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(54) **Title**: METHOD OF PRODUCING POLYSTYRENE BEADS CONTAINING ATHERMANOUS PARTICLES

(57) **Abstract**: The present invention provides a method of producing polystyrene beads, wherein styrene monomers, and optionally co-monomers, are subjected to a polymerisation reaction in the presence of a polymerisation initiator to produce polystyrene beads, said method comprising adding at least a part of the monomers and the athermanous material in particulate form as a mixture together with a dilatanting agent.

METHOD OF PRODUCING POLYSTYRENE BEADS CONTAINING ATHERMANOUS PARTICLES

FIELD OF THE INVENTION

The present invention relates to polystyrene beads. In particular, the invention relates to the production of expandable polystyrene beads with fire-resistant properties and insulating properties. Thus, the invention relates to a method according to the preamble portion of claim 1 as well as expandable polystyrene beads according to the preamble of claim 19 and uses thereof.

BACKGROUND ART

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.

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, hexabromocyclododecane is used in typically polystyrene building insulation, both extruded and expanded as a flame-retarding agent.

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 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 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.

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. Grey EPS, however, has poor light reflecting capability and absorbs a considerable amount of light, thus heating up when exposed to sunlight.

AIM OF THE INVENTION

It is an aim of the present invention to provide EPS, containing athermanous particles, having good thermally-insulating and improved light-reflecting properties employing a simple novel process.

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

SUMMARY

The invention relates to methods of producing polystyrene beads, wherein styrene monomers, and optionally co-monomers are subjected to a polymerisation reaction in the presence of athermanous material and a polymerisation initiator to produce polystyrene beads. The method comprises adding at least a part of the monomers and the athermanous material in particulate form as a mixture together with a dilatanting agent.

It has surprisingly been found that the thus produced beads exhibit a greater than expected ability to reflect light while maintaining the level of resistivity expected in grey EPS, *i.e.* high resistivity or low thermal conductivity.

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

More specifically, the method according to the present invention is characterised by what is stated in claim 1. The EPS beads are characterised by what is stated in the characterising part of claim 19. Articles comprising expanded PS are characterized by what is stated in claims 20, 21 and 24.

BENEFITS

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 yet of light colour.

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

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 comprises photographs of the samples (cross-sections of panels) produced in Example 1 and Comparative Examples 2 and 3 (upper portion); reflectivity measurements corresponding to the samples (intermediate portion) as well as micrographs of the samples.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Various embodiments described herein provide a method of producing EPS beads, including a method and process for the incorporation of a dilatanting agent as well as athermanous particles into the beads.

The present technology comprises a method of producing expandable polystyrene beads containing athermanous particles and a dilatanting agent and having a reflective surface.

As mentioned above, the method according to the present technology is based on polymerisation of styrene monomers. A first portion of the styrene monomers to be polymerised is subjected to polymerisation in the presence of a polymerisation initiator and a premix of a second portion of the monomers to be polymerised, carbon black and a dilatanting agent. The addition of the premix to the polymerisation process results in the production of a light in colour grey EPS. The light in colour grey EPS produced has a similar thermal conductivity to grey EPS and a considerably lower conductivity than the corresponding white EPS.

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

In a preferred embodiment the dilatanting agent acts as a flocculent causing the athermanous particles of the premix to agglomerate. This agglomeration allows the athermanous particle size in the EPS to be selected and therefore maintained. This size selection is what allows the produced EPS to be lighter in colour and, thus, more reflective than grey EPS produced by other methods. The number of separate athermanous particles in each EPS bead is reduced while the mass of athermanous particles in each bead is maintained. The premix can be added to the polymerisation at any time and is in one embodiment added at a conversion rate of 0.1 to 70.0 %, in particular about 1 to 50.0 %, especially about 10.0 to 30.0 %, calculated from the total mass of the styrene monomer.

In a further embodiment the dilatanting agent is a polymeric fire-retarding agent. In a preferred embodiment the dilatanting 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.

KR20090038314 discloses a method of forming an outer layer of polystyrene containing flame retardant and an inorganic filler on the surface of a foamed polystyrene bead. Styrene monomers, and optionally comonomers, are subjected to a polymerisation reaction in the presence of athermanous material and a polymerisation initiator in a continuous stirred tank reactor (CSTR) in which polystyrene beads are present.

US2012252914 discloses flame-retardant polymer expandable styrene polymers comprising at least one halogenated polymer as a flame retardant and processes for producing the same. The process of the above-mentioned publication comprises heating a mixture of demineralized water, sodium pyrophosphate, styrene, tert-butyl 2-ethylperoxyhexanoate, tert-butyl perbenzoate, graphite powder, and also flame retardant to 90° C in a pressure-resistant stirred tank, with stirring.

In neither of the publications is there any teaching on the use of the flame-retarding polymer as a dilatanting agent as a flocculent for causing the athermanous particles of the premix to agglomerate.

In one embodiment polymerisation is carried out in a static mixer.

In a further embodiment the polymerisation is carried out in a liquid phase into which the styrene monomers are suspended. In a preferred embodiment the liquid phase is an aqueous phase.

Thus, in one embodiment of the indicated kind, flame-retardant polystyrene beads are produced by suspension polymerisation. Thus, a portion of the styrene monomers to be polymerised are mixed with athermanous material and a dilatanting agent into a premix. The remaining portion of the monomers to be polymerised is suspended in a liquid phase to form a suspension and is subjected to a polymerisation reaction in the presence of a polymerisation initiator to produce expandable polystyrene (EPS) beads. The premix is added to the suspension at a preselected point of time, and polymerisation is continued in order to produce EPS beads. On addition of the dilatanting agent to the premix, the premix itself becomes a dilatant or shear-thickening premix that becomes more viscous with increasing shear rate, *i.e.* the viscosity of the dilatant premix is dependent on shear rate. The foamed polystyrene articles made from the above described beads have excellent properties; in particular they exhibit fire-resistant properties, a light, aesthetically-pleasing colour, as well as a more reflective surface than is typical in grey EPS and still they maintain excellent thermal insulation properties.

Dilatanting agent is used synonymously with “shear-thickening” and denotes any agent capable of achieving an anti-thixotropic effect, *i.e.* viscosity increases when agitation, exemplified by any of the following: stirring; mixing; beating; whipping or any other form of shear stress; or shaking is applied.

The dilatanting agent can be added in various forms and in one embodiment the dilatanting 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 the styrene monomers of the premix.

In a preferred embodiment the dilatanting agent is a flame retarding agent, selected from the group of polymeric compounds which exhibit a shear-thickening effect. Examples of suitable flame retarding agents include halogenated, in particular chlorinated or preferably brominated polymers and polymeric compounds. Specific embodiments of the flame retarding agents are represented by halogenated, in particular brominated polystyrene, halogenated, in particular brominated block copolymers, containing styrene and/or butadiene and/or tetrabromo-bisphenol A units or blocks of such units, e.g. styrene-butadiene block copolymers. Typically, the halogen content of such polymers is up to 90 % by weight of the halogenated polymer. In preferred embodiments, the bromine concentration is about 10 to 85 % by weight, in particular about 30 to 80 % by weight, of the brominated polymer (e.g. polystyrene or styrene-butadiene block copolymer).

The production of halogenated polymeric flame retardants is disclosed in WO 2007/058736.

Naturally, as has been discussed above, it is required that the flame retarding agent selected has a dilatanting effect and that it is added in such a way that it is capable of exerting such an effect.

In addition to halogenated polymeric flame retardants, it is also possible to use conventional flame retardants, such as organochlorines and organobromines.

In one embodiment a method is provided for producing expandable polystyrene beads in which styrene monomers are polymerised in a suspension at a first temperature in the range of about 75 to 110 °C until a preselected degree of conversion has been reached. The premix is added to the suspension. In the said embodiment a blowing agent is added and the suspension is heated to a second, higher temperature during the addition of the blowing agent.

Polymerisation is continued until a preselected final conversion degree has been reached. In a further embodiment the temperature of the suspension is raised to a third temperature higher than the second temperature. In a further embodiment the premix is added over a time period smaller than that needed for increasing the conversion rate of the polymerisation by 10 % units, preferably over a time period corresponding to the time needed for increasing the conversion rate by 10 to 30 % units.

In one example the polymerisation is continued to a conversion rate of at least 95 %, calculated from the styrene monomer and in a preferred embodiment the EPS beads are recovered from the liquid phase.

A blowing agents is added during the implementation of the process or afterwards. The blowing agent typically comprises a hydrocarbon, such as an aliphatic hydrocarbon having 3 to 10 carbon atoms. Typical examples of such hydrocarbons comprise C3 to C6 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.

In another example the polymerisation is carried out in the presence of a radical initiator or initiators, typically 1 to 4 initiators being used.

In one embodiment polymerisation is carried out in the presence of additives selected from the group of emulsifiers, preferably stabilizers, more preferably fillers *e.g.* talc, as well as combinations thereof, each additive providing its own additional property to the produced EPS beads. *e.g.* making the beads more stable.

In one embodiment the styrene monomers are polymerised in the presence of comonomers. The addition of comonomers varies the quality of the resultant polystyrene beads. In a further embodiment the athermanous particles are selected from the group of carbon black particles, graphite, graphene and other carbon-based materials. The content of athermanous particles is typically 0.1 to 15 parts by weight, for example 1 to 10, or 2 to 5, parts by weight, based on 100 parts by weight of styrene.

In a further embodiment expanded polystyrene beads or articles that are produced exhibit a reflectance that is 30 to 70 %, preferably 40 to 60 %, more preferably 45 to 55 %, which is two to three times the reflectance of expanded polystyrene beads produced in the absence of said premix.

In a further embodiment, expanded polystyrene beads are provided. In one embodiment articles are produced from the expanded polystyrene beads. In a preferred embodiment the articles comprise insulating board composed of expanded polystyrene beads said insulating board having a reflective surface and a thermal conductivity value corresponding to its thermal insulating properties.

The production of expanded product from polystyrene beads is well-known in the art.

Thus, in one alternative, for producing 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, swelling of the beads is achieved and porous particles created, which can be moulded together to form articles, such as panels, sheets and boards, by using traditional shape or block moulding methods.

In one embodiment the insulating board composed of expanded polystyrene beads comprises 0.01 to 5.0 %, preferably 0.05 to 4.0 % more preferably 0.1 to 3.0 %, advantageously 0.2 to 2.0 % by total mass of the styrene of dilatanting agent, and 0.1 to 15.0 %, preferably 1.0 to 10.0 %, advantageously 3.0 to 6.0 % by total mass of the styrene of agglomerated carbon black particles.

The agglomeration of the carbon black particles of the composition provides thermal insulating properties and provides the composition with a lighter colour and, thus, higher reflectivity than compositions in which added carbon black particles are not agglomerated.

Generally, the thermal conductivity of an insulating board according to the present invention, composed of expanded polystyrene beads is, measured at a density of about15 kg/m^3, roughly 15 ± 2 kg/m^3, 0.025 to 0.045 W/(m K), preferably 0.027 to 0.035 W/(m K).

Based on the above, article produced from expanded polystyrene beads as described herein exhibit a reflectivity at 700 nm of at least 20 % higher than a corresponding article produced from expanded polystyrene beads in the absence of a dilatant agent.

In one embodiment, articles produced from the present expanded polystyrene beads exhibit a reflectivity at 700 nm of at least 25 %, for example 30 to 70 %, preferably 40 to 60%, more preferably 45 to 55%, at a content of athermanous particles of up to typically 6 %, or up to 5 %, in particular about 1 to 4.5 %, for example 1 to 3.5 %, by weight of the polystyrene, measured at a density of 10 to 30 kg/m^3.

The λ value of the insulating board composed of expanded polystyrene beads is, measured using standard methods (EN12667 or ISO 8301) at a density of about 15 kg/m^3, 0.015 to 0.05 W/m K, preferably 0.02 to 0.04 W/m K, advantageously 0.025 to 0.035 W/m K (e.g. 0.027 to 0.034 W/m K).

Thus, one particularly preferred embodiment comprises an insulating panel, board or sheet of expanded polystyrene, containing athermanous particles, which exhibits in combination a reflectivity of better than 30 % and a λ value of 0.025 to 0.035 W/m K (e.g. 0.027 to 0.034 W/m K), measured at about 15 kg/m^3.

In the present context, the expression "about 15 kg/m^3 is used include a 10 to 20 % variation of the exact value, thus about 15 kg/m^3 can be interpreted as being typically 15 ± 2 kg/m^3.

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

Heat insulation has been 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.

The reflectance of visible light (from 360 to 740 nm) of this plate was determined with Konica Minolta Spectrophotometer cm-2600d.

Flame retarding properties were tested according to DIN 4102 B2.

EXAMPLES

Example 1

Preparation of styrene/carbon black premix

28.5 g of polymeric flame retardant Emerald 3000 (dilatanting agent) was dissolved in 250 g of styrene, whereafter 57 g of carbon black Lamp Black 101 was mixed in it.

Polymerisation

2.3 l of ion-exchanged water, 3.8 g of sodium acetate, and 3.8 g of sodium bentonite were added to a stirred 6 l autoclave. The mixture was heated to 90 °C within 1h, while 1.65 kg styrene, 1.9 g polyethylene, 7.6 g tert-butyl peroxy-2-ethylhexanoate, 5.7 g tert-butylperoxy 2-ethylhexyl carbonate, 5.7 g dicumylperoxide, and 3.8 g pig skin gelatine were added to the autoclave. After the mixture was kept at 90°C for 30 min, the styrene/carbon black premix was added. After the mixture was kept at 90°C for 315 min, 3.8 g of pig skin gelatine was added.

Altogether the mixture was kept at 90°C for 320 min whereafter it was heated to 120°C within 2h. While heating to 120°C, 152 g of pentane was added. The mixture was kept at 120°C for 2h whereafter it was cooled to 37°C within 90 min. The reaction mixture was removed from the autoclave and the polystyrene beads were washed thoroughly with water. The beads were sieved and the sizes from 0.8 mm to 1.4 mm were pre-expanded to 15 kg/m^3 from which a 50 mm thick sample plate was moulded. The reflectance of visible light (from 360 to 740 nm) of this plate was determined with Konica Minolta Spectrophotometer cm-2600d. In addition, the thermal conductivity of this plate was determined.

Results (density 15.6 kg/m^3): Thermal conductivity 33.4 mW/(m K), 48,0 % reflectance at 700 nm.

Fire test according to DIN 4102 B2 was passed.

Comparative Example 2

Preparation of styrene/carbon black premix

Styrene/carbon black (Lamp Black 101) premix was prepared by mixing 57 g of carbon black in 250 g of styrene.

Polymerisation

2.3 l of ion-exchanged water, 3.8 g of sodium acetate, and 3.8 g of sodium bentonite were added to a stirred 6 l autoclave. The mixture was heated to 90 °C within 1h, while 1.65 kg styrene, 1.9 g polyethylene, 7.6 g tert-butyl peroxy-2-ethylhexanoate, 5.7 g tert-butylperoxy 2-ethylhexyl carbonate, 5.7 g dicumylperoxide, 28.5 g of flame retardant Emerald 3000 (dilatanting agent) and 3.8 g pig skin gelatine were added to the autoclave. After the mixture was kept at 90°C for 30 min, the styrene/carbon black premix was added. After the mixture was kept at 90°C for 315 min, 3.8 g of pig skin gelatine was added. Altogether the mixture was kept at 90°C for 320 min whereafter it was heated to 120°C within 2h. While heating to 120°C, 152 g of pentane was added. The mixture was kept at 120°C for 2h whereafter it was cooled to 37°C within 90 min. The reaction mixture was removed from the autoclave and the polystyrene beads were washed thoroughly with water. The beads were sieved and the sizes from 0.8 mm to 1.4 mm were pre-expanded to 15 kg/m^3 from which a 50 mm thick sample plate was moulded. The reflectance of visible light (from 360 to 740 nm) of this plate was determined with Konica Minolta Spectrophotometer cm-2600d. In addition, the thermal conductivity of this plate was determined.

Results (density 19.6 kg/m^3): Thermal conductivity 32.4 mW/(m K), 28.2 % reflectance at 700 nm.

Comparative Example 3

Example 2 was repeated without polymeric flame retardant agent Emerald 3000.

Results (density 14.4 kg/m^3): Thermal conductivity 33.9 mW/mK, 22.0 % reflectance at 700 nm.

INDUSTRIAL APPLICABILITY

The present technology can be employed to provide thermally-insulating, light-reflecting expanded polystyrene articles for application in *e.g.* the construction industry.

CITATION LIST

Patent Literature

ALGOSTAT GmbH & CO. KG – EP0620246 – Polystyrene Hard Foam Moulded Articles

Glück Guiscard *et al.* – EP0981574 – Expandable Polystyrene Polymers Containing Graphite Particles

Glück Guiscard *et al.* – EP0981575 – Method For Producing Expandable Polystyrene Polymers Containing Graphite Particles

Ponticiello Antonio *et al.* – EP1608698 – Expandable Vinyl Aromatic Polymers and Process For Their Preparation

Dongbu Hitek Co Ltd. – KR20090038314 – Expandable Polystyrene Bead and Method for Providing the Same

Hahn *et al.* – US2012252914 – Flame Protected Polymer Foams

King *et al.* – WO 2007/058736 – Brominated Butadiene/Vinyl Aromatic Copolymers, Blends of Such Copolymers with a Vinyl Aromatic Polymer, and Polymeric Foams Formed From Such Blends

CLAIMS:

1. Method of producing polystyrene beads, wherein styrene monomers, and optionally co-monomers are subjected to a polymerisation reaction in the presence of athermanous material and a polymerisation initiator to produce polystyrene beads, said method comprising

    – adding a premix of at least a part of the monomers and the athermanous material in particulate form as a mixture together with a dilatanting agent.

2. The method according to claim 1, wherein the dilatanting agent acts as a flocculent causing the athermanous material particles of the premix to agglomerate.

3. The method according to either of claims 1 or 2, wherein the premix is added when the polymerisation has reached a conversion rate of at 0.1 to 70.0 %, in particular about 1.0 to 50.0 %, especially about 10.0 to 30.0 %, calculated from the total mass of the styrene monomer.

4. The method according to any of the preceding claims, wherein the dilatanting agent is a polymeric flame-retarding agent, in particular a brominated polymeric flame-retarding agent.

5. The method according to any of the preceding claims wherein the dilatanting 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.

6. The method according to any of the preceding claims wherein the polymerisation is carried out in a static mixer.

7. The method according to any of the preceding claims, wherein the polymerisation is carried out in a liquid phase into which the styrene monomers are suspended.

8. The method according to any of the preceding claims wherein the liquid phase is an aqueous phase.

9. The method according to any of the preceding claims, wherein the dilatanting 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. The method according to any of the preceding claims for producing expandable polystyrene beads, comprising

- polymerising styrene monomer in a suspension at a first temperature in the range of about 75 to about 110 °C until a preselected degree of conversation of at least 50 %, calculated from the molar amount of the styrene monomer, has been reached,
- adding a blowing agent,
- heating the suspension to a second temperature higher than the first temperature during the addition of the blowing agent,
- optionally raising the temperature of the suspension to a third temperature higher than the second temperature, and
- continuing polymerisation until a preselected final conversion degree has been reached,

said premix being added to the suspension before addition of the blowing agent.

11. The method according to any of the preceding claims, wherein the premix is added over a time period which is smaller than needed for increasing the conversion rate of the polymerisation with 10 % units.

12. The method according to any of the preceding claims, wherein the premix is added over a time interval corresponding to the time needed for increasing the conversion rate with 10 to 30 % units.

13. The method according to any of the preceding claims, wherein the polymerisation is continued up to a conversion rate of at least 95 %, calculated from the styrene monomer.

14. The method according to any of the preceding claims, wherein the polystyrene beads are recovered from the liquid phase.

15. The method according to any of the preceding claims, wherein the polymerisation is carried out in the presence of a radical initiator or combinations of radical initiators.

16. The method according to any of the preceding claims, wherein the polymerisation is carried out in the presence of additives selected from the group of emulsifiers, stabilizers, fillers, such as talc, as well as combinations thereof.

17. The method according to any of the preceding claims, wherein the styrene monomers are polymerised in the presence of comonomers.

18. The method according to any of the preceding claims, wherein the athermanous material particles are selected from the group of carbon black particles, graphite, graphene and other carbon-based materials, wherein such particles are in an amount of 0.1 to 15 % parts by weight per 100 parts by weight of styrene monomers.

19. Expandable polystyrene beads obtained by a method according to any of the preceding claims.

20. Article produced from expanded polystyrene beads according to claim 19, exhibiting a reflectivity at 700 nm of at least 20 % higher than the corresponding article produced from expanded polystyrene beads in the absence of a dilatanting agent.

21. Article produced from expanded polystyrene beads according to claim 19, exhibiting a reflectivity at 700 nm of 30 to 70 %, preferably 40 to 60 %, more preferably 45 to 55 %, at a content of athermanous particles of up to 6 % by weight of the polystyrene, measured at a density of 10 to 30 kg/m^3.

22. The articles according to any of claims 20 to 21 wherein the insulating board composed of expanded polystyrene beads comprises 0.01 to 3.0 %, preferably 0.05 to 2.5 % more

preferably 0.1 to 2.0 %, advantageously 0.5 to 1.5 % by total mass of the styrene of dilatanting agent, and 1.0 to 6.0 %, preferably 2.0 to 5.0 %, advantageously 2.5 to 4.0 % by total mass of the styrene of agglomerated athermanous particles.

23. The articles according to any of claims 20 to 22, wherein the λ value of the insulating board composed of expanded polystyrene beads is, measured at a density of 15 kg/m^3, 0.015 to 0.05 W/m K, preferably 0.02 to 0.04 W/m K, advantageously 0.025 to 0.035 W/m K.

24. An article of expanded polystyrene, containing athermanous particles, which exhibits in combination a reflectivity of better than 30 % and a λ value of 0.025 to 0.035 W/m K, measured at a density of about 15 kg/m^3.

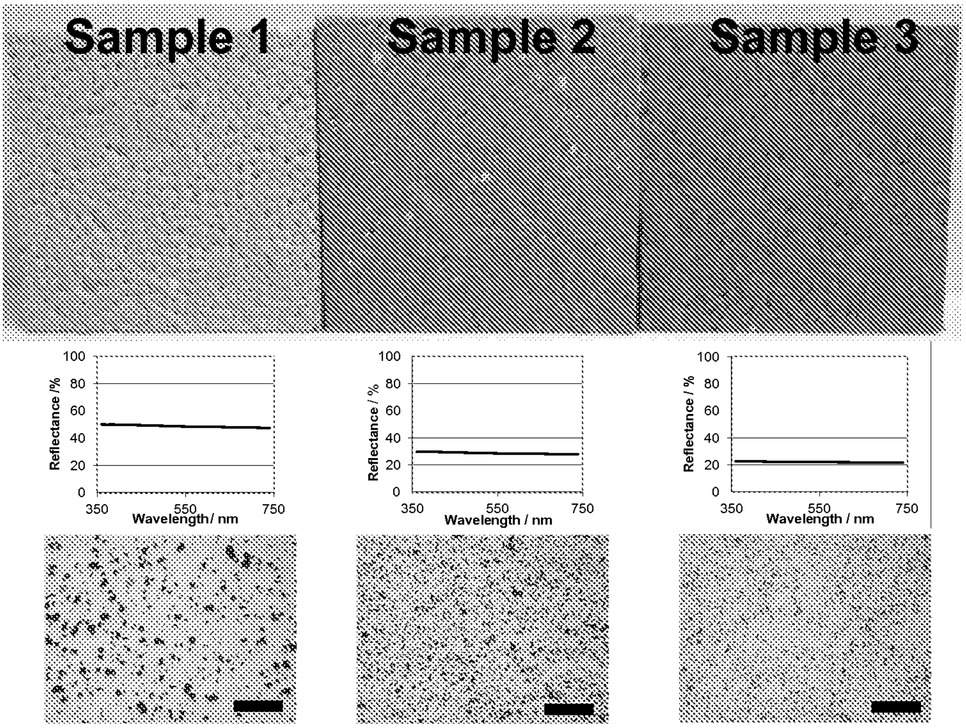
Sample 1
Sample 2
Sample 3
Reflectance /%
Reflectance / %
Reflectance / %
100
80
60
40
20
0
350
550
750
Wavelength / nm

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2014/050044

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J9/00 C08J9/16 C08L25/04 C08J9/20 C08F12/08
C08F2/44
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 C08L C08F

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/061571 A1 (INNOVENE EUROP LTD [GB]; GALEWSKI JEAN-MARC [FR]; LABASTIE COEYREHOURC) 15 June 2006 (2006-06-15)	1-3,5-24
Y	page 4, line 13 - page 6, line 12 page 7, line 29 - page 9, line 25 page 10, lines 17-29 examples 1-3 -----	4
X	US 6 387 968 B1 (GLUECK GUISCARD [DE] ET AL) 14 May 2002 (2002-05-14) column 1, line 37 - column 3, line 12 claims 1-6 -----	1-3,5-24
X	US 2010/099782 A1 (LEE LY JAMES [US] ET AL) 22 April 2010 (2010-04-22) paragraphs [0042] - [0047], [0070]; examples 1-3 ----- -/--	1-3,5-24

☒ 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

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"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 28 May 2014	Date of mailing of the international search report 06/06/2014
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 Mayer, Anne

INTERNATIONAL SEARCH REPORT

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PCT/FI2014/050044

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012/252914 A1 (HAHN KLAUS [DE] ET AL) 4 October 2012 (2012-10-04) cited in the application paragraphs [0008] - [0023], [0029] - [0030], [0035] - [0039] paragraphs [0044] - [0052] examples 1-4 -----	4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FI2014/050044

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006061571 A1	15-06-2006	NONE	
US 6387968 B1	14-05-2002	DE 19812856 A1	30-09-1999
		EP 1082382 A1	14-03-2001
		US 6387968 B1	14-05-2002
		WO 9948957 A1	30-09-1999
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		DE 102009059781 A1	22-06-2011
		EP 2513209 A1	24-10-2012
		JP 2013514397 A	25-04-2013
		KR 20120107114 A	28-09-2012
		RU 2012130168 A	27-01-2014
		US 2012252914 A1	04-10-2012
		WO 2011073141 A1	23-06-2011