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(71) Applicant (for all designated States except US): **TOTAL PETROCHEMICALS RESEARCH FELUY** [BE/BE]; Zone Industrielle C, B-7181 Seneffe (Feluy) (BE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **NOWE, Stéphane** [FR/BE]; rue du Lac 37 Bte 31, B-1000 Bruxelles (BE). **LODEFIER, Philippe** [BE/BE]; Rue Marlène Dietrich 4/16, B-1090 Bruxelles (BE). **URBANCZYK, Laetitia** [BE/BE]; Rue Molinvaux 19, B-4000 Liège (BE).

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(54) Title: EXPANDABLE VINYL AROMATIC POLYMERS

(57) Abstract: The present invention is an expandable vinyl aromatic polymer which comprises: a) a matrix of a vinyl aromatic polymer, b) 1-10% by weight calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix, c) 0.1 to 5% by weight calculated with respect to the polymer (a), of PiB (polyisobutene), homogeneously distributed in the polymeric matrix, d) 0-20% by weight, calculated with respect to the polymer (a), of one or more fillers, other than PiB, homogeneously distributed in the polymeric matrix, Wherein the proportion of PiB is adjusted to increase the Melt Flow Index (MFI) from an initial index to a final index such as the 10% compression strength of the foam made with said expandable vinyl aromatic polymer of the final index is essentially the same or higher than the foam made with said expandable vinyl aromatic polymer of the initial index. The expandable vinyl aromatic polymer of the invention is produced in the form of beads or granules. In an embodiment the expandable vinyl aromatic polymer comprises carbon black in a proportion sufficient for the foamed material obtained from the expandable vinyl aromatic polymer to have a thermal conductivity λ of about 34 mW/m²K or lower.



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EXPANDABLE VINYL AROMATIC POLYMERS

5 [Field of the invention]

The present invention relates to expandable vinyl aromatic polymers with an enhanced heat insulation capacity and comprising polyisobutene (PiB).

Expandable vinyl aromatic polymers, and among these, in particular,
10 expandable polystyrene (EPS), are known products which have been used for a long time for preparing expanded articles which can be adopted in various applicative fields, among which one of the most important is the field of heat insulation. These expanded products are obtained by swelling beads of expandable polymer impregnated with a gas and molding the swollen particles
15 contained inside a closed mould by means of the contemporaneous effect of pressure and temperature. The swelling of the particles is generally effected with water vapour, or another gas, maintained at a temperature slightly higher than the glass transition temperature (T_g) of the polymer.

A particular applicative field of expanded polystyrene is that of thermal
20 insulation in the building industry where it is generally used in the form of flat sheets. The flat expanded polystyrene sheets are normally used with a density of about 15 to 30 g/l.

[Background of the invention]

25

The term "expandable beads based on vinyl aromatic polymers" as used in the present description and claims, means vinyl aromatic polymers in the form of granules, containing an expanding system and other additives.

These expandable thermoplastic polymers in the form of granules are
30 particularly used, after expansion and moulding, in the production of household appliances or other industrial equipment, in packaging and thermal insulation in the building industry, due to their thermo-insulating properties. Thermoplastic

vinyl aromatic polymers such as polystyrene can be made expandable by incorporating an expandable agent in the polymeric matrix. Typical expanding agents for vinyl aromatic polymers include at least one liquid hydrocarbon containing from 3 to 7 carbon atoms, a halogenated hydrocarbon, carbon dioxide or water. The quantity of expanding agent usually ranges from 2 to 15% by weight. Expandable polymers are produced in general as beads or granules which, under the action of heat, supplied, for example, by steam, are first expanded until a desired density is reached and, after a certain aging period, are sintered in closed moulds to produce blocks or the desired final products.

The making of such expandable beads has already been described in EP 126459, US 2006 211780, US 2005 156344, US 6 783 710 and WO 2008 141766.

The production of beads of PS incorporating pentane is difficult due to the balance required between ease of extrusion/granulation and foam process and compression resistance of the blocks made with the sintered expanded beads (the insulation boards etc ...).

When performing granulation to make the beads, the flowability of polymer mixtures containing fillers is critical especially if micro-beads have to be produced. A usual method to modify the rheology and decrease the viscosity is to lower the molecular weight. This technique is showing limitations because of the lack of entanglements of the low molecular weight chains. An alternative is to add oil, however when using a material containing oil in foams application the compression resistance is reduced. The present invention uses polyisobutylene (also called polyisobutene or PiB) instead of oil. PiB allows to decrease the viscosity of the polymer while maintaining the same or a higher 10% compression resistance. By way of example the MFI (see in the examples the measurements standart) is increased by 0.5 to 2.5 units. A higher molecular weight can then advantageously be used.

EP 770632 B1 describes a high impact monovinylaromatic polymeric compound comprising an impact resistant rubber modified monovinylaromatic

polymer with improved environmental stress crack resistance, said polymeric compound formed by the polymerization of a monovinylaromatic compound in the presence of a rubber and an additive consisting essentially of low/medium to high molecular weight polyisobutylene as measured by a viscosity of from
5 about 48 up to about 4380 cst at 99°C. It also describes high impact monovinylaromatic polymeric compound consisting essentially of an impact resistant rubber modified polymer having improved environmental stress crack resistance, said polymer formed by the polymerization of the monovinylaromatic compound in the presence of the rubber and a mixture of about equal portions
10 of two additives comprising mineral oil and polyisobutylene. Said prior art doesn't relate to expandable monovinylaromatic polymer.

DE 2019945 describes polystyrene foam made by extrusion. Mixtures of polystyrene, di-iso-decanyl-phthalate, PiB, pentane and citric acid are mixed in
15 an extruder and foamed. Said prior art doesn't relate to expandable monovinylaromatic polymer.

US 3,929,686 describes a composition and process for the preparation of expandable styrene polymers wherein low molecular weight isobutylene
20 polymers are employed in an amount of from about 0.02 to about 0.15% by weight based upon the styrene polymer as a nucleating agent to produce an expanded styrene polymer having a very small average cell size. There is no mention of the insulation boards obtained and compression resistance thereof.

25 [Brief summary of the invention]

The present invention is an expandable vinyl aromatic polymer which comprises:

- a) a matrix of a vinyl aromatic polymer,
- 30 b) 1-10% by weight calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix,

c) 0.1 to 5% by weight calculated with respect to the polymer (a), of PiB (polyisobutene), homogeneously distributed in the polymeric matrix,

d) 0-20% by weight, calculated with respect to the polymer (a), of one or more fillers, other than PiB, homogeneously distributed in the polymeric matrix,

5 Wherein the proportion of PiB is adjusted to increase the Melt Flow Index (MFI) from an initial index to a final index such as the 10% compression strength of the foam made with said expandable vinyl aromatic polymer of the final index is essentially the same or higher than the foam made with said expandable vinyl aromatic polymer of the initial index.

10

The expandable vinyl aromatic polymer of the invention is produced in the form of beads or granules.

15 In an embodiment the expandable vinyl aromatic polymer comprises carbon black in a proportion sufficient for the foamed material obtained from the expandable vinyl aromatic polymer to have a thermal conductivity λ of about 34 mW/m^{°K} or lower.

20 The thermal conductivity λ of about 34 mW/m^{°K} means that it could be in the range 33.5 to 34.5 mW/m^{°K}. Advantageously the thermal conductivity λ is between about 33 and 34 mW/m^{°K}, more advantageously between about 32 and 33 mW/m^{°K}, preferably between about 31 and 32 mW/m^{°K} and more preferably between about 30 and 31 mW/m^{°K}.

25 The present invention also relates to a process for preparing the composition wherein it is carried out by mixing the vinyl aromatic polymer in the melted state with the blowing agent or agents, PiB, optionally carbon black and optionally the fillers. In an embodiment PiB can be introduced in the molten vinyl aromatic polymer or with the expanding agent, or with the carbon black if any or with the fillers if any or any combination thereof. In another embodiment PiB can
30 be introduced during the polymerization of the vinyl aromatic monomer. In another embodiment PiB can be introduced in part during the polymerization of the vinyl aromatic monomer and in part in the already polymerized vinyl

aromatic monomer as explained above or with the expanding agent, or with the carbon black if any or with the fillers if any or any combination thereof.

In an advantageous embodiment the mixing is carried out in a chamber
5 equipped with at least one stirring means and under temperature and pressure conditions which are capable of preventing expansion of the composition, preferably in an extruder, in particular a single-screw or twin-screw extruder, or in one or more static mixers at a temperature greater than the glass transition temperature of the polymer, in particular a temperature ranging from 120 to
10 250°C and under an absolute pressure ranging from 0.1 to 10 MPa.

The present invention also relates to the use of the expandable vinyl aromatic polymer to make expanded articles, in particular insulation boards.

In an embodiment the moulded and expanded article is produced by a
15 process comprising the following steps:

(i) a step of pre-expansion, by contacting and mixing the composition, which is in the form in particular of expandable particles or, preferably, expandable beads, with water vapour, in particular in a stirred tank, under pressure and temperature conditions capable of forming expanded particles or
20 expanded beads having in particular a bulk density ranging from 5 to 200 kg/m³, preferably from 5 to 100kg/m³ and in particular from 5 to 50 kg/m³,

(ii) a step of stabilizing the particles or beads thus expanded, by contacting them with ambient air, and

(iii) a step of moulding the particles or beads thus stabilized, by
25 introducing them into a mould and by heating the mould so as to weld the particles or beads to one another and so to produce a moulded and expanded article having in particular the desired bulk density and, preferably a bulk density substantially identical to that of the expanded particles or expanded beads obtained in step (i).

30

The present invention also relates to a process to increase the Melt Flow Index of an expandable vinyl aromatic polymer while maintaining the same or a higher 10% compression resistance.

- In an embodiment the present invention is a process to increase the Melt Flow Index of an expandable vinyl aromatic polymer while maintaining the same or a higher 10% compression resistance, comprising,
- a) providing a vinyl aromatic polymer in the molten state,
 - b) introducing 1-10% by weight calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix,
 - 10 c) introducing 0.1 to 5% by weight calculated with respect to the polymer (a), of PiB (polyisobutene), homogeneously distributed in the polymeric matrix,
 - d) introducing 0-20% by weight, calculated with respect to the polymer (a), of one or more fillers, other than PiB, homogeneously distributed in the polymeric matrix,

- 15 Wherein the proportion of PiB is adjusted to increase the Melt Flow Index (MFI) from an initial index to a final index such as the 10% compression strength of the foam made with said expandable vinyl aromatic polymer of the final index is essentially the same or higher than the foam made with said expandable vinyl aromatic polymer of the initial index.

20

The expandable vinyl aromatic polymer can be recovered as beads by any means, advantageously through an under water pelletizer.

- 25 [Detailed description of the invention]

As regards the vinyl aromatic polymer, mention may be made of :

- polystyrene, elastomer-modified polystyrene,
 - copolymers of styrene and acrylonitrile (SAN), elastomer-modified
- 30 SAN, in particular ABS, which is obtained, for example, by grafting (graft polymerization) of styrene and acrylonitrile on a backbone of polybutadiene or of butadiene-acrylonitrile copolymer,

- mixtures of SAN and ABS,
- copolymers with styrene blocks and blocks made of butadiene or isoprene or of a mixture butadiene /isoprene, these block copolymers can be linear blocks copolymers or star blocks copolymers, they can be hydrogenated and/or functionalized. These copolymers are described in ULLMANN'S
5 ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY, fifth edition (1995) Vol A26, pages 655-659, They are sold by Total Petrochemicals under the trade mark Finaclear®, by BASF under the trade mark Styrolux®, under the trade mark K-Resin® by Chevron Phillips Chemical,
- 10 - SBR (Styrene butadiene rubber),

Possible examples of the abovementioned elastomers are EPR (the abbreviation for ethylene-propylene rubber or ethylene- propylene elastomer), EPDM (the abbreviation for ethylene- propylene-diene rubber or ethylene-
15 propylene-diene elastomer), polybutadiene, acrylonitrile- butadiene copolymer, polyisoprene, isoprene-acrylonitrile copolymer and copolymers with styrene blocks and blocks made of butadiene or isoprene or of a mixture butadiene /isoprene. These block copolymers can be linear blocks copolymers or star blocks copolymers, they can be hydrogenated and/or functionalized (see
20 above).

In the above vinyl aromatic polymer just mentioned, part of the styrene may be replaced by unsaturated monomers copolymerizable with styrene, for example alpha- methylstyrene or (meth)acrylates, Other examples of styrene copolymers which may be mentioned are chloropolystyrene, poly-alpha-
25 methylstyrene, styrene- chlorostyrene copolymers, styrene-propylene copolymers, styrenebutadiene copolymers, styrene-isoprene copolymers, styrene-vinyl chloride copolymers, styrene-vinyl acetate copolymers, styrene-alkyl acrylate copolymers (methyl, ethyl, butyl, octyl, phenyl acrylate), styrene-alkyl methacrylate copolymers (methyl, ethyl, butyl, phenyl methacrylate),
30 styrene methyl chloroacrylate copolymers and styrene-acrylonitrile-alkyl acrylate copolymers.

In a specific embodiment the vinyl aromatic polymer comprises :

i) from 60 to 100 weight % of one or more C₈₋₁₂ vinyl aromatic monomers;
and

ii) from 0 to 40 weight % of one or more monomers selected from the group consisting of C₁₋₄ alkyl esters of acrylic or methacrylic acid and acrylonitrile and methacrylonitrile; which polymer may be grafted onto or
5 occluded within from 0 to 20 weight % of one or more rubbery polymers.

By way of example rubbery polymers can be selected from the group consisting of:

- a) co- and homopolymers of C₄₋₆ conjugated diolefins,
- 10 b) copolymers comprising from 60 to 85 weight % of one or more C₄₋₆ conjugated diolefins and from 15 to 40 weight % of a monomer selected from the group consisting of acrylonitrile and methacrylonitrile and
- c) copolymers comprising from 20 to 60, preferably from 40 to 50 weight % of one or more C₈₋₁₂ vinyl aromatic monomers which are unsubstituted or
15 substituted by a C₁₋₄ alkyl radical and from 60 to 40, preferably from 60 to 50 weight % of one or more monomers selected from the group consisting of C₄₋₆ conjugated diolefins.

The rubber may be prepared by a number of methods, preferably by emulsion or solution polymerization. These processes are well known to those
20 skilled in the art. The vinyl aromatic polymers may be prepared by a number of methods. This process is well known to those skilled in the art.

If present, preferably the rubber is present in an amount from about 3 to 10 weight %. Polybutadiene is a particularly useful rubber.

In the specific embodiment in which the vinyl aromatic polymer is polystyrene, it could be a crystal polystyrene or a rubber modified polystyrene.
25 The rubber modified polystyrene is called HIPS (High Impact Polystyrene). The process for making HIPS is well known to those skilled in the art. The rubber is "dissolved" in the styrene monomer (actually the rubber is infinitely swollen with the monomer). This results in two co- continuous phases. The resulting
30 "solution" is fed to a reactor and polymerized typically under shear. When the degree of polymerization is about equal to the weight % of rubber in the system it inverts (e.g. the styrene/styrene polymer phase becomes continuous and the

rubber phase becomes discontinuous. After phase inversion the polymer is finished in a manner essentially similar to that for finishing polystyrene. The polymer is prepared using conventional bulk, solution, or suspension polymerization techniques.

5 The vinyl aromatic polymers of the present invention may be co- or homopolymers of C₈₋₁₂ vinyl aromatic monomers. Some vinyl aromatic monomers may be selected from the group consisting of styrene, alpha methyl styrene and para methyl styrene. Preferably the vinyl aromatic monomer is styrene. The vinyl aromatic polymer may be a copolymer comprising from 60 to
10 100 weight % of one or more C₈₋₁₂ vinyl aromatic monomers; and from 0 to 40 weight % of one or more monomers selected from the group consisting of C₁₋₄ alkyl esters of acrylic or methacrylic acid and acrylonitrile and methacrylonitrile. Suitable esters of acrylic and methacrylic acid include methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate and butyl
15 methacrylate. The vinyl aromatic polymers of the present invention may be rubber modified.

Advantageously the vinyl aromatic polymer is a monovinylaromatic polymer.

20 In an embodiment the vinyl aromatic polymer can be a branched aromatic ionomer. As regards the branched aromatic ionomer, it is described in WO 2006 081295 the content of which is incorporated in the present application. the branched aromatic ionomer comprises the product of co-polymerizing a first monomer comprising an aromatic moiety and an
25 unsaturated alkyl moiety and a second monomer comprising an ionic moiety and at least two unsaturated moieties, wherein the ionic moiety has at least two ionizable groups, a cationic group that ionizes to form cations and an anionic group that ionizes to form anions, and wherein the cationic group is polyvalent and one capable of forming bridges to other molecules.

30 Advantageously the first monomer is selected from the group consisting of styrene, alphas methyl styrene, t-butylstyrene, p-methylstyrene, vinyl toluene, and mixtures thereof. Preferably the first monomer is styrene.

Components that may be used as the second monomer include, but are not limited to: zinc diacrylate, zinc dimethacrylate, zinc di-vinylacetate, zinc di-ethylfumarate, and the like; copper diacrylate, copper dimethacrylate, copper di-vinylacetate, copper di-ethylfumarate, and the like; aluminum triacrylate, aluminum trimethacrylate, aluminum tri-vinylacetate, aluminum tri-ethylfumarate, and the like; zirconium tetraacrylate, zirconium tetramethacrylate, zirconium tetra-vinylacetate, zirconium tetra-ethylfumarate, and the like. For components having monovalent cationic groups the second monomer may be sodium acrylate, sodium methacrylate, silver methacrylate, and the like. These components and any component useful as the second monomer may be prepared by, for example, reacting an organic acid or an anhydride with a metal or metal salt.

Advantageously the second monomer is selected from the group consisting of: zinc diacrylate, zinc dimethacrylate, zinc di-vinylacetate, zinc di-ethylfumarate, and the like; copper diacrylate, copper dimethacrylate, copper di-vinylacetate, copper di-ethylfumarate, and the like; aluminum triacrylate, aluminum trimethacrylate, aluminum tri-vinylacetate, aluminum tri-ethylfumarate, and the like; zirconium tetraacrylate, zirconium tetramethacrylate, zirconium tetra-vinylacetate, zirconium tetra-ethylfumarate, and mixtures thereof. Preferably the second monomer is zinc diacrylate or zinc dimethacrylate.

The first monomer can be a mixture of various aromatic monomers comprising an aromatic moiety and an unsaturated alkyl moiety and /or can be used alone or in a mixture of up to 50% by weight with other co-polymerizable monomers. Examples of said monomers are (meth) acrylic acid, C₁-C₄ alkyl esters of methacrylic acid, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isopropyl acrylate, butyl acrylate, amides and nitriles of (meth)acrylic acid, such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, butadiene, ethylene, divinyl benzene, maleic anhydride, etc.. Preferred co polymerizable monomers are acrylonitrile and methyl methacrylate.

The monomers used to prepare the branched aromatic ionomers may interact in several ways to affect the physical properties of the ionomers. A first way is the formation of covalent bonds due to the polymerization of the unsaturated moieties. A second way that the monomers used to prepare the
5 branched aromatic ionomers may interact is by the formation of a bridge wherein a polyvalent cationic group is coordinated to two anionic groups which are integrated into the backbones of at least two separate chains. This coordination may, in effect, cross link the two chains thereby increasing that segment's total effective molecular weight to the sum of the two chains. A third
10 way that that the monomers used to prepare the branched aromatic ionomers may interact is by the formation of multiple bridges as described immediately above. The more crosslinking that occurs, the less flexible the three dimensional structure of the ionomer, which may result in lower melt flow values and increased melt strength. In yet a fourth way of interacting, when the cationic
15 groups are mono-valent, the ionic moieties, while not fully bridged, may still associate due to hydrophobic-hydrophilic forces.

In these embodiments, this weaker but still measurable force may result from the comparatively non-polar hydrophobic, non-ionic parts of the molecule being mutually attracted and repelled from the polar hydrophilic ionic parts of
20 the ionomer. These forces are more noticeable as the proportion of the second monomer is increased in concentration. These four are not all of the possible interactions of the monomers. In addition, most of the properties of the ionomers associated with its primary, secondary, and even tertiary structure, such as the ionomers' glass transition temperatures "T_g" may be affected.

25

Both the amount of second monomer and the type of interaction with the first monomer will dictate the amount of second monomer used. Therefore, in some embodiments where the interaction is weak, such as when the cationic group of the second monomer is mono-valent, and a significant amount of effect
30 is desired from the second monomer, the branched ionomers are prepared with a comparatively large amount of the second monomer, typically with a ratio of first monomer to second monomer of from about 999:1 to about 40:60. In other

such embodiments, the ratio is from about 95:5 to about 50:50. In still other such embodiments, the ratio is from about 90:10 to about 60:40. Other embodiments have a ratio of from 80:20 to 70:30. Where the interaction is very strong, such as when the cationic group is di-or tri-valent, or only small changes to the properties of the ionomer due to the second monomer are desired, the amount of the second monomer is quite small ranging from about 10 parts per million "ppm" to about 10,000 ppm. In other such ionomers, the range is from about 100 ppm to about 1000 ppm. In still other such ionomers, the range is from about 250 ppm to about 800 ppm.

The branched aromatic ionomer is prepared by co-polymerizing the first and second monomers. Each of these monomers has at least one polymerizable unsaturation. The polymerization may be carried out using any method known to those of ordinary skill in the art of performing such polymerizations. For example, the polymerization may be carried out by using a polymerization initiator. Examples of the polymerization initiators are, for instance, radical polymerization initiators such as benzoyl peroxide, lauroyl peroxide, t-butyl peroxybenzoate and 1,1-di-t-butylperoxy-2,4-di-t-butylcyclohexane. The amount of the polymerization initiator is from about 0 to about 1 percent by weight of the monomers. In one embodiment, the amount of polymerization initiator is from about 0.01 to about 0.5 percent by weight of the monomers. In another embodiment, the amount of polymerization initiator is from about 0.025 to about 0.05 percent by weight of the monomers.

Alternatively, rather than using an initiator, the ionomer may be prepared using heat as an initiator. The ionomer may be prepared using a non-conventional initiator such as a metallocene catalyst as is disclosed in US. Patent No. 6,706,827 to Lyu, et al., which is incorporated herein in its entirety by reference. In one embodiment, the monomers may be admixed with a solvent and then polymerized. In another embodiment, one of the monomers is dissolved in the other and then polymerized. In still another embodiment, the monomers may be fed concurrently and separately to a reactor, either neat or dissolved in a solvent, such as mineral oil.

In yet another embodiment, the second monomer may be prepared in-situ or immediately prior to the polymerization by admixing the raw material components, such as an unsaturated acid or anhydride and a metal alkoxide, in-line or in the reactor. Any process for polymerizing monomers having polymerizable unsaturation know to be useful to those of ordinary skill in the art in preparing such polymers may be used. For example, the process disclosed in U.S. Patent No. 5,540,813 to Sosa, et al., may be used and is incorporated herein in its entirety by reference. The processes disclosed in U.S. Patent No. 3,660,535 to Finch, et al., and U. S. Patent No. 3,658,946 to Bronstert, et al., may be used and are both incorporated herein in their entirety. Any process for preparing general purpose polystyrene may be used to prepare the branched aromatic ionomers.

The branched aromatic ionomer can be mixed with up to 50%w of a GPPS.

The ionomers may be admixed with additives prior to being used in end use applications. For example, the ionomers may be admixed with fire retardants, antioxidants, lubricants, UV stabilizers, antistatic agents, and the like. Any additive known to be useful to those of ordinary skill in the art of preparing ionomers to be useful may be used with the branched ionomers.

As regards an advantageous vinyl aromatic polymer, one can cite polystyrene such as crystal polystyrene and HiPS. Polystyrene has advantageously a $\overline{M_w}$ from 130000 to 210000 and a MFI (Measured at 200°C with a weight of 5Kg, according to norm DIN ISO 1133) ranging from 4 to 20.

As regards the expanding agent, it is selected from aliphatic or cyclo-aliphatic hydrocarbons containing from 3 to 6 carbon atoms such as n-pentane, iso-pentane, cyclopentane or blends thereof; halogenated derivatives of aliphatic hydrocarbons containing from 1 to 3 carbon atoms, such as, for example, dichlorodifluoromethane, 1,2,2- trifluoroethane, 1,1,2-trifluoroethane; carbon dioxide and water. As regards pentane advantageously a mixture of n

and iso is used. The proportion of pentane is advantageously in the range 4 to 7w%.

As regards PiB, the isobutylene polymers according to the present invention are preferably homopolymers of isobutylene but include also C2-C5 lower olefin hydrocarbons containing at least about 85% isobutylene monomer units and typically including minor amounts of normal-butylene monomer units and relatively small amounts of other lower olefins. The isobutylene polymers employed in the present invention are those having a molecular weight (number average) of between about 500 and 5000, although it is preferred that the molecular weight thereof range between about 900 and 3000. The polymers are characterized as long chain hydrophobic molecules with methyl side group chains. The proportion of PiB can be adjusted easily by checking the MFI of the expandable vinyl aromatic polymer. It seems that an increase of about 1 or 2 g/10 min is enough to make easily the beads or granules. Advantageously the proportions (w% with respect to polymer (a)) of PiB are from 0.5 to 2.5, preferably from 0.8 to 2.2 more preferably from 1 to 2.

The isobutylene polymers employed in accordance with the present invention can be prepared by means of known procedures, and suitable products are available commercially. In a typical method for the preparation of the subject isobutylene polymers, a hydrocarbon feed consisting essentially of isobutylene monomer is contacted with a Friedel-Crafts catalyst at a temperature above about -45°F, whereupon a suitable low molecular weight polymer is produced. See, for example, the disclosure of U.S. Pat. No. 2,957,930. Polymers falling within the upper portion of the molecular weight range specified hereinabove may be produced by further contacting the foregoing low molecular weight polyisobutylene with about 1 to 10% of a Friedel-Crafts catalyst for periods of about 15 minutes to 2 hours and at a temperature of from about 10° to 200°F see, for example, U.S. Pat. No. 3,375,295. Other suitable procedures for the preparation of low molecular weight isobutylene polymers are described in U.S. Pat. Nos. US 3, 501,551, US 3,073, 876, US 3,242,158, and US 3,356,661.

As regards the carbon black, the proportion can be determined easily by the man skilled in the art. The thermal conductivity of the foam decreases with the increasing proportion of carbon black. The range can be from about 1 to about 5 w%. It is easy with a reduced number of experiments to find the proportion to get a thermal conductivity λ of about 34 mW/m^{°K} or lower of the foam. The carbon black has advantageously a surface area (preferably the BET nitrogen surface area), measured according to ASTM D-6556, ranging from 5 to 1000 m²/g, more advantageously from 5 to 800 m²/g. Preferably said surface area ranges from 50 to 100 m²/g and more preferably from 45 to 75 m²/g. One can cite the Ensaco® 150, Ensaco® 210, Ensaco® 250, Ensaco® 260 and Ensaco® 350 supplied by the company Timcal.

As regards the fillers, one can cite any material capable to reduce the thermal conductivity and/or to enhance the properties of the expanded vinyl aromatic polymer. One can cite talc, graphite, mica, silica, titanium dioxide and barium sulfate.

As regards talc, in an embodiment, one can cite those having a mean diameter above about 8 μ m, said mean diameter being measured by Laser Mastersizer according to standard ISO 13320-1, one can cite the 20M00S supplied by the company Rio Tinto Minerals (Talcs de Luzenac). Advantageously the talc has a mean diameter above about 8 μ m and under 100 μ m, more advantageously in the range 8-50 μ m, preferably in the range 8-30 μ m, more preferably in the range 9-12 μ m. Advantageously the D(95) is around 100 μ m or below, more advantageously around 50 μ m, much more advantageously around 40 μ m, preferably around 30 μ m. D(95) means that 95% of particles are smaller than this value. Advantageously the BET of the talc is in the range 0.5-5 m²/g and preferably in the range 3-4 m²/g. The proportion of talc is advantageously from 0.1 to 2w% and preferably around 1%.

One can cite also flame retardants, nucleating agents, plasticizers and agents which facilitate the demoulding of the moulded and expanded articles. In particular it may comprise at least one flame retardant selected in particular

from halogenated hydrocarbons, preferably brominated hydrocarbons, in particular C6 to C12 hydrocarbons, such as hexabromocyclohexane, pentabromomonochlorocyclohexane or hexabromocyclododecane, in an amount which can range from 0.05 to 2 parts, preferably from 0.1 to 1.5 parts, by weight, per 100 parts by weight of the styrene polymer. The composition may further comprise at least one nucleating agent selected in particular from synthetic waxes, in particular Fischer-Tropsch waxes and polyolefin waxes such as polyethylene waxes or polypropylene waxes, in an amount which can range from 0.05 to 1 part, preferably from 0.1 to 0.5 part, by weight per 100 parts by weight of the vinyl aromatic polymer. The composition may likewise comprise at least one plasticizer, selected in particular from mineral oils and petroleum waxes such as paraffin waxes, in an amount which can range from 0.1 to 1 part, preferably from 0.1 to 0.8 part, by weight per 100 parts by weight of the vinyl aromatic polymer. The composition may additionally comprise at least one agent which facilitates the demoulding of the moulded and expanded articles, selected in particular from inorganic salts and esters of stearic acid, such as glycerol mono-, di or tristearates and zinc stearate, calcium stearate or magnesium stearate, in an amount which can range from 0.05 to 1 part, preferably from 0.1 to 0.6 part, by weight per 100 parts by weight of the vinyl aromatic polymer.

As regards the mechanical properties of the foam, a parameter of importance is the 10% compression strength as a function of the density of the foam. The advantage of the compositions of the invention is they have a high 10% compression strength.

The proportion of PiB is adjusted to increase the Melt Flow Index (MFI) from an initial index to a final index such as the 10% compression strength of the foam made with said expandable vinyl aromatic polymer of the final index is essentially the same or higher than the foam made with said expandable vinyl aromatic polymer of the initial index. "Essentially the same" means that the difference is less than 5%, advantageously less than 4%, more advantageously less than 3% and preferably less than 2%.

Advantageously, for polystyrene, the 10% compression strength (or strain value at 10% deformation) in kPa which is at least $[7.14 \times \text{density of the foam in kg/m}^3 - 28]$. Which means about 50 kPa for a density of 11 kg/m³ and
5 about 150 kPa for a density of 25 kg/m³.

As regards the process to make said expandable polymer, it is carried out by mixing the vinyl aromatic polymer in the melted state with the blowing agent or agents, PiB, talc if any, carbon black if any and the fillers.

10 In an advantageous embodiment the mixing is carried out in a chamber equipped with at least one stirring means and under temperature and pressure conditions which are capable of preventing expansion of the composition, preferably in an extruder, in particular a single-screw or twin-screw extruder, or in one or more static mixers at a temperature greater than the glass transition
15 temperature of the polymer, in particular a temperature ranging from 120 to 250°C and under an absolute pressure ranging from 0.1 to 10 MPa.

The making of such expandable beads has already been described in EP 126459, US 2006 211780, US 2005 156344, US 6 783 710 and WO 2008
20 141766, the content of which is incorporated in the present invention.

According to an embodiment the present invention relates to a process for preparing in mass and in continuous, expandable vinyl aromatic polymers, which comprises the following steps in series: (i) feeding the vinyl aromatic
25 polymer, as described above, to an extruder, optionally together with fillers, (ii) heating the vinyl aromatic polymer to a temperature higher than the relative melting point; (iii) injecting the expanding agent and possible additives (PiB) into the molten polymer before extrusion through a die; and (iv) forming expandable beads, through a die, with an average diameter ranging from 0.2 to 2 mm and
30 advantageously made with an underwater pelletizer. The expandable beads produced are subjected to pre-treatment generally applied to conventional expandable beads and which essentially consists in:

1. coating the beads with an antistatic agent such as amines, tertiary ethoxylated alkylamines, ethylene oxide-propylene oxide copolymers, etc. The purpose of this agent is to facilitate the adhesion of the coatings
 2. applying the "coating" to the above beads, said coating essentially consisting
- 5 of a mixture of mono-, di-and tri-esters of glycerin (or other alcohols) with fatty acids and of metallic stearates such as zinc and/or magnesium stearate.

[Examples]

10

In all examples the melt index of polystyrene is measured at 200°C under a 5kg load (DIN ISO 1133).

Example 1 : reference, MFI =7

15

A mixture containing 99 parts of polystyrene ($M_w = 170$ Kg/mol, Polydispersity Index (PI)=2.3), and 1 part of talc from Luzenac® are fed in an extruder. 6w% of pentane (80/20 n-/iso pentane) is injected in the extruder through a specific line. The melt flow index of this melt equals 7 g/10min, according to DIN ISO 1133.

20

The sample is finally granulated at die exit with an underwater pelletizer. The recovered beads, whose diameter is in the range 0.3-2mm, are then treated with a coating agent like zinc stearate and optionally glycerol mono- bi- or tri-stearate. The treated beads are pre-expanded with steam at 100°C, left to age for 1 day and finally used to mold the board. After 1 day, the density of the

25 board, determined by weighing the board and measuring its dimensions, is 19 g/l. After at least 30 ageing days, the sample is subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standart, is 113 kPa. The thermal conductivity of the board, measured according to norm ISO 8301, is 0.035 W/mK

30

Example 2: reference MFI= 8.5

A mixture containing 99 parts of polystyrene ($M_w = 155$ Kg/mol, $PI = 2.2$), and 1 part of talc from Luzenac® are fed in an extruder. 6w% of pentane (80/20 n-/iso pentane) is injected in the extruder through a specific line. The melt flow index of this melt equals 8.5 g/10min according to DIN ISO 1133. The sample is finally
5 granulated at die exit with an underwater pelletizer. The recovered beads, whose diameter is in the range 0.3-2mm, are then treated with a coating agent like zinc stearate and optionally glycerol mono- bi- or tri-stearate. The treated beads are pre-expanded with steam at 100°C, left to age for 1 day and finally used to mold the board. After 1 day, the density of the board, determined by
10 weighing the board and measuring its dimensions, is 19.1 g/l. After at least 30 ageing days, the sample is subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standart, is 101.4 kPa.

Example 3: according to the invention PS+ 0.5% PiB MFI= 8.5

15

Expandable beads are produced with the same conditions as described in Example 1, except that the initial mixture contains 98.5 parts of polystyrene ($M_w = 170$ Kg/mol, $PI = 2.3$), 1 part of talc from Luzenac®, and 0.5 part of polyisobutene Glissopal 1000 from BASF. Glissopal 1000 is a polyisobutene of
20 $\overline{M_n}$ 1000. The melt flow index of this melt equals 8.5 g/10min, according to DIN ISO 1133. The board obtained after pre-expansion and molding steps has a density of 19.9 g/l. After at least 30 ageing days, the sample is subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standart, is 117.3 kPa.

25

Comparative Example 3: PS+ 1% huile Primol MFI= 8.1

Expandable beads are produced with the same conditions as described in Example 2, except that the initial mixture contains 98 parts of polystyrene ($M_w =$
30 170 Kg/mol, $PI = 2.3$), 1 part of talc from Luzenac®, and 1 part of Primol 352 oil from Exxon. Primol 352 is a white mineral oil (CAS number: 8042-47-5 EINECS

number: 232-455-8) of average Molecular Weight 480 (ASTM D 2502) having a percentage carbon Paraffinic / Naphthenic/ Aromatic 66 / 34 / 0 (ASTM D 2140). The melt flow index of this melt equals 8.1 g/10min, according to DIN ISO 1133. The board obtained after pre-expansion and molding steps has a density of 18.8 g/l. After at least 30 ageing days, the sample is subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standart, is 103.8 kPa.

Example 4: according to the invention PS+ 1% PiB MFI =9

10

Expandable beads are produced with the same conditions as described in Example 1, except that the initial mixture contains 98 parts of polystyrene (Mw= 170 Kg/mol, PI=2.3), 1 part of talc from Luzenac®, and 1 part of polyisobutene Glissopal 1000 from BASF. The melt flow index of this melt equals 9 g/10min, according to DIN ISO 1133. The board obtained after pre-expansion and molding steps has a density of 19.5 g/l. After at least 30 ageing days, the sample is subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standart, is 112.2 kPa.

20 Comparative Example 4: PS+ 2% Primol 352, MFI =8.9

Expandable beads are produced with the same conditions as described in Example 3, except that the initial mixture contains 97 parts of polystyrene (Mw= 170 Kg/mol, PI=2.3), 1 part of talc from Luzenac®, and 2 parts of Primol 352 oil from Exxon. The melt flow index of this melt equals 8.9 g/10min, according to DIN ISO 1133. The board obtained after pre-expansion and molding steps has a density of 20 g/l. After at least 30 ageing days, the sample is subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standart, is 99 kPa.

30

Example 5: according to the invention PS+ 3%CB + 1% PiB, MFI= 9.3

Expandable beads are produced with the same conditions as described in Example 3, except that the initial mixture contains 95 parts of polystyrene ($M_w = 170$ Kg/mol, $PI = 2.3$), 1 part of talc from Luzenac®, 1 part polyisobutene Glissopal 1000 from BASF and 3% of carbon black Ensaco® 260G from Timcal.

- 5 The melt flow index of this melt equals 9.3 g/10min, according to DIN ISO 1133. The board obtained after pre-expansion and molding steps has a density of 20.2 g/l. After at least 30 ageing days, the sample is subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standart, is 116 kPa. The thermal conductivity of the board, measured according to norm
- 10 ISO 8301, is 0.0318 W/mK.

Comparative Example 5: + 3%CB + 2% Primol 352 MFI =10.2

Expandable beads are produced with the same conditions as described in

15 Example 3, except that the initial mixture contains 95 parts of polystyrene ($M_w = 170$ Kg/mol, $PI = 2.3$), 1 part of talc from Luzenac®, 2 parts of Primol 352 oil from Exxon and 3% of carbon black Ensaco® 260G from Timcal. The melt flow index of this melt equals 9.6 g/10min, according to DIN ISO 1133. The board obtained after pre-expansion and molding steps has a density of 20 g/l. After at least 30

20 ageing days, the sample is subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standart, is 95.1 kPa. The thermal conductivity of the board, measured according to norm ISO 8301, is 0.0324 W/mK.

Example	Polystyrene Mw (Kg/mol)	Additive nature	Additive amount (%)	Carbon black content (%)	MFI ¹ (g/10min)	Board density (g/l)	10% compression strength ² (kPa)
1 reference	170	No add.	-	0	7	19	113
2 reference	155	No add.	-	0	8.5	19.1	101.4
3	170	PIB	0.5	0	8.5	19.9	117.3
Comp. 3	170	Oil	1	0	8.1	18.8	103.8
4	170	PIB	1	0	9	19.5	112.2
Comp. 4	170	Oil	2	0	8.9	20	99
5	170	PIB	1	3	9.3	20.2	116
Comp. 5	170	Oil	2	3	9.6	20	95.1

¹ Measured at 200°C with a weight of 5Kg, according to norm DIN ISO 1133.

² Measured according to norm EN826.

5

Discussion about the examples

Example 1 illustrates the preparation of white EPS beads with a standard polystyrene grade by extrusion with the use of an underwater pelletizer. A good control over the melt flow is critical in order to facilitate melt cutting and to obtain spherical beads of narrow size distribution. The melt flow index of the PS used (MI=7 g/10min, 170 Kg/mol, PI=2.3) is too low and necessitates higher pelletizing temperature in order to prevent any plugging of the die plate. However, increasing the temperature leads to irregular beads shape and broad size distribution. Therefore, the strategy envisaged is to find a way to lower the melt viscosity, which would allow an easy granulation without plugging issues or beads deformation.

One way of reducing the melt viscosity is to choose PS of lower molecular weight, as illustrated in Example 2 (MI=8.5 g/10min, 155 Kg/mol, PI=2.2). With this melt flow, pelletization becomes much easier and very regular beads are obtained. However, the boards obtained suffer from weaker compression resistance (101.4 kPa), due to lower PS Mw.

Another classical way of reducing melt viscosity is to add some oil (see Comparative Examples 3 and 4). With 1 and 2wt% of oil, the MFI is successfully increased to 8.1 and 8.9 g/10min respectively, which greatly facilitates underwater pelletization. However, the oil added decreases the foam mechanical resistance (103.8 and 99 kPa respectively).

In the present invention, we have found that polyisobutene addition can increase the melt flow index of the PS while not negatively impacting the final foam mechanical resistance. In fact, as shown in Examples 3 and 4, the addition of 0.5 and 1wt% of PiB leads to MI of 8.5 and 9 g/10min, respectively.

This higher melt flow facilitates the underwater granulation step (no plugging observed). The mechanical resistance of the boards prepared is similar than boards of Example 1, where no plasticizer is added (117.3 and 112.2 kPa, respectively). Polyisobutene addition thus helps the granulation process without negatively impacting the final foam mechanical properties.

The same experiment has been performed with the addition of a filler able to decrease the foam thermal conductivity, namely carbon black, for insulation purpose. In Example 5, a satisfactory MFI is obtained with the addition of 1% of PiB and 3% of carbon black (9.3 g/10min). The compression resistance of the boards prepared is not affected by these additives (116 kPa) and the thermal conductivity of the boards is lowered (0.0318 W/mK compared to 0.035 W/mK without carbon black, see Example 1). In contrast, Comparative Example 5 shows that mechanical resistance of foams containing 1% of oil and 3% of carbon black is detrimentally affected (95.1 kPa), while the thermal conductivity remains acceptable (0.0324 W/mK).

CLAIMS

- 1 Expandable vinyl aromatic polymer which comprises:
- a) a matrix of a vinyl aromatic polymer,
 - 5 b) 1-10% by weight calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix,
 - c) 0.1 to 5% by weight calculated with respect to the polymer (a), of PiB (polyisobutene), homogeneously distributed in the polymeric matrix,
 - 10 d) 0-20% by weight, calculated with respect to the polymer (a), of one or more fillers, other than PiB, homogeneously distributed in the polymeric matrix,
- Wherein the proportion of PiB is adjusted to increase the Melt Flow Index (MFI) from an initial index to a final index such as the 10% compression strength of the foam made with said expandable vinyl aromatic polymer of the final index is essentially the same or higher than the foam made with said
- 15 expandable vinyl aromatic polymer of the initial index.
- 2 Expandable vinyl aromatic polymer according to claim 1 wherein it is in the form of beads or granules.
- 20 3 Expandable vinyl aromatic polymer according to any one of the preceding claims wherein it comprises carbon black in a proportion sufficient for the foamed material obtained from the expandable vinyl aromatic polymer to have a thermal conductivity λ of about 34 mW/m^{°K} or lower.
- 25 4 Expandable vinyl aromatic polymer according to claim 3 wherein the thermal conductivity λ of the foamed material obtained from the expandable vinyl aromatic polymer is between about 33 and 34 mW/m^{°K}.
- 30 5 Expandable vinyl aromatic polymer according to claim 3 wherein the thermal conductivity λ of the foamed material obtained from the expandable vinyl aromatic polymer is between about 32 and 33 mW/m^{°K}.

6 Expandable vinyl aromatic polymer according to claim 3 wherein the thermal conductivity λ of the foamed material obtained from the expandable vinyl aromatic polymer is between about 30 and 31 mW/m²K.

5 7 Expandable vinyl aromatic polymer according to any one of the preceding claims wherein the PiB are those having a molecular weight (number average) of between about 500 and 5000.

8 Expandable according to claim 7 wherein the molecular weight
10 ranges between about 900 and 3000.

9 Expandable vinyl aromatic polymer according to any one of the preceding claims wherein the vinyl aromatic polymer is polystyrene such as crystal polystyrene and HiPS.

15

10 Use of the expandable vinyl aromatic polymer according to any one of the preceding claims to make expanded articles, in particular insulation boards.

20 11 Process to increase the Melt Flow Index of an expandable vinyl aromatic polymer while maintaining the same or a higher 10% compression resistance, comprising,

- a) providing a vinyl aromatic polymer in the molten state,
- b) introducing 1-10% by weight calculated with respect to the polymer (a),
25 of an expanding agent englobed in the polymeric matrix,
- c) introducing 0.1 to 5% by weight calculated with respect to the polymer (a), of PiB (polyisobutene), homogeneously distributed in the polymeric matrix,
- d) introducing 0-20% by weight, calculated with respect to the polymer (a), of one or more fillers, other than PiB, homogeneously distributed in the
30 polymeric matrix,

Wherein the proportion of PiB is adjusted to increase the Melt Flow Index (MFI) from an initial index to a final index such as the 10% compression

strength of the foam made with said expandable vinyl aromatic polymer of the final index is essentially the same or higher than the foam made with said expandable vinyl aromatic polymer of the initial index.

- 5 12 Process according to claim 11 wherein the PiB are those having a molecular weight (number average) of between about 500 and 5000.

 13 Process according to claim 12 wherein the molecular weight ranges between about 900 and 3000.

10

 14 Process according to any one of claims 11 to 13 wherein the vinyl aromatic polymer is polystyrene such as crystal polystyrene and HiPS.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/068165

A. CLASSIFICATION OF SUBJECT MATTER
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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

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 practical, search terms used)

EP0-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 397 001 A1 (BASF AG [DE]) 14 November 1990 (1990-11-14) example 1	1-10
X	DE 26 21 448 A1 (BASF AG) 1 December 1977 (1977-12-01) example 4	1-10
X	DE 12 82 938 B (BASF AG) 14 November 1968 (1968-11-14) example 1	1-10
X	US 3 660 321 A (PRAETZEL HANS EBERHARD ET AL) 2 May 1972 (1972-05-02) example 1	1-10
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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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

Andriollo, Giovanni

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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