

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
16 April 2015 (16.04.2015)

(10) International Publication Number
WO 2015/052384 A1

(51) International Patent Classification:

C08J 9/00 (2006.01) *C08K 5/00* (2006.01)
C08J 9/16 (2006.01) *F16L 59/00* (2006.01)
C08K 3/04 (2006.01) *C08K 3/22* (2006.01)

(21) International Application Number:

PCT/FI2014/050774

(22) International Filing Date:

13 October 2014 (13.10.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

20136018 11 October 2013 (11.10.2013) FI

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(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: POLYSTYRENE BEADS WITH LOW THERMAL CONDUCTIVITY

(57) Abstract: The present invention provides expandable polystyrene beads and methods for producing the same. The beads comprise 0.001 to 0.5% of particulate solid material, calculated from the weight of the polystyrene, said beads being capable, when expanded, of providing polystyrene foams having an average cell size in the range of about 100 to 300µm and exhibiting a thermal conductivity λ of 37 mW/(m·K) or less at a density of 16kg/m³.



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POLYSTYRENE BEADS WITH LOW THERMAL CONDUCTIVITY

FIELD OF THE INVENTION

5 The present invention relates to polystyrene beads. In particular, the invention relates to the production of expandable polystyrene beads having good insulating properties containing particulate matter. Thus, the invention relates to expandable polystyrene beads according to the preamble of claim 1 as well as an article produced from the expandable polystyrene beads, according to the preamble of claims 15 and 31, and methods for the preparation of expandable
10 polystyrene beads according to the preamble of claims 16 and 30.

BACKGROUND ART

The thermal conductivity of articles formed from expandable polystyrene beads depends, to a
15 large extent, on the cell size of the final product. The cell size of expanded products is normally adjusted with a variety of crystalline polyethylene waxes. Optimising cell size and creating a uniform cell structure with polyethylene waxes is, however, difficult, often leading to great variation in cell sizes in the final product.

20 Expandable Polystyrene beads are traditionally produced by the suspension polymerisation of styrene, which involves the mechanical dispersion of styrene in water and polymerisation of the resultant monomer droplets by use of a monomer-soluble initiator. Styrene is kept in suspension by continuous agitation and the use of stabilisers. Polystyrene is obtained in the form of beads.

25

Expanded articles have been used for some time, for example to improve the thermal insulation of buildings. Generally, these articles are prepared by either extrusion or moulding through the swelling of polymer beads. Additives can be used to improve the desired properties of the articles. For example, solid particulate matter is added to improve the thermal
30 insulating capabilities of expanded polystyrene insulation boards.

Expanded polystyrene (EPS) is becoming increasingly common for use in such articles. EPS is a rigid and tough, closed-cell foam, generally made of pre-expanded polystyrene beads.

Common uses of these EPS beads include moulded sheets for building insulation and packing material for cushioning fragile items. The latest advances in the technology related to these

5 EPS beads concern improving the thermal insulation of the articles prepared from the beads.

In order to improve the thermal insulating properties of polystyrene beads, athermanous particles, such as graphite and carbon black, are incorporated into the polystyrene to produce what is known as grey EPS. The production of grey EPS moulded articles is disclosed in

10 EP 0 620 246. Athermanous material can be added directly to the polymerisation process, on the surface of the unexpanded EPS beads or to pre-foamed EPS beads before they are moulded. Further processes for the production of such materials are described in EP 0 981 574 and EP 0 981 575, as well as EP 1 608 698.

15 WO 2005/105905 discloses one such process for the preparation of a composition of an expandable styrene polymer in the form of beads. The process comprises a polymerisation of styrene in aqueous suspension carried out in the presence of dibenzyl peroxide, dicumyl peroxide, the dimer of α -methyl styrene, a Fischer-Tropsch wax, at least one suspending agent, and at least one pore-forming agent.

20

US 2010 148 110 discloses an expandable particle composite material suitable for the preparation of expanded materials having a density lower than 40 g/l and a content of closed cells of at least 60%, including heterophase cavities and/or heterophase domains, whose matrix is a synthetic thermoplastic resin having at least 60% by weight of a vinyl aromatic

25 polymer and in which an expanding system is contained, together with a heterogeneously distributed graphite material, having a graphitization degree, calculated by means of the Maire and Mering formula, of at least 0.2.

US 6,340,713 discloses particulate expandable styrene polymers that contain homogeneously

30 distributed graphite particles and that can be processed to give self-extinguishing foams having a density of ≤ 35 g/l.

Due to the addition of athermanous material, the colour of the granules is black and the colour of the corresponding expanded beads is grey. Grey EPS is more thermally efficient than white polystyrene and provides improved insulation achieving lower lambda values than that of white EPS.

5

Grey EPS, however, has poor light reflecting capability and absorbs a considerable amount of light, thus heating up when exposed to sunlight. The addition of any particulate material changes the colour of final products and increases production costs significantly..

10 AIM OF THE INVENTION

It is an aim of the present invention to eliminate at least a part of the problems of the art. It is particularly an aim to provide EPS containing particulate matter, having good thermally-insulating properties in the absence of significant amounts of athermanous particles.

15

It is also an aim of the present invention to provide expanded, flame-retardant, thermally insulating boards that still have light-reflecting properties.

SUMMARY

20

The invention relates to expandable polystyrene beads comprising 0.001 to 0.5 % of particulate solid material, calculated from the weight of the polystyrene. It has surprisingly been found that the beads of the invention are capable, when expanded, of providing polystyrene foams having a relatively large average cell size and exhibiting a relatively low thermal conductivity λ at a relatively low density.

25

Methods of producing polystyrene beads are also provided, wherein styrene monomers, and optionally co-monomers, are subjected to a polymerisation reaction in the presence of particulate material to produce polystyrene beads. The method comprises adding at least a part of the monomers and the particulate material as a mixture together.

30

It has been found that the thus produced beads exhibit a lower than expected thermal conductivity.

5 By means of the invention, articles of expanded polystyrene are provided which exhibit a high reflectivity combined with good heat-insulation properties because of a relatively large cell size.

10 More specifically, the EPS beads according to the present invention are characterised by what is stated in claim 1. The methods according to the present invention are characterised by what is stated in the characterising part of claims 16 and 30. Articles comprising expanded polystyrene are characterized by what is stated in claims 15 and 31.

BENEFITS

15 Considerable benefits are gained with the aid of the present invention. The present invention provides expandable polymer beads that can be used to prepare foamed articles of low thermal conductivity and of low density that are light in colour.

20 Compared to conventional expandable polystyrene beads which do not contain particulate matter in the indicated ranges, the present beads provide better thermal insulation properties while maintaining density, employing a simple novel process.

25 In one aspect of the invention, the size of the particles of the particulate matter is directly related to the quantity of particles to be added. A small particle size means a large number of particles can be added while only adding a small amount by weight of particles. The particles are preferably homogeneously distributed throughout the beads and act as a nucleant for a blowing agent. On expansion large cells are provided in a non-grey expanded foam.

30 As will appear, with a material according to the present invention, a low thermal conductivity value can be obtained with a relatively small amount of material. By contrast, for a conventional material, the same heat insulation properties require that the density and therefore amount of material used are relatively high.

Other features and advantages will become apparent from the following description.

EMBODIMENTS

5

Various embodiments hereinafter described provide expandable polystyrene beads comprising particulate solid material that when expanded are capable of providing polystyrene foams with large cell size, low thermal conductivity or high thermal resistivity, and low density.

10 In the present context, “large cell size” means an average cell size greater than 120 μm and up to about 400 μm , in particular in the range of 150 to 300 μm .

“Low thermal conductivity” means a conductivity, which preferably is lower than 37 mW/m K, in particular it is in the range of 32 to 37 mW/(m K), typically 33 to 35 mW/(m·K). At a
15 density of 16 kg/m³, the low thermal conductivity stands for about 34 to 36.5 mW/(m·K), typically about 34 to 35 mW/(m·K).

“Low density” means a density below 20 kg/m³, preferably it stands for a density generally in the range of 15 to 19 kg/m³.

20

A first embodiment provides expandable polystyrene beads comprising 0.001 to 0.5 %, preferably 0.002 to 0.1 %, particularly 0.005 to 0.05 % of particulate solid material, calculated from the weight of the polystyrene. Preferably the beads are capable, when expanded, of providing polystyrene foams having an average cell size in the range of about 100 to 300 μm .

25 Such expanded foams are capable of exhibiting a thermal conductivity λ of not more than 37 mW/(m·K) at a density of 16 kg/m³.

In one embodiment the particulate solid material comprises particles having an average particle size of 0.1 to 50 μm , preferably 1 to 10 μm . The size range of the particles determines
30 the quantity of particles to be added, individual particles assumingly work as a nucleant for a blowing agent.

In a still further embodiment the particulate solid material comprises platy particles. The shape of the particles contributes to the effects mentioned above in relation to particle size.

5 In one embodiment the solid material comprises particulate material selected from the group of talc, titanium dioxide and combinations thereof.

In a further embodiment the solid material comprises particulate athermanous material. The addition of athermanous material provides the beads with superb properties of thermal resistivity and correspondingly low thermal conductivity λ values.

10

The athermanous material of a preferred embodiment is selected from the group of carbon black, graphite, coke, graphene and any carbon-based material and combinations thereof, said combinations varying the qualities of the beads produced.

15 In one embodiment the particulate solid material comprises athermanous material selected from the group of carbon black, graphite, coke, graphene and any carbon-based material and combinations thereof, forming a first solid material component, in combination with further particulate material selected from the group of talc, titanium dioxide and combinations thereof, forming a second solid material component. The mass ratio of the first solid material
20 component to the second material component is typically 1:100 to 1000:0.1, in particular 10:10 to 10 to 0.1.

A further embodiment provides expandable polystyrene beads comprising about 0.005 to 0.5
25 %, by weight of the polystyrene, of particulate solid material, the expanded product therefrom preferably having an average cell size in the range of about 150 to 250 μm .

In another embodiment the expandable polystyrene beads further comprise a blowing agent selected from the group of pentane, isopentane and cyclopentane and combinations thereof. The beads may comprise other blowing agents typical in the manufacture of expandable
30 polystyrene beads *e.g.* a hydrocarbon, such as an aliphatic hydrocarbon having 3 to 10 carbon atoms. Typical examples of such hydrocarbons comprise C_3 to C_6 aliphatics and isomers thereof. Specific examples are propane, butane, pentane and hexane and isomers thereof, such

as isobutane, isopentane and isohexane. The blowing agent is added in amounts of about 0.1 to about 15 parts by weight per 100 parts by weight of styrene.

5 In an alternative embodiment the expandable polystyrene beads further comprise a fire-retarding agent selected from the group of organochlorines, organobromines and polymeric brominated flame retardants and combinations thereof. The fire-retarding agent provides the capability of the expanded product to self extinguish when subjected to flame.

10 In a further embodiment the expandable polystyrene beads comprise 0.01 to 5.0 %, in particular 0.05 to 4.0 %, preferably about 0.1 to 3.0 %, advantageously 0.2 to 2.0 % of fire-retarding agent, calculated from the total mass of the styrene monomer.

15 Based on the foregoing, in an embodiment of the present technology, expandable polystyrene beads are provided that contain about 0.01 to 5.0 % of polymeric brominated flame retardants together with 0.01 to 0.4 % of particles selected from graphite, graphene and carbon black or talc or titanium dioxide.

20 In a preferred embodiment the particles are graphite particles ranging in size from 0.1 to 50 μm in size added in an amount of 0.01 to 0.4 % of particles calculated from the total mass of the styrene. The particle size is indirectly proportional to the amount by mass added. For example, 30 to 50 μm particles are added in an amount of 0.01 to 0.2 % calculated from the total mass of the styrene and 0.1 to 30 μm particles are added in an amount of 0.2 to 0.4 %, calculated from the total mass of the styrene.

25 A yet further embodiment provides expandable polystyrene beads wherein the particulate athermanous material is homogenously distributed.

Further embodiments provide thermo-insulating expanded articles formed from the expandable polystyrene beads of any of the above embodiments.

In one embodiment a thermo-insulating expanded article is formed from the expandable polystyrene beads. The production of expanded product from polystyrene beads is well-known in the art.

5 Thus, in one alternative, for forming expanded products, the expandable beads are heated, for example by using a heat transfer medium such as steam, to a temperature high enough to soften the beads, preferably to a temperature above the glass transition point of polystyrene. Typically, the temperature is in excess of 95 °C, in particular 100 °C or higher. The heating will cause the blowing agent to boil and while the blowing agent is evaporated off the beads,
10 swelling of the beads is achieved and porous particles are created, which can be moulded together to form articles, such as panels, sheets and boards, by using traditional shape or block moulding methods.

The thermo-insulating expanded articles have excellent properties. They are light in colour
15 providing IR radiation reflection properties that are almost as good as those for conventional white EPS and have low densities in the range of about 10 to 30 kg/m³. Due to the large average cell size, in the range of about 100 to 300 µm the thermo-insulating expanded articles have excellent insulation properties without the addition of significant amounts of athermanous materials. Lower densities can be used in the expanded articles of the present
20 invention than can be used in conventional white EPS to achieve the same required thermal conductivity values. The lower densities provide remarkable savings in raw materials costs.

Further embodiments provide a method for the preparation of the expandable polystyrene beads. As mentioned above, the method according to the present technology is based on
25 polymerisation of styrene monomers. The styrene monomers to be polymerised are subjected to polymerisation in the presence of a polymerisation initiator and solid particulate material. The addition of the solid particulate material to the polymerisation process results in the production of a light in colour non-grey EPS. The light in colour non-grey EPS produced has a considerably lower thermal conductivity than the corresponding white EPS.

30

In a further embodiment, the thermo-insulating expanded article is non-grey and has a reflectivity measured at 700 nm of at least 50 %, preferably at least 60 %, suitably at least

75 %, more preferably at least 80 % or even at least 85 %. Typically, the reflectivity of the articles referred to in the fore-going is measured at a density of 10 to 30 kg/m³.

5 The solid particulate material is added when the polymerisation reaction has reached a preselected conversion rate and the polymerisation is continued in order to produce EPS beads.

10 In a preferred embodiment the particulate material is added at a conversion rate no greater than 40 %, preferably at a conversion rate of 1 to 30 %, advantageously 5 to 20 %, especially 8 to 12 %, calculated from the molar amount of the styrene monomer.

15 One embodiment provides a method for the preparation of the expandable polystyrene beads, wherein styrene monomers, and optionally co-monomers, suspended in a liquid phase to form a suspension, are subjected to a polymerisation reaction in the presence of a polymerisation initiator to produce expandable polystyrene beads, said polymerisation reaction having a conversion rate, said method comprising adding 0.001 to 0.5 parts by weight, preferably 0.002 to 0.1 parts by weight, particularly 0.005 to 0.05 parts by weight of particulate material to the suspension for each 100 parts by weight of styrene monomers with optional co-monomers when the polymerisation has reached a pre-selected conversion rate and continuing the
20 polymerisation to produce expandable polystyrene beads.

25 In a further embodiment the polymerisation is carried out in an aqueous phase into which a first portion of the styrene monomer is suspended and into which a premix comprising a second portion of the styrene monomer mixed with the particulate material is added.

In another embodiment a blowing agent selected from the group of pentane, isopentane and cyclopentane is added, although other blowing agents as detailed above may be added either alone or in combination.

30 In a still further embodiment a fire-retarding agent selected from the group of organobromines, organochlorines and polymeric brominated flame retardants and combinations thereof is added.

In a preferred embodiment the fire-retarding agent is added in an amount of 0.01 to 5.0 %, in particular 0.05 to 4.0 %, preferably about 0.1 to 3.0 %, advantageously 0.2 to 2.0 % by total mass of the styrene monomer.

5

In an alternative embodiment the fire-retarding agent is added as a dry powder, or optionally as pellets, preferably dissolved, more preferably dispersed in a liquid, for example in a solvent corresponding to the liquid phase of the suspension, more particularly preferably dissolved in the portion of styrene monomers of the premix.

10

In another embodiment the polymerisation is continued up to a conversion rate of at least 95 %, calculated from the styrene monomer.

In further embodiment the added particulate solid material comprises particles having an average particle size of 0.1 to 50 μm , preferably 1 to 10 μm .

15

In a still further embodiment the added particulate solid material comprises platy particles.

In one embodiment the added particulate solid material comprises material selected from the group of talc, titanium dioxide and combinations thereof.

20

In a further embodiment the added particulate solid material comprises particulate athermanous material.

In a preferred embodiment the added athermanous material is selected from the group of carbon black, graphite, graphene and any carbon-based material, and combinations thereof.

25

In a still further embodiment, the particulate solid material comprises material selected from the group of talc, titanium dioxide carbon black, graphite, coke, graphene and any carbon-based material, and combinations thereof.

30

A still further embodiment provides a thermo-insulating expanded article formed from the expandable polystyrene beads produced by the method of any of the above embodiments.

Further embodiments provide methods of producing expandable polystyrene beads of any of
5 the above embodiments by extrusion.

One embodiment provides a method for the production of expandable polystyrene beads, wherein polystyrene containing a blowing agent and particulate solid material is subjected to extrusion in an extruder to produce extruded polystyrene, said method comprising pelletizing
10 said extruded polystyrene with an underwater pelletizer to produce expandable polystyrene beads. Expandable beads produced by such a method are, similar to expandable beads of any of the embodiments described above, suited to be formed into thermo-insulating expanded articles and thus in one embodiment a thermo-insulating expanded article as described in the above embodiments is formed from the extruded expandable polystyrene by a method
15 according to any of the above-described embodiments.

The following non-limiting examples are intended to merely illustrate the methods according to preferred embodiments of the invention.

20 Heat insulation was determined by ISO Standard 8301 using a Heat Flow Meter device, with a mean temperature of 10 °C and a temperature difference of 20 °C. The samples were kept in an oven at 70 °C for 7 days before measuring of λ value.

Flame retarding properties were tested according to DIN 4102 B2.

25

EXAMPLES

Reference Example 1

Polymerization

30

2.1 l of ion-exchanged water and 4.2 g of sodium acetate were added in stirred 6 l autoclave. The mixture was heated to 90 °C within 45 min, while 2.1 kg styrene, 2.73 g sodium

bentonite, 21 g polymeric fire retardant agent (Emerald 3000), 6.1 g benzoylperoxide, 2.1 g tert-butylperoxy 2-ethylhexyl carbonate, and 8.4 g dicumylperoxide were added in the autoclave. After the mixture was kept for 45 min at 90°C 2.73 g of pig skin gelatine was added. After the mixture was kept for 265 min at 90°C 2.1 g of pig skin gelatine was added.

5 Altogether the mixture was kept at 90°C for 270 min whereafter it was heated to 120°C within 2h. While heating to 120°C 157.5 g of pentane was added. The mixture was kept at 120°C for 2h whereafter it was cooled down to 37°C within 90 min. The reaction mixture was removed from the autoclave, the polystyrene beads were washed thoroughly with water, and finally the beads were dried using an air blower. The dry beads were sieved and the sizes from 0.8 mm to

10 1.4 mm were pre-expanded to 16 kg/m³ from which a 50 mm thick sample plate was moulded. Finally, the thermal conductivity of this plate was determined and the cell size was determined micrographically.

Results (density 16 kg/m³): Thermal conductivity 37 mW/(m·K), cell size <100 μm

15

Example 2

Polymerization

As reference example 1, but when the mixture was kept for 40 min at 90 °C 0.84 g (0.04 %) of synthetic graphite (TimCal SFG6) was added.

20

Results (density 16 kg/m³): Thermal conductivity 35 mW/(m·K), cell size ~ 150 μm

As will appear, with a material according to the present invention, a thermal conductivity of 35 mW/(m·K) can be obtained at a density as low as 16 kg/m³. By contrast, for a conventional

25 material, the same heat insulation properties require that the density is increased to about 20 kg/m³.

INDUSTRIAL APPLICABILITY

The present technology can be employed to provide thermally-insulating, low density, non-grey expanded polystyrene articles for application in *e.g.* the construction industry. The
5 articles are also useful for storage and transport of perishable goods such as foodstuffs, in particular as heat-insulating casings for foodstuff that needs to be transported and maintained at temperatures below 8 °C, and breakables such as glassware. Any and all of these applications may be realised by any of the embodiments described above.

10

CITATION LIST

Patent Literature

- EP 0 620 246
EP 0 981 574
15 EP 0 981 575
EP 1 608 698.
EP 1 758 591
US 6,340,713
WO 2005/105908
20 US 2008 221 230
US 2010 148 110

CLAIMS:

1. Expandable polystyrene beads comprising 0.001 to 0.5 % of particulate solid material, calculated from the weight of the polystyrene, said beads being capable, when expanded, of providing polystyrene foams having an average cell size in the range of about 100 to 300 μm and exhibiting a thermal conductivity λ of not more than 37 mW/(m·K) at a density of 16 kg/m³.
5
2. The expandable polystyrene beads according to claim 1, wherein the particulate solid material comprises particles having an average particle size of 0.1 to 50 μm , preferably 1 to 10 μm .
10
3. The expandable polystyrene beads according to any of the preceding claims, wherein said particulate solid material comprises platy particles.
15
4. The expandable polystyrene beads according to any of the preceding claims, wherein said solid material comprises particulate material selected from the group of talc, titanium dioxide and combinations thereof.
- 20 5. The expandable polystyrene beads according to any of claims 1 to 4, wherein said solid material comprises particulate athermanous material.
6. The expandable polystyrene beads according to claim 5, wherein the athermanous material is selected from the group of carbon black, graphite, coke, graphene and any carbon-based material, and combinations thereof.
25
7. The method according to any of the preceding claims, wherein the particulate solid material comprises material selected from the group of talc, titanium dioxide carbon black, graphite, coke, graphene and any carbon-based material, and combinations thereof.
30

8. The expandable polystyrene beads according to any of the preceding claims, comprising about 0.005 to 0.5 %, by weight of the polystyrene, of particulate solid material, and preferably having an average cell size when expanded in the range of about 150 to 250 μm .
- 5 9. The expandable polystyrene beads according to any of the preceding claims, further comprising a blowing agent selected from the group of $\text{C}_3\text{-C}_7$, preferably pentane, isopentane and cyclopentane and combinations thereof.
- 10 10. The expandable polystyrene beads according to any of the preceding claims, further comprising a fire-retarding agent selected from the group of organochlorines, organobromines and polymeric brominated flame retardants and combinations thereof.
- 15 11. The expandable polystyrene beads according to any of the preceding claims, comprising 0.01 to 5.0 %, in particular 0.05 to 4.0 %, preferably about 0.1 to 3.0 %, advantageously 0.2 to 2.0 % of fire-retarding agent, calculated from the total mass of the styrene monomer.
12. The expandable polystyrene beads according to any of the preceding claims, wherein the particulate athermanous material is homogenously distributed.
- 20 13. The expandable polystyrene beads according to any of the preceding claims, comprising 0.002 to 0.1 %, particularly 0.005 to 0.05 % of particulate solid material calculated from the weight of the polystyrene.
- 25 14. A thermo-insulating expanded article formed from the expandable polystyrene beads of any of claims 1 to 13.
- 30 15. The thermo-insulating expanded article according to claim 14, wherein the expanded article is non-grey and has a reflectivity measured at 700 nm of at least 50 %, preferably at least 60%, suitably at least 75%, more preferably at least 80% or even at least 85%, preferably when measured at a density of 10 to 30 kg/m^3 .

16. A method for the preparation of the expandable polystyrene beads according to any of claims 1 to 13, wherein styrene monomers, and optionally co-monomers, suspended in a liquid phase to form a suspension, are subjected to a polymerisation reaction in the presence of a polymerisation initiator to produce expandable polystyrene beads, said polymerisation reaction
5 having a conversion rate, said method comprising adding 0.001 to 0.5 parts by weight of particulate material to the suspension for each 100 parts by weight of styrene monomers with optional co-monomers when the polymerisation has reached a pre-selected conversion rate and continuing the polymerisation to produce expandable polystyrene beads.
- 10 17. The method according to claim 16, wherein the polymerisation is carried out in an aqueous phase into which a first portion of the styrene monomer is suspended and into which a premix comprising a second portion of the styrene monomer mixed with the particulate material is added.
- 15 18. The method according to claim 17 or 16, further comprising adding a blowing agent selected from the group of pentane, isopentane and cyclopentane.
19. The method according to any of claims 16 to 18, comprising the additional step of adding a fire-retarding agent selected from the group of organobromines, organochlorines and
20 polymeric brominated flame retardants and combinations thereof.
20. The method according to any of claims 16 to 19, wherein the fire-retarding agent is added in an amount of 0.01 to 5.0 %, in particular 0.05 to 4.0 %, preferably about 0.1 to 3.0 %, advantageously 0.2 to 2.0 % by total mass of the styrene monomer.
25
21. The method according to any of claims 16 to 20, wherein the fire-retarding agent is added as a dry powder, or optionally as pellets, preferably dissolved, more preferably dispersed in a liquid, for example in a solvent corresponding to the liquid phase of the suspension, more particularly preferably dissolved in the portion of styrene monomers of the premix.
30
22. The method according to any of claims 16 to 21, wherein the polymerisation is continued up to a conversion rate of at least 95 %, calculated from the styrene monomer.

23. The method according to any of claims 16 to 22, wherein the particulate solid material comprises particles having an average particle size of 0.1 to 50 μm , preferably 1 to 10 μm .
- 5 24. The method according to any of claims 16 to 23, wherein the particulate solid material comprises platy particles.
25. The method according to any of claims 16 to 24, wherein the particulate solid material comprises material selected from the group of talc, titanium dioxide and combinations thereof.
- 10 26. The method according to any of claims 16 to 25, wherein the particulate solid material comprises particulate athermanous material.
27. The method according to claim 26, wherein the athermanous material is selected from the
15 group of carbon black, graphite, coke, graphene and any carbon-based material, and combinations thereof.
28. The method according to any of claims 16 to 27, wherein the particulate solid material
20 comprises material selected from the group of talc, titanium dioxide carbon black, graphite, coke, graphene and any carbon-based material, and combinations thereof.
29. The method according to any of claims 16 to 28, comprising adding 0.002 to 0.1,
particularly 0.005 to 0.05 parts by weight of particulate material to the suspension for each
100 parts by weight of styrene monomers with optional comonomers
- 25 30. A method for the production of expandable polystyrene beads according to any of claims 1 to 13, wherein polystyrene comprising a blowing agent and particulate solid material is subjected to extrusion in an extruder to produce extruded polystyrene, said method comprising pelletizing said extruded polystyrene with an underwater pelletizer to produce expandable
30 polystyrene beads.

31. A thermo-insulating expanded article formed from expandable polystyrene beads produced by the method according to any of claims 16 to 30.

5 32. The thermo insulating expanded article according to claim 31, wherein the expanded article is non-grey and has a reflectivity measured at 700 nm of at least 50 %, preferably at least 60 %, suitably at least 75 %, more preferably at least 80 % or even at least 85 %, in particular when measured at a density of 10 to 30 kg/m³.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2014/050774

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08J9/00 C08J9/16 C08K3/04 C08K5/00 F16L59/00
 C08K3/22
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C08J C08K F16L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/264836 A1 (FELISARI RICCARDO [IT] ET AL) 18 October 2012 (2012-10-18)	1-3, 5-15, 30-32
A	paragraphs [0089] - [0092], [0112] - [0114]; claims 1-15; example 1	4,16-29
X	WO 2012/175345 A1 (TOTAL RES & TECHNOLOGY FELUY [BE]; NOWE STEPHANE [BE]; LODEFIER PHILIP) 27 December 2012 (2012-12-27) paragraph [0019]; claims 1-5; examples 2-6; table III	1,4,14
X	WO 2007/114529 A1 (KOREA KUMHO PETROCHEM CO LTD [KR]; LEE JIN HEE [KR]; LEE SEOK WON [KR]) 11 October 2007 (2007-10-11) claims 1, 8; examples 1-3; table 1	1,14
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 15 December 2014	Date of mailing of the international search report 22/12/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Clement, Silvia
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INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2014/050774

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/030096 A1 (LEE JIN-HEE [KR] ET AL) 29 January 2009 (2009-01-29) paragraph [0030]; claims 1-7; tables 1, 2 -----	1,14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/FI2014/050774

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012264836	A1	18-10-2012	CN 102666686 A
			EP 2486085 A1
			JP 2013507477 A
			RU 2012116879 A
			US 2012264836 A1
			WO 2011042800 A1

WO 2012175345	A1	27-12-2012	CN 103703062 A
			EA 201400050 A1
			EP 2591044 A1
			US 2014221513 A1
			WO 2012175345 A1

WO 2007114529	A1	11-10-2007	NONE

US 2009030096	A1	29-01-2009	CA 2639270 A1
			CN 101353439 A
			EP 2025691 A2
			ES 2400244 T3
			JP 2009536687 A
			KR 100801275 B1
			PT 2025691 E
			RU 2376318 C1
			US 2009030096 A1
			WO 2009014279 A1
