/80) were pressed into the autoclave by nitrogen pressurization in 30 minutes, maintaining the state for three hours.

[0044] Later, the inside of the autoclave was cooled down to 25°C. Flame retardant expandable polystyrene beads were taken out from the autoclave and repeatedly washed and dehydrated multiple times. After passing through a drying process, the flame retardant expandable polystyrene beads were classified, thereby obtaining flame retardant expandable polystyrene beads having a particle diameter of 0.85 to 1.2 mm, an average particle diameter of 1.1 mm and a weight average molecular weight of 300,000. It is noted that all the powdery flame retardant of the flame retardant A was impregnated into the polystyrene particles.

[0045]

(Example 2)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that the amount of tetrabromocyclooctane was set to be 220 g in the preparation of the flame retardant A.

[0046]

(Example 3)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that the amount of tetrabromocyclooctane was set to be 660 g in the preparation of the flame retardant A.

[0047]

(Example 4)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that the amount of tetrabromocyclooctane was set to be 880 g in the preparation of the flame retardant A.

[0048]

(Example 5)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that hydrophilic silica was used in amount of 4.48 g instead of 2.24 g in the preparation of the flame retardant A.

[0049]

(Example 6)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that hydrophilic silica was used in amount of 6.72 g instead of 2.24 g in the preparation of the flame retardant A.

[0050]

(Example 7)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that hydrophilic silica (under the trade name "AEROSIL 300" manufactured by AEROSIL Japan Inc.) was used as a fluidizer in the preparation of the flame retardant A.

[0051]

(Example 8)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that hydrophobic silica (under the trade name "AEROSILR 974" manufactured by AEROSIL Japan Inc.) was used as a fluidizer in the preparation of the flame retardant A.

[0052]

(Comparative Example 1)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that the amount of tetrabromocyclooctane was set to be 88 g in the preparation of the flame retardant A.

[0053]

(Comparative Example 2)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that the amount of tetrabromocyclooctane was set to be 1320 g in the preparation of the flame retardant A.

[0054]

(Comparative Example 3)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that hydrophilic silica was not used in the preparation of the flame retardant A.

[0055]

(Comparative Example 4)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that the amount of hydrophilic silica was set to be 0.22 g instead of 2.24 g in the preparation of the flame retardant A.

[0056]

(Comparative Example 5)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that the amount of hydrophilic silica was set to be 8.96 g instead of 2.24 g in the preparation of the flame retardant A.

[0057]

(Comparative Example 6)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that hydrophilic silica (under the trade name "AEROSIL 130" manufactured by AEROSIL Japan Inc.) was used as a fluidizer in the preparation of the flame retardant A.

[0058]

(Comparative Example 7)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that hydrophilic silica (under the trade name "AEROSIL 380" manufactured by AEROSIL Japan Inc.) was used as a fluidizer in the preparation of the flame retardant A.

[0059]

(Comparative Example 8)

Flame retardant expandable polystyrene beads were obtained as in Example 1 except that 88.0 g of tetrabromobisphenol A-bis(2,3-dibromopropyl ether) was used instead of 2.24 g of hydrophilic silica in the preparation of the flame retardant A.

[0060] Each evaluation of the above Examples and Comparative Examples was made in the following manner as shown in Table 1 and Table 2.

[Table 1]

[0061]

[Table 2]

	Comparative Example					
	1	2	3	4	5	6
TBCO (part by weight)/ resin particles (100 parts by weight)	0.2	3	1	1	1	1
TBCO (part by weight)	99.5	99.5	100	99.95	98	80
Fluidizer	Hydrophilic silica	Hydrophilic silica	None	Hydrophilic silica	Hydrophilic silica	Tetrabromobisphenol A-bis(2,3-dibromopropyl ether)
Specific surface area of silica (m ² /g)	200	200		200	200	
Silica (part by weight)	0.5	0.5		0.05	2	20
Blocking evaluation of flame retardant A	○	×	×	×	○	△
Bonding when pre-expanded	○	○	×	×	○	×
Flame retardant test	Flame-out time (sec.)	0.3	0.3	0.3	0.6	Burning
	Result of flame retardant test	×	⊙	⊙	⊙	×
Appearance evaluation of expansion molded article	○	○	○	○	×	○
Heat fusion property	⊙	×	○	○	○	○
Remarks					Large scattering of silica powder	

[0062]**[Method of measuring silica specific surface area]**

All methods of measuring specific surface area of silica fine powders used in the present invention are based on the BET method.

[0063]**[Blocking evaluation of flame retardant A]**

Evaluations were made in a way that 100 g of flame retardant was put in a polyethylene bag, packed into a tube having a diameter of 50 mm, on which 1.1 kg of spindle was put, and stored in an oven having 40°C for one month, followed by taking it out from there to observe the state.

× . . . A flame retardant is hardened in a very hard state, which can not be fully crumbled even if gripping it by hand.

△ . . . A flame retardant is hardened in a hard state, but crumbled even if gripping it by hand.

○ . . . A flame retardant provides tightening feeling, but no lumps, which is in a powder state.

[0064]**[Molding of polystyrene expansion molded articles]**

40kg of the obtained flame retardant expandable polystyrene beads and as coating agents, 20 g of polyethylene glycol, 60 g of zinc stearate, 40

g of fatty acid triglyceride (under the trade name "RIKEMAL VT-50" manufactured by RIKEN VITAMIN CO., LTD.) and 20g of fatty acid monoglyceride (under the trade name "RIKEMAL S-100P" manufactured by RIKEN VITAMIN CO., LTD.) were supplied into a tumbler mixer and stirred for 30 minutes, thereby coating the surfaces of the flame retardant expandable polystyrene beads with the coating agents.

Next, after the flame retardant expandable polystyrene beads were stored in a cooling warehouse having 15°C for 48 hours, 5.8 kg of the flame retardant expandable polystyrene beads per shot were supplied into a cylindrical batch-type pressurized prefoamer having a volume to a detection sensor installed in the upper part of prefoamer tank of 350 liters as set forth in page 39 of the official gazette 57(1982)-133[3347], well-known and conventional art collection (expansion molding) and heated by water vapor for two minutes, thereby obtaining polystyrene pre-expanded particles.

After that, the polystyrene pre-expanded particles were left under a room temperature atmosphere for 24 hours, while a block molding machine (under the trade name "PEONY · 205DS" manufactured by KASAHARA INDUSTRY CO., LTD.) equipped with a mold having a cavity with a rectangular parallelepiped shape of 840 mm length × 930 mm width × 530 mm height was prepared. The polystyrene pre-expanded particles were filled into the cavity of this mold and water vapor of 0.07 MPa (gauge pressure) was pressed into the cavity of the mold for 20 seconds, thereby secondarily expanding the polystyrene pre-expanded particles. Next, the mold was cooled down until the pressure in the mold becomes -0.01 MPa, thereby obtaining flame

retardant polystyrene expansion molded articles of rectangular parallelepiped shape. Subsequently, the flame retardant polystyrene expansion molded articles were stored in a drying room having 70°C for three days.

[0065]

[Bonding of pre-expanded particles]

A weight W_1 (g) of the polystyrene pre-expanded particles obtained by the above procedures were prepared and sieved using a sieve with an aperture of 1cm. A weight W_2 (g) of the polystyrene pre-expanded particles left on the sieve were measured, calculating the bonding degree of the pre-expanded particles according to the following formula. The obtained results were shown in Tables 1 and 2. It is noted that the bonding degree of not greater than 1% by weight was evaluated as ○ and the bonding degree exceeding 1% by weight was evaluated as ×.

$$\text{Bonding degree of pre-expanded particles (\% by weight)} = 100 \times W_2 / W_1$$

[0066]

[Flame retardant test]

Five test specimens each having a rectangular parallelepiped shape of 200 mm length × 25 mm width × 10 mm height were cut out from the obtained flame retardant polystyrene expansion molded articles by a vertical cutter. After aging at an oven having 60°C for one day, measurements were made according to a measuring method A of JIS A9511-2006 to determine the average value of the five test specimens.

By defining the determined average value as a flame-out time, evaluations were comprehensively made according to the following standard. The obtained results were shown in Tables 1 and 2. It is noted that the flame-out time is required to be within three seconds according to the JIS standard. Therefore, the flame-out time is preferably to be within two seconds, more preferably within one second.

× . . . Flame-out time exceeds three seconds, or even in one test specimen, afterglow exists or flame spreads beyond the indicating line of flammability limit.

○ . . . Flame-out time is over one second and within three seconds and in all of the five test specimens, neither afterglow exists nor flame spreads beyond the indicating line of flammability limit.

◎ . . . Flame-out time is within one second and in all of the five test specimens, neither afterglow exists nor flame spreads beyond the indicating line of flammability limit.

[0067]

[Appearance evaluation of expansion molded articles]

Each appearance of expansion molded articles was visually observed and evaluated according to the following standard.

○ . . . A part where expanded particles were fused with each other was flat and smooth.

× . . . Concavities and convexities were generated in the fused part of the expanded particles.

[0068]

[Heat fusion property]

Sliced articles (each having 1840 mm length × 980 mm width × 50 mm thickness) were obtained by cutting using a nichrome wire cutter. At the center portion in the long side direction on the upper surface of the sixth element of the sliced article from the bottom, a broken cut line having a depth of 5 mm was formed along the short side direction by using a cutter knife. Then, the sliced article was divided into two along this broken cut line by hand, thereby obtaining divided pieces each having 920 mm length × 930 mm width × 50 mm thickness.

In the broken surface of the obtained divided pieces, particles (a) broken in the expanded particles and particles (b) broken on the interfaces among the expanded particles were counted to calculate the fusion ratio according to the following formula. The obtained results were shown in Tables 1 and 2. It is note that the fusion ratio of not less than 70% is evaluated as ◎, the fusion ratio of from 50% to less than 70% is evaluated as ○, and the fusion ratio of less than 50% is evaluated as ×.

Fusion ratio (%) = $100 \times \text{particle number (a)} / (\text{particle number (a)} + \text{particle number (b)})$

[0069] From Table 1, 0.45 to 2.0 parts by weight of the tetrabromocyclooctane is added relative to 100 parts by weight of the polystyrene resin. Examples containing 0.3 to 1.5 parts by weight of the silica fine powders relative to 98.5 to 99.7 parts by weight of the tetrabromocyclooctane which is the powdery flame retardant are recognized as good results with regard to any of blocking evaluation, bonding of pre-expanded particles, flame retardant test (self-extinguishing property), result of flame retardant test, appearance evaluation of expanded molded articles and heat fusion property.

On the other hand, from Table 2, Comparative Example 1 containing 0.2 parts by weight of the tetrabromocyclooctane relative to 100 parts by weight of the polystyrene resin shows bad results in the flame retardant test (self-extinguishing property) and × in the result of flame retardant test. In Comparative Example 2 containing 3.0 parts by weight of the tetrabromocyclooctane relative to 100 parts by weight of the polystyrene resin, the blocking evaluation is × and the heat fusion property is ×. Also, in Comparative Example 3 not containing hydrophilic silica, the blocking evaluation is × and the bonding of pre-expanded particles is also ×. In Comparative Example 4 where the content of the silica fine powders are 0.05 parts by weight, the blocking evaluation is × and the bonding of pre-expanded particles is × as well. In Comparative Example 5 where the content of the silica fine powders are 2 parts by weight, there is a problem in terms of appearance evaluation of an expanded molded article. Scattering of the silica fine powders is large. Comparative Example 6 replacing a fluidizer with tetrabromobisphenol A-bis(2,3-dibromopropyl ether) also

shows × in the bonding of pre-expanded particles, bad results in the flame retardant test (self-extinguishing property) and × in the result of flame retardant test

INDUSTRIAL APPLICABILITY

[0070] The flame retardant expandable polystyrene beads of the present invention has been used for a wide range of purposes such as in the fields of agricultural and fishing, home electronics, architectural and civil engineering and the like. Particularly, they are used as heat-insulating materials for walls or floors in the architectural field.

WHAT IS CLAIMED IS:

1. Flame retardant expandable polystyrene beads, wherein polystyrene resin particles dispersed in an aqueous suspension are impregnated with a powdery flame retardant of tetrabromocyclooctane dispersed by silica fine powders before or during impregnation of the polystyrene resin particles with a blowing agent, the flame retardant expandable polystyrene beads are taken out from the aqueous suspension,

the tetrabromocyclooctane is added in an amount of 0.45 to 2.0 parts by weight relative to 100 parts by weight of the polystyrene resin and

the silica fine powders are contained in an amount of 0.3 to 1.5 parts by weight relative to 98.5 to 99.7 parts by weight of the tetrabromocyclooctane that is the powdery flame retardant.

2. The flame retardant expandable polystyrene beads according to claim 1, wherein the specific surface area of the silica fine powders is 170 to 330 m²/g.

3. A method of producing flame retardant expandable polystyrene beads comprising steps of

impregnating polystyrene resin particles dispersed in an aqueous suspension with 0.45 to 2.0 parts by weight of a powdery flame retardant of tetrabromocyclooctane dispersed by silica fine powders before or during impregnation of the polystyrene resin particles with a blowing agent and

taking out the flame retardant expandable polystyrene beads from the aqueous suspension,

wherein the powdery flame retardant contains 0.3 to 1.5 parts by weight of the silica fine powders relative to 98.5 to 99.7 parts by weight of the tetrabromocyclooctane.

4. Pre-expanded particles wherein the flame retardant expandable polystyrene beads according to claim 1 are preliminarily expanded.
5. Expansion molded articles obtained by filling the pre-expanded particles according to claim 4 into a mold and expanding them.