

DESCRIPTION

FLAME-RETARDANT EXPANDABLE STYRENE RESIN PARTICLE AND METHOD FOR PRODUCTION THEREOF

TECHNICAL FIELD

5 [0001]

The present invention relates to a flame-retardant expandable styrene based resin particle and a method for producing the same. More particularly, the present invention relates to a flame-retardant expandable styrene based resin particle and a method for producing
10 the same using tetrabromocyclooctane as a flame retardant.

BACKGROUND ART

[0002]

Styrene based resin expanded molded articles have been used for construction materials to a great extent as having excellent strength
15 and heat insulation. Such styrene based resin expanded molded articles were produced by suspending and polymerizing a styrenic monomer to obtain styrene based resin particles; impregnating the obtained styrene based resin particles with a physical blowing agent to obtain expandable styrene based resin particles; pre-expanding the
20 obtained expandable styrene based resin particles to obtain styrene based resin pre-expanded particles; charging the obtained pre-expanded particles into a metal mold having a desired shape for expansion; and thermally fusing and integrating the pre-expanded particles by the action of their blowing pressure.

25 [0003]

On the other hand, the above-described styrene based resin expanded molded articles have a problem; they are inflammable. When used for construction materials, in particular, they may cause spread of flame in case of a fire. Therefore, resolution of the problem
5 has been attempted by adding a flame retardant to a styrene based resin expanded molded article.

Examples of known methods for adding a flame retardant include a method in which the flame retardant is dissolved in a styrenic monomer and a method in which impregnation of styrene based resin
10 particles with the flame retardant is performed simultaneously with impregnation with a physical blowing agent. Examples of the former method include methods disclosed in Japanese Unexamined Patent Publication No. 2003-335891 (Patent Document 1) and Japanese Unexamined Patent Publication No. 2002-194130 (Patent Document 2),
15 and examples of the latter method include methods disclosed in Japanese Examined Patent Publication No. HEI 6(1994)-18918 (Patent Document 3) and Japanese Unexamined Patent Publication No. 2007-246606 (Patent Document 4).

Patent Document 1: Japanese Unexamined Patent Publication No.
20 2003-335891

Patent Document 2: Japanese Unexamined Patent Publication No.
2002-194130

Patent Document 3: Japanese Examined Patent Publication No. HEI
6(1994)-18918

25 Patent Document 4: Japanese Unexamined Patent Publication No.

2007-246606

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0004]

5 In the former method, hexabromocyclododecane (HBCD) is mainly used as a flame retardant. The HBCD is a substance for which accumulation in living organisms is concerned about, and it is therefore desired to reduce the use thereof. Since the impregnation with the flame retardant is performed on the styrene based resin particles in the latter method, the impregnation amount is limited, and
10 it is therefore desired to increase the impregnation amount of the flame retardant to improve the flame retardancy.

 In addition, there is another problem; when the impregnation amount of the flame retardant is too large for the styrene based resin particles, the flame retardant works as a nucleating agent to make the
15 size of foams in the obtained styrene based resin expanded article too small. This problem has an adverse effect on the latter method, in particular. That is, in the latter method, more flame retardant resides around the surface of the styrene based resin particles to cause the forms formed in the pre-expanded particles to be small only in a surface
20 region. As a result, the foams may be unable to resist heat during production of an expanded molded article by molding to cause melting, having an adverse effect on the appearance of the expanded molded article. In addition, residing more around the surface of the styrene
25 based resin particles, the flame retardant has tended to cause so-called

blocking, that is, fusion and binding among the pre-expanded particles upon the pre-expansion. Furthermore, in some cases, the flame retardant experienced secondary aggregation in a solution for the impregnation with a blowing agent to make dispersion of the flame retardant nonuniform. As a result, absorption of the flame retardant to the styrene based resin particles could be nonuniform. Nonuniform absorption will allow presence of particles that have absorbed more flame retardant in part, and such particles will have inferior heat resistance. As a result, the particles could be unable to resist heating during production of an expanded molded article by molding to contract to be hardened particles. Expanded molded articles are usually shaped into a predetermined shape by cutting with a heated nichrome wire, and on this occasion, the nichrome wire could bounce at the hardened particles to generate lines having uneven shapes on a face that has gone through the cutting, significantly reducing the value of the article produced. In addition, the lines having uneven shapes could result in insufficient adhesive strength when the expanded molded article and a panel were pasted together for a use.

Furthermore, there is another problem; thermal fusion among the styrene based resin pre-expanded particles may be poor.

MEANS FOR SOLVING THE PROBLEMS

[0005]

The inventors of the present invention have found that it is possible to provide expandable styrene based resin particles that have, when expanded, excellent thermal fusibility among particles and that

allow production of an expanded molded article having excellent flame retardancy by using a specific flame retardant in a specific amount and setting the temperature for the impregnation with the physical blowing agent to a specific temperature, to achieve the invention.

5 The present invention therefore provides a method for producing a flame-retardant expandable styrene based resin particle, the method comprising: adding, in suspension polymerization of a styrenic monomer to obtain a styrene based resin particle, 0.45 parts by weight to 2.0 parts by weight of tetrabromocyclooctane with respect
10 to 100 parts by weight of the styrenic monomer; and then impregnating the styrene based resin particle with a physical blowing agent while adjusting an impregnation temperature to 80°C to 110°C during or after the suspension polymerization of the styrenic monomer to obtain the flame-retardant expandable styrene based resin particle.

15 [0006]

 The present invention further provides a flame-retardant expandable styrene based resin particle comprising: a styrene based resin particle; and a physical blowing agent and tetrabromocyclooctane contained in the styrene based resin particle,

20 the tetrabromocyclooctane being contained in the styrene based resin particle so as to satisfy a relationship of a formula $a \leq 1.1 \times b$ when a content percentage of the tetrabromocyclooctane contained in a surface region of the styrene based resin particle is "a" (% by weight) and a content percentage of the tetrabromocyclooctane
25 contained in a whole of the styrene based resin particle is "b" (% by

weight),

the tetrabromocyclooctane being contained in the whole of the styrene based resin particle in an amount of 0.45 parts by weight to 2.00 parts by weight with respect to 100 parts by weight of the styrene based resin particle, and

the flame-retardant expandable styrene based resin particle giving an expanded article having an average foam size of 50 μm to 350 μm when expanded by an expansion ratio of 50.

EFFECTS OF THE INVENTION

[0007]

The production method of the present invention can provide a flame-retardant expandable styrene based resin particle that is capable of controlling the foam size, free from variation of the foam density when expanded, and has satisfactory thermal fusibility when molded.

In addition, use of a surfactant in the suspension polymerization allows improvement of dispersion stability of droplets of a monomer mixture in the suspension polymerization system.

Inclusion of a flame retardant auxiliary agent in the monomer mixture allows improvement of the flame retardancy of the expandable styrene based resin particle.

[0008]

Adjustment of the impregnation temperature so that the expanded molded article to be obtained by expanding the above-described flame-retardant expandable styrene based resin particle by a factor of 50 will have an average foam size of 50 μm to

350 μ m allows provision of an expandable styrene based resin particle that has more satisfactory thermal fusibility.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

5 FIG. 1 is an electron micrograph of a cross section of a pre-expanded particle of Example 1.

 FIG. 2 is an electron micrograph of a cross section of a pre-expanded particle of Example 3.

10 FIG. 3 is an electron micrograph of a cross section of a pre-expanded particle of Comparative Example 4.

 FIG. 4 is an electron micrograph of a cross section of a pre-expanded particle of Comparative Example 5.

 FIG. 5 is an electron micrograph of a cross section of a pre-expanded particle of Comparative Example 6.

15 BEST MODE FOR CARRYING OUT THE INVENTION

[0010]

 First, in the present invention, suspension polymerization of a styrenic monomer is carried out to obtain styrene based resin particles, and on this occasion, tetrabromocyclooctane (TBCO) and a
20 polymerization initiator are added to the styrenic monomer.

 Examples of the styrenic monomer include styrene, α -methylstyrene, p-methylstyrene, t-butylstyrene, chlorstyrene, and the like. These monomers may be used independently or in combination of two or more kinds thereof. Of these monomers, styrene
25 is particularly preferable. In addition, an ester of acrylic or

methacrylic acid such as methylacrylate, butylacrylate, methyl methacrylate, ethyl methacrylate, and cetyl methacrylate; or a monomer such as acrylonitrile, dimethyl fumarate, and ethyl fumarate may be copolymerized with the styrenic monomer. Further, a
5 bifunctional monomer such as divinylbenzene and alkylene glycol dimethacrylate may be copolymerized with the styrenic monomer.

The TBCO is used in a range of 0.45 parts by weight to 2.00 parts by weight with respect to 100 parts by weight of the styrenic monomer. This range can ensure the flame retardancy and the
10 thermal fusibility in molding, and inhibit variation of the foam density.
[0011]

The polymerization initiator is not particularly limited and a suitable polymerization initiator may be appropriately selected according to the polymerization temperature. Examples thereof
15 include organic peroxides such as benzoyl peroxide, lauroyl peroxide, t-butyl perbenzoate, t-butyl perpivalate, t-butyl peroxyisopropyl carbonate, t-butyl peroxyacetate, 2,2-di-t-butyl peroxybutane, t-butyl peroxy-3,3,5-trimethylcyclohexanoate, di-t-butyl peroxyhexahydrotelephthalate, and
20 1,1-di-t-butylperoxy-3,3,5-trimethylcyclohexane; and azo compounds such as azobisisobutyronitrile and azobisdimethylvaleronitrile. These polymerization initiators may be used independently or in combination of two or more kinds thereof. The polymerization initiator can be used in a range of 0.05 parts by weight to 3.0 parts by weight with respect to
25 100 parts by weight of the styrenic monomer.

[0012]

A monomer mixture is obtained by dissolving the TBCO in the styrenic monomer. The monomer mixture may contain a flame retardant auxiliary agent. Examples of the flame retardant auxiliary agent include cumene hydroperoxide, dicumyl peroxide, t-butyl hydroperoxide, 2,3-dimethyl-2,3-diphenylbutan, and the like. The flame retardant auxiliary agent can be used in a range of 0.1 parts by weight to 0.5 parts by weight with respect to 100 parts by weight of the styrenic monomer.

10 [0013]

The monomer mixture is dispersed in an aqueous medium and subjected to suspension polymerization.

Examples of the aqueous medium include water, and a mixture of water and a water-soluble organic medium (for example, methyl alcohol and ethyl alcohol). The aqueous medium may contain an additive such as a surfactant and a dispersant.

Examples of the surfactant include anionic surfactants, cationic surfactants, amphi-ionic surfactants, and non-ionic surfactants.

20 [0014]

Examples of the anionic surfactants include, fatty acid oils such as sodium oleate and castor oil potassium; alkyl sulfuric acid ester salts such as sodium laurylsulfate and ammonium laurylsulfate; alkylbenzene sulfonates such as sodium dodecyl benzenesulfonate; alkyl naphthalenesulfonates; alkanesulfonates; dialkyl

sulfosuccinates; alkylphosphoric acid ester salts; naphthalenesulfonic acid-formalin condensed products; polyoxyethylene- alkyl phenyl ether sulfuric acid ester salts; polyoxyethylenealkyl sulfuric acid ester salts; and the like.

5 [0015]

Examples of the non-ionic surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene fatty acid esters, sorbitane fatty acid esters, polyoxysorbitane fatty acid esters, polyoxyethylene alkyl amines, glycerine fatty acid esters, oxyethylene-oxypropylene block polymers, and the like.

Examples of the cationic surfactants include alkyl amine salts such as laurylamine acetate and stearylamine acetate; quarternary ammonium salts such as lauryltrimethyl ammonium chloride; and the like.

15 Examples of the amphi-ionic surfactants include lauryl dimethylamine oxides and phosphate ester or phosphorous acid ester surfactants.

[0016]

The above-mentioned surfactants may be used independently or in combination of two or more kinds thereof. The surfactant can be used in a range of 0.002 parts by weight to 1.0 part by weight with respect to 100 parts by weight of the aqueous medium.

Examples of the dispersant include water-soluble polymers such as polyvinyl alcohol, methylcellulose, polyvinylpyrrolidone, and polyacrylamide; and hardly soluble inorganic salts such as magnesium

pyrophosphate, tricalcium phosphate, and hydroxyapatite. These dispersants may be used independently or in combination of two or more kinds thereof. The dispersant can be used in a range of 0.2 parts by weight to 10 parts by weight with respect to 100 parts by weight of the styrenic monomer.

The styrenic monomer is subjected to suspension polymerization. The suspension polymerization is usually carried out at 50°C to 120°C for 1 hour to 20 hours. As a result of the suspension polymerization, styrene based resin particles are obtained.

10 [0017]

Further, during or after the suspension polymerization, the styrene based resin particles are impregnated with a physical blowing agent, thereby obtaining flame-retardant expandable styrene based resin particles. Here, the impregnation temperature for the impregnation is adjusted to 80°C to 110°C. Such adjustment allows provision of flame-retardant expandable styrene based resin particles that are capable of controlling the foam size, free from variation of the foam density when expanded, and have satisfactory thermal fusibility when molded.

20 The impregnation of the styrene based resin particles with the physical blowing agent during the suspension polymerization can be performed by pressing the physical blowing agent into the aqueous medium. On the other hand, when the impregnation of the styrene based resin particles with the physical blowing agent is performed after
25 the suspension polymerization, the styrene based resin particles are

taken out from the aqueous medium for the impregnation or left in the aqueous medium for the impregnation.

[0018]

The physical blowing agent means a blowing agent having a blowing function as is without decomposing, that is, a so-called volatile blowing agent. Examples of the physical blowing agent include aliphatic hydrocarbons such as propane, normal butane, isobutane, normal pentane, isopentane, and hexane. These physical blowing agents can be used independently or in combination of two or more kinds thereof.

The average particle diameter of the obtained flame-retardant expandable styrene based resin particles may be, for example, 0.3 mm to 2.0 mm.

The flame-retardant expandable styrene based resin particles go through a commonly known pre-expansion process and expansion-molding process to be an expanded molded article. When the particles are expanded by a factor of 50, in particular, the average diameter of the foams that constitute the expanded molded article can be in a range of 50 μm to 350 μm . This range allows the expanded particles that constitute the expanded molded article to have satisfactory thermal fusibility.

The present invention also provides a flame-retardant expandable styrene based resin particle obtained by the above-described method. The flame-retardant expandable styrene based resin particle contains tetrabromocyclooctane so as to satisfy the

relationship of the formula $a \leq 1.1 \times b$ when the content percentage of the tetrabromocyclooctane contained in a surface region of the styrene based resin particle is "a" (% by weight) and the content percentage of the tetrabromocyclooctane contained in the whole of the styrene based resin particle is "b" (% by weight). By satisfying the relationship, a flame-retardant expandable styrene based resin particle that satisfies both the flame retardancy and the thermal fusibility can be provided. More preferably, the relationship is represented by the formula $a \leq 1.05 \times b$.

Here, the content percentage "a" of the tetrabromocyclooctane in the surface region of the particle is a value measured by the following method, as being difficult to be measured directly. That is, a test piece having a thickness of 0.2 mm is cut out from a surface of an expanded molded article obtained by expanding flame-retardant expandable styrene based resin particles by a factor of 50. Since the surface of the expanded molded article is formed of the surface region of the flame-retardant expandable styrene based resin particles, the test piece shows a state of the surface region of the flame-retardant expandable styrene based resin particles. The amount of the tetrabromocyclooctane in the test piece is measured and the ratio thereof to the total weight of the test piece is calculated, thereby obtaining the content percentage "a" (% by weight) of the tetrabromocyclooctane contained in the surface region of each particle. The detail of the measurement method is described in Examples.

On the other hand, the content percentage "b" of the

tetrabromocyclooctane contained in the whole of each particle means a ratio of the amount of the tetrabromocyclooctane to the amount of the styrenic monomer as materials for the production of the flame-retardant expandable styrene based resin particle.

5 EXAMPLES

[0019]

Hereinafter, the present invention will be described in detail based on Examples; however, the present invention is not limited to these Examples. Measurement methods for the molecular weight of
10 styrene based resin particles, the bulk expansion ratio, the expansion ratio, the flame retardancy, the average foam size, and the thermal fusibility are as follows.

(Molecular weight of styrene based resin particle)

The weight average molecular weight (Mw) is measured by gel
15 permeation chromatography (GPC). The measurement method is as follows. The weight average molecular weight (Mw) herein means a weight average molecular weight indicated as the molecular weight of polystyrene (PS).

The measurement is carried out by using a chromatograph after
20 dissolving 50 mg of a sample in 10 ml of tetrahydrofuran (THF) and filtering it with a non-aqueous 0.45 μ m chromatography disc. The conditions for the chromatograph are as follows.

[0020]

Liquid chromatograph: trade name "Gel permeation
25 chromatograph HLC -8020" produced by Tosoh Corporation

Column: trade name "TSKgel GMH-XL-L", ϕ 7.8 mm $\times$ 30 cm $\times$
2 columns, produced by Tosoh Corporation

Column temperature: 40°C

Carrier gas: Tetrahydrofuran (THF)

5 Carrier gas flow rate: 1 ml/minute

Injection pump temperature: 35°C

Detection: RI

Injection amount: 100 microliters

Standard polystyrene for calibration curve: trade name
10 "Shodex" manufactured by SHOWA DENKO K.K., weight average
molecular weight: 1030000; and product by Tosoh Corporation, weight
average molecular weight: 5480000, 3840000, 355000, 102000, 37900,
9100, 2630, 870
[0021]

15 (Bulk expansion ratio)

The bulk expansion ratio is calculated according to the
following formula after allowing pre-expanded particles as a sample to
free fall into a graduated cylinder, tapping on the bottom of the
graduated cylinder to even the sample volume, and measuring the
20 volume and the mass of the sample. In the case of styrene based resin,
the specific gravity of the resin is 1.0.

Bulk expansion ratio (times) = Sample volume (ml) in graduated
cylinder / Sample mass (g) $\times$ Specific gravity of resin
[0022]

25 (Expansion ratio)

The expansion ratio was calculated according to the following formula after measuring the dimension and the mass of a test piece (for example, 50 mm × 50 mm × 25 mm) of an expanded molded article so as to be indicated to three or more significant figures. In the case of styrene based resin, the specific gravity of the resin is 1.0.

Expansion ratio (times) = Test piece volume (cm³) / Test piece mass (g)
× Specific gravity of resin

[0023]

(Flame retardancy)

Five test pieces each having a thickness of 10 mm, a length of 200 mm, and a width of 25 mm are cut out from an expanded molded article and given a prescribed ignition limit index line and flammability limit index line. Each test piece is burnt up to the ignition limit index line by using a candle for a fire source, and then the flame is reversed to measure the time (seconds) from that moment to the moment when the flame goes out. Articles are evaluated as pass when the average time until the flame goes out among the five tests was not more than 3 seconds and no test piece is burnt beyond the flammability limit index line. The candle used for the fire source is that giving a flame having a length of 50 mm or more and a width of approximately 7 mm or more in stationary burning when the wick thereof has a length of approximately 10 mm.

[0024]

(Average foam size)

An expanded molded article is cut and photographed by

enlarging 100 times a cut area 1/10 to 9/10 or more inside from the outside of the cut surface with a scanning electron microscope (S-3000N produced by Hitachi, Ltd.). The photographed images are printed onto A4 paper sheets so that each paper sheet has 4 images, and from the number of forms on an arbitrary straight line (60mm in length), the average chord length (t) of the foams is calculated according to the following formula. The arbitrary straight line is set so as to allow as few foams as possible not to contact with the line only at a point of contact (when contacting at a point, the foam is counted in). The measurement is performed on six places.

Average chord length $t = 60 / (\text{Number of foams} \times \text{Multiplication factor of photograph})$

Then, the foam size D is calculated according to the following formula.

$$D = t / 0.616$$

[0025]

(Thermal fusibility)

After molding, an expanded molded article is dried at 70°C for 48 hours, and then a piece around the center in the thick direction is cut out to have a thickness of 50 mm by using a slicer with a nichrome wire. The molded article in a plate-like shape of 350 mm × 450 mm × 50 mm cut out is broken in half at the center in the long direction. The percentage (%) of particles that were broken in the expanded particles themselves to all particles that are present in the breaking area is calculated. The percentage of fusion is evaluated as "excellent" when it is 80% or more, "good" when it is 60% or more and less than 80%,

"acceptable " when it is 40% or more and less than 60%, and "poor×" when it is less than 40%.

[0026]

Example 1

5 Into a 100-liter autoclave, 40 kg of a styrene monomer in which
200 g of tetrabromocyclooctane (Pyrogard FR-200 manufactured by
DAI-ICHI KOGYO SEIYAKU CO., LTD.), 120 g of dicumyl peroxide, 140
g of benzoyl peroxide (purity: 75%), and 30 g of t-butyl peroxybenzoate
were dissolved was set after being mixed with 40 kg of ion-exchange
10 water containing 60 g of tricalcium phosphate (TCP-10 manufactured
by Taihei Chemicals) as a dispersant and 0.8 g of sodium dodecyl
benzenesulfonate as a suspension stabilizing auxiliary agent
(surfactant), and then dissolved and dispersed under stirring to form a
suspension.

15 [0027]

Next, the styrene monomer was subjected to polymerization
reaction at 90°C for 6 hours and further at 110°C for 4 hours under
stirring at 70 rpm. During the reaction at 90°C, that is, 2 hours and 3
hours from the initiation of the reaction, 6 g of tricalcium phosphate
20 (TCP-10, manufactured by Taihei Chemicals) was further added to the
suspension, respectively. After completion of the reaction, the
temperature was decreased to room temperature (25°C), and the
content was taken out of the autoclave to be subjected to a centrifugal
separation process and dried to obtain styrene resin particles.

25 The obtained styrene resin particles were classified to give

particles of 0.6 mm to 0.7 mm.

[0028]

Into a 5-liter autoclave, 2000 g of water, 9 g of magnesium pyrophosphate, and 0.3 g of sodium dodecyl benzenesulfonate were set
5 to prepare an aqueous medium, and 2000 g of the above-described particles were added thereto to be stirred at 300rpm.

Subsequently, the temperature was raised to 95°C, and 180 g of butane was pressed in at the same temperature being retained. The particles were impregnated with the butane for 3 hours, and then
10 cooled to obtain expandable styrene resin particles. The obtained expandable styrene resin particles were allowed to stand at 15°C for 4 days for aging, and then subjected to a pre-expansion process. The pre-expansion process was carried out under a certain condition, that is, the expandable styrene based resin particles were put into a
15 pre-expander and pre-expanded with the use of steam. As a result of the pre-expansion, particles pre-expanded by a bulk expansion ratio of 50 were obtained. FIG. 1 shows an SEM (scanning electron microscope) photograph of a cross section of the pre-expanded particle obtained. FIG. 1 indicates that a pre-expanded particle in which
20 variation of the foam density is inhibited was obtained in Example 1.

[0029]

Furthermore, the pre-expanded particles were allowed to stand at normal temperature for 24 hours for aging, charged into a mold cavity of a commonly known steam molding machine for expandable
25 polystyrene, heated with steam of 0.6 kg/cm²G for 30 seconds, and

cooled with water for 20 seconds to obtain a molded article in a block shape of 300 mm × 450 mm × 100 mm expanded by an expansion ratio of 50.

Table 1 shows the flame retardancy, the average foam size, and
5 the thermal fusibility of the block-shaped expanded molded article obtained.

[0030]

Example 2

An expanded molded article was obtained in the same manner
10 as in Example 1 except that the amount of the tetrabromocyclooctane was changed to 400 g.

Example 3

An expanded molded article was obtained in the same manner
as in Example 1 except that the amount of the tetrabromocyclooctane
15 was changed to 600 g. FIG. 2 shows an SEM photograph of a cross section of the pre-expanded particle obtained. FIG. 2 indicates that a pre-expanded particle in which variation of the foam density is inhibited was obtained in Example 3.

Example 4

20 An expanded molded article was obtained in the same manner as in Example 1 except that the amount of the tetrabromocyclooctane was changed to 800 g.

[0031]

Example 5

25 An expanded molded article was obtained in the same manner

as in Example 2 except that the impregnation temperature was changed to 80°C.

Example 6

5 An expanded molded article was obtained in the same manner as in Example 2 except that the impregnation temperature was changed to 100°C.

Example 7

10 An expanded molded article was obtained in the same manner as in Example 2 except that the impregnation temperature was changed to 110°C.

[0032]

Example 8

An expanded molded article was obtained in the same manner as in Example 3 except that the dicumyl peroxide was not added.

15 Example 9

An expanded molded article was obtained in the same manner as in Example 5 except that 2.2 g of α -olefin sulfonate was used instead of the sodium dodecyl benzenesulfonate.

Example 10

20 An expanded molded article was obtained in the same manner as in Example 9 except that the impregnation temperature was changed to 110°C.

[0033]

Example 11

25 An expanded molded article was obtained in the same manner

as in Example 2 except that the tricalcium phosphate was changed from TCP-10 manufactured by Taihei Chemicals to C13-09 manufactured by Budenheim.

Example 12

5 An expanded molded article was obtained in the same manner as in Example 2 except that the tricalcium phosphate was not used and 85 g of magnesium pyrophosphate was used.

Example 13

10 An expanded molded article was obtained in the same manner as in Example 3 except that the tricalcium phosphate was not used and 85 g of magnesium pyrophosphate was used.

[0034]

Comparative Example 1

15 An expanded molded article was obtained in the same manner as in Example 1 except that the amount of the tetrabromocyclooctane was changed to 80 g.

Comparative Example 2

20 An expanded molded article was obtained in the same manner as in Example 1 except that the amount of the tetrabromocyclooctane was changed to 160 g.

Comparative Example 3

 An expanded molded article was obtained in the same manner as in Example 2 except that the impregnation temperature was changed to 115°C.

25 Comparative Example 4

An expanded molded article was obtained in the same manner as in Example 1 except that the amount of the tetrabromocyclooctane was changed to 1200 g. FIG. 3 shows an SEM photograph of a cross section of the pre-expanded particle obtained. FIG. 3 indicates that the size of the foams is smaller, because the amount of the flame retardant used is larger in Comparative Example 4.

Comparative Example 5

Styrene resin particles were obtained in the same manner as in Example 1 except that the tetrabromocyclooctane was not added. The obtained styrene resin particles were classified to give particles of 0.6 mm to 0.7 mm.

An expanded molded article was obtained in the same manner as in Example 1 except that 10 g of tetrabromocyclooctane was added to the aqueous medium under stirring at 300 rpm. FIG. 4 shows an SEM photograph of a cross section of the pre-expanded particle obtained. FIG. 4 indicates that the size of the foams in a surface region is smaller and the size of the foams in a central region is larger, causing variation of the foam density, because more flame retardant is present in the surface region in Comparative Example 5.

Comparative Example 6

Styrene resin particles were obtained in the same manner as in Example 1 except that the tetrabromocyclooctane was not added. The obtained styrene resin particles were classified to give particles of 0.6 mm to 0.7 mm. An expanded molded article was obtained in the same manner as in Example 1 except that 30 g of tetrabromocyclooctane was

added to the aqueous medium under stirring at 300 rpm. FIG. 5 shows an SEM photograph of a cross section of the pre-expanded particle obtained. FIG. 5 indicates that the size of the foams in a surface region is smaller and the size of the foams in a central region is larger, causing variation of the foam density, because more flame retardant is present in the surface region in Comparative Example 6.

Table 1 shows the flame retardancy, the average foam size, and the thermal fusibility of the block-shaped expanded molded articles obtained in Examples 2 to 13 and Comparative Examples 1 to 6.

10 [0035]

Table 1

		TBCO part	Dispersant	Surfactant	Impregnation temp. °C	Molecular weight Mw	Flame retardancy seconds		Average foam size µm	Thermal fusibility
Ex.	1	0.5	TCP-10	Sodium dodecyl benzenesulfonate	95	265000	1.7	Pass	280	⊙
	2	1.0	TCP-10	Sodium dodecyl benzenesulfonate	95	256000	1.1	Pass	290	⊙
	3	1.5	TCP-10	Sodium dodecyl benzenesulfonate	95	246000	0.3	Pass	170	○
	4	2.0	TCP-10	Sodium dodecyl benzenesulfonate	95	228000	0.3	Pass	180	○
	5	1.0	TCP-10	Sodium dodecyl benzenesulfonate	80	268000	0.6	Pass	340	⊙
	6	1.0	TCP-10	Sodium dodecyl benzenesulfonate	100	247000	0.9	Pass	180	○
	7	1.0	TCP-10	Sodium dodecyl benzenesulfonate	110	241000	1.0	Pass	73	○
	8	1.5	TCP-10	Sodium dodecyl benzenesulfonate	95	252000	0.6	Pass	210	○
	9	1.0	TCP-10	α-olefin sulfonate	90	239000	0.5	Pass	190	○
	10	1.0	TCP-10	α-olefin sulfonate	110	237000	0.3	Pass	110	○
	11	1.0	C13-09	Sodium dodecyl benzenesulfonate	95	252000	0.6	Pass	220	○
	12	1.0	Mg pyrophosphate	Sodium dodecyl benzenesulfonate	95	248000	0.4	Pass	270	⊙
	13	1.5	Mg pyrophosphate	Sodium dodecyl benzenesulfonate	95	251000	0.3	Pass	250	○
Comp. Ex.	1	0.2	TCP-10	Sodium dodecyl benzenesulfonate	95	283000	Burnt	Fail	450	⊙
	2	0.4	TCP-10	Sodium dodecyl benzenesulfonate	95	281000	3.7	Fail	350	⊙
	3	1.0	TCP-10	Sodium dodecyl benzenesulfonate	115	223000	1.3	Pass	41	×
	4	3.0	TCP-10	Sodium dodecyl benzenesulfonate	95	191000	0.3	Pass	35	×
	5	0.5	TCP-10	Sodium dodecyl benzenesulfonate	95	262000	3.3	Fail	320	○
	6	1.5	TCP-10	Sodium dodecyl benzenesulfonate	95	224000	0.8	Pass	150	×

[0036]

Table 1 indicates that it is possible to provide expandable styrene based resin particles that have, when expanded, excellent thermal fusibility among particles and that allow production of an expanded molded article having excellent flame retardancy by using a specific flame retardant in a specific amount and setting the temperature for the impregnation with the physical blowing agent to a specific temperature.

[0037]

The content percentages of the tetrabromocyclooctane in the surface region and in the whole of the expandable styrene based resin particles obtained in Examples 1 to 13 and Comparative Examples 1 to 6 were measured by the following method, and Table 1 shows the results.

(Method for measuring content percentage of tetrabromocyclooctane)

A surface of a molded article expanded by a factor of 50 is sliced into a shape having a thickness of 0.2 mm, a length of 20 cm, and a width of 20 cm with a slicer (FK-4N, produced by FUJISHIMA KOKI CO., LTD.), to be treated as a surface region of the flame-retardant expandable styrene resin particle. The sliced surface is measured for the content percentage of the tetrabromocyclooctane. The measurement for the content percentage of the tetrabromocyclooctane is carried out by an order analysis method (thin film method) with the use of a fluorescent X-ray analyzer (RIX-2100, produced by Rigaku Corporation). Specifically, 2 g to 3 g of the sliced surface is

heat-pressed at 200°C to 230°C to prepare a film having a thickness of 0.1 mm to 1 mm, a length of 5 cm, and a width of 5 cm. The film is measured for the weight to calculate the basis weight, and the amount of Br is calculated from the X-ray intensity by the order analysis method with C_8H_8 as a balancing component. In view of the fact that the percentage of Br contained in the tetrabromocyclooctane is 75%, the amount of the tetrabromocyclooctane in the film is calculated from the obtained Br amount. The result of the calculation is determined as the content percentage of the tetrabromocyclooctane contained in the surface region of the flame-retardant expandable styrene resin particle.

The content percentage of the tetrabromocyclooctane contained in the whole of the flame-retardant expandable styrene resin particle is the same as that set for the impregnation with the tetrabromocyclooctane.

Table 2 shows the content percentages of the tetrabromocyclooctane contained in the surface region and in the whole of the flame-retardant expandable styrene resin particle, and the ratio of the content percentage of the tetrabromocyclooctane contained in the surface region to the content percentage of the tetrabromocyclooctane contained in the whole.

Table 2

	TBCO content "b" in whole (wt%)	TBCO content "a" in surface region (wt%)	TBCO content "a" in surface region /TBCO content "b" in whole	b×1.1
Ex. 1	0.50	0.49	0.98	0.55
Ex. 2	1.00	1.01	1.01	1.1
Ex. 3	1.50	1.52	1.01	1.65
Ex. 4	2.00	2.01	1.01	2.2
Ex. 5	1.00	0.99	0.99	1.1
Ex. 6	1.00	1.03	1.03	1.1
Ex. 7	1.00	1.01	1.01	1.1
Ex. 8	1.50	1.50	1.00	1.65
Ex. 9	1.00	1.01	1.01	1.1
Ex. 10	1.00	1.00	1.00	1.1
Ex. 11	1.00	1.00	1.00	1.1
Ex. 12	1.00	0.99	0.99	1.1
Ex. 13	1.50	1.55	1.03	1.65
Com. Ex. 1	0.20	0.20	1.00	0.22
Com. Ex. 2	0.40	0.41	1.01	0.44
Com. Ex. 3	1.00	1.01	1.01	1.1
Com. Ex. 4	3.00	2.95	0.98	3.3
Com. Ex. 5	0.50	0.56	1.12	0.55
Com. Ex. 6	1.50	1.71	1.14	1.65

Table 2 indicates that it is possible to provide expandable styrene based resin particles that have, when expanded, excellent thermal fusibility among particles and that allow production of an expanded molded article having excellent flame retardancy in

5 Examples that satisfy the formula " $a \leq 1.1 \times b$ ". Table 2 also indicates that, on the other hand, the expanded molded articles in Comparative Examples 5 and 6 that do not satisfy the formula have inferior thermal fusibility and/or flame retardancy.

CLAIMS

1. A method for producing a flame-retardant expandable
styrene based resin particle, the method comprising: adding, in
5 suspension polymerization of a styrenic monomer to obtain a styrene
based resin particle, 0.45 parts by weight to 2.0 parts by weight of
tetrabromocyclooctane with respect to 100 parts by weight of the
styrenic monomer; and then impregnating the styrene based resin
particle with a physical blowing agent while adjusting an impregnation
10 temperature to 80°C to 110°C during or after the suspension
polymerization of the styrenic monomer to obtain the flame-retardant
expandable styrene based resin particle.

2. The method for producing a flame-retardant expandable
15 styrene based resin particle according to Claim 1, wherein the
suspension polymerization is carried out in the presence of a
surfactant.

3. The method for producing a flame-retardant expandable
20 styrene based resin particle according to Claim 1, wherein the styrenic
monomer further contains a flame retardant auxiliary agent.

4. The method for producing a flame-retardant expandable
styrene based resin particle according to Claim 3, wherein the flame
25 retardant auxiliary agent is selected from cumene hydroperoxide,

dicumyl peroxide, t-butyl hydroperoxide, and 2,3-dimethyl-2,3-diphenylbutan.

5 5. The method for producing a flame-retardant expandable styrene based resin particle according to Claim 3 or 4, wherein the flame retardant auxiliary agent is used in an amount of 0.1 parts by weight to 0.5 parts by weight with respect to 100 parts by weight of the styrenic monomer.

10 6. The method for producing a flame-retardant expandable styrene based resin particle according to any one of Claims 1 to 5, wherein the impregnation temperature is adjusted so that an expanded molded article to be obtained by expanding the flame-retardant expandable styrene based resin particle by an expansion ratio of 50 will
15 have an average foam size of 50 μm to 350 μm .

7. The method for producing a flame-retardant expandable styrene based resin particle according to any one of Claims 1 to 6, wherein the styrenic monomer is selected from styrene,
20 α -methylstyrene, p-methylstyrene, t-butylstyrene, and chlorstyrene.

8. A flame-retardant expandable styrene based resin particle comprising: a styrene based resin particle; and a physical blowing agent and tetrabromocyclooctane contained in the styrene based resin
25 particle,

the tetrabromocyclooctane being contained in the styrene based resin particle so as to satisfy a relationship of a formula $a \leq 1.1 \times b$ when a content percentage of the tetrabromocyclooctane contained in a surface region of the styrene based resin particle is "a" (% by weight) and a content percentage of the tetrabromocyclooctane contained in a whole of the styrene based resin particle is "b" (% by weight),

the tetrabromocyclooctane being contained in the whole of the styrene based resin particle in an amount of 0.45 parts by weight to 2.00 parts by weight with respect to 100 parts by weight of the styrene based resin particle, and

the flame-retardant expandable styrene based resin particle giving an expanded article having an average foam size of 50 μm to 350 μm when expanded by an expansion ratio of 50.

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