Abstract:
Invention relates to expandable vinyl aromatic polymers which comprise: a) a matrix of 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 talc having a mean diameter above about 8 μm, said mean diameter being measured by Laser Mastersizer according to standard ISO 13320-1, the BET of the talc being in the range 0.5-25m²/g, d) 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 m W/m°K or lower, e) 0-20% by weight, calculated with respect to the polymer (a), of one or more fillers, other than talc and carbon black, homogeneously distributed in the polymeric matrix. The expandable vinyl aromatic polymer of the invention is obtained in the form of beads or granules. The thermal conductivity λ of about 34 m W/m°K means that it could be in the range 33.5 to 34.5 m W/m°K. Advantageously the thermal conductivity λ between about 33 and 34 m W/m°K, more advantageously between about 32 and 33 m W/m°K, preferably between about 31 and 32 m W/m°K and more preferably between about 30 and 31 m W/m°K.
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 carbon black and talc.

Expandable vinyl aromatic polymers, and among these, in particular, 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 contained inside a closed mould by means of the contemporaneous effect of pressure and temperature. The swelling of the particles is generally effected with vapour, or another gas, maintained at a temperature slightly higher than the glass transition temperature (Tg) of the polymer.

A particular applicative field of expanded polystyrene is that of thermal 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 30 g/l as the thermal conductivity of the polymer has a minimum at these values.

25 [Background of the invention]

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 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 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 ...).

EP 372343 A1 at page 12 describes EPS comprising carbon black 0, 4, and 10 weight percent and talc: 0 to 0.20 weight percent. It is mentioned that the use of 10% carbon black reduces the thermal conductivity by 15%.

WO 97 45477 A1 describes an EPS comprising 2-8% carbon black having an area ranging from 10 to 500 m2/g. In examples 4 and 5 for 6w% carbon black the thermal conductivity $\lambda$ is 30-33 mW/m°K. There is no talc.

EP 620 246 B1 describes moulding comprising expanded polystyrene foam and an athermanous material, where the expanded polystyrene foam has a density of less than 20 kg/m³ and the athermanous material absorbs infrared radiation. In an example for 2w% carbon black and a foam density of 10 kg/m³ the thermal conductivity $\lambda$ is 35 mW/m°K. There is no talc.
WO 2004-087798 A1 relates to expandable vinylaromatic polymers which comprise:

a) a matrix obtained by polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0-50% by weight of a copolymerizable monomer;

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

c) 0.01-20% by weight, calculated with respect to the polymer (a), of carbon black homogeneously distributed in the polymeric matrix having an average diameter ranging from 30 to 2000 nm, a surface area ranging from 5 to 40 m²/g, a sulfur content ranging from 0.1 to 2000 ppm and an ash content ranging from 0.001 to 1%. In an example for 1w% carbon black the thermal conductivity $\lambda$ is 36.5 mW/m°K. There is no talc.

WO 2006-058733 A1 relates to expandable styrene polymer granulates, which contain

a) between 5 and 50 wt. % of a filler, selected from pulverulent inorganic materials such as talc, chalk, kaolin, aluminium hydroxide, aluminium nitrite, aluminium silicate, barium sulphate, calcium carbonate, titanium dioxide, calcium sulphate, silicic acid, quartz powder, aerosil, alumina or wollastonite and

b) between 0.1 and 10 wt. % carbon black or graphite.

In example 2 there are 1w% carbon black and 10w% chalk, the thermal conductivity $\lambda$ is 32 mW/m°K.

WO 2006 108672 A2 describes a process for improving the insulating capacity of expanded vinyl aromatic which comprises:

1) preparing beads of expandable vinyl aromatic polymers containing 1-10% by weight, calculated with respect to the polymer, of an expanding agent englobed in the polymeric matrix and 0.001-25% by weight, calculated with respect to the polymer (a), of an athermanous additive comprising carbon black homogeneously distributed in the polymeric matrix;
2) treating the surface of the beads, before deposition of the coating, with a liquid lubricating agent; and
3) thermally treating the beads with hot air at a temperature ranging from 30 to 60°C.

In an example for 1w% carbon black the thermal conductivity \( \lambda \) is 35.2 mW/m\( \cdot \)°K. In an example for 1w% carbon black the thermal conductivity \( \lambda \) is 33 mW/m\( \cdot \)°K. In an example for 1w% carbon black + 1w% graphite the thermal conductivity \( \lambda \) is 32 mW/m\( \cdot \)°K. There is no talc.

US 2007 0112082 A1 relates to a moldable-foam molding with a density from 8 to 200 g/l, obtainable via fusion of prefoamed foam beads comprising expandable pelletized thermoplastic polymer materials, wherein the pelletized polymer materials comprise from 1 to 50% by weight, of one or more fillers selected from the group consisting of talc, chalk, kaolin, aluminum hydroxide, magnesium hydroxide, aluminum nitrite, aluminum silicate, calcium carbonate, calcium sulfate, silica, powdered quartz, Aerosil, alumina and glass beads. In an embodiment the moldable foam molding further comprises from 0.1 to 10% by weight of carbon black or graphite. In an example for 1w% carbon black and 10w% chalk, a foam density of 18.8 kg/m\( ^3 \) the thermal conductivity \( \lambda \) is 35.2 mW/m\( \cdot \)°K.

WO 2007 045454 A1 relates to expandable granulates, having compositions based on vinyl-aromatic polymers, essentially consisting of:

a) 65-99.8% by weight of a copolymer obtained by polymerizing 85-100% by weight of one or more vinyl-aromatic monomers having general formula (I) and 0-1.5% by weight of an \( \alpha \)-alkylstyrene in which the alkyl group contains from 1 to 4 carbon atoms;
b) 0-25% by weight, calculated with respect to the polymer (a), of a carbon black having an average diameter ranging from 10 to 1000 nm and a surface area ranging from 5 to 200 m\( ^2 \)/g;
c) at least one of the following additives (cl)-(c3): ci) 0.01-5% by weight, calculated with respect to the polymer (a), of graphite having an average diame-
term ranging from 0.5 to 50 μm; c2) 0.01-5% by weight, calculated with respect to the polymer (a), of oxides and/or sulfates and/or lamellar dichalcogenides of metals of groups hA, lIIA, MB, lV E, VIE or VIII B, c3) 0.01-5% by weight, calculated with respect to the polymer (a), of inorganic derivatives of silicon of the lamellar type;
d) 0-5% by weight, calculated with respect to the polymer (a), of a nucleating agent; and
e) 1-6% by weight, calculated with respect to 100 parts of the total of (a)-(d), of one or more expanding agents.

In an example there is 4w% of carbon black. There is no talc and no thermal conductivity is cited.

WO 2008 141766 A1 relates to a process to make EPS. In the examples at table 2 there is 5.2% of graphite or 4.7% of talc. There are no examples in which talc and graphite or carbon black are simultaneously present.

WO 2008 061678 A2 relates to expandable vinyl aromatic polymers which comprise:

a) a matrix obtained by polymerizing 50-100% by weight of one or more vinyl aromatic monomers and 0-50% by weight of at least one copolymerizable monomer;
b) 1-10% by weight calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix;
c) 0.01-20% by weight, calculated with respect to the polymer (a), of a filler including carbon black electrically conductive and homogeneously distributed in the polymeric matrix, with a surface area, measured according to ASTM D-3037/89, ranging from 5 to 200 m2/g.

In the examples for 1 to 4w% carbon black, a foam density of 17 kg/m3 the thermal conductivity λ is ranging from 31 to 33.3 mW/m°K. In an example for 1w% carbon black and 0.2w% graphite, a foam density of 18.3 kg/m3 the thermal conductivity λ is 30.1 mW/m°K. There is no talc.
It has now been discovered that by selecting a talc having a mean
diameter above about 8 μm, said mean diameter being measured by Laser
Mastersizer according to standard ISO 13320-1, the proportion of carbon black
can be lowered. Simultaneously the 10% compression strength is maintained
over a wide range of foam density.

[Brief summary of the invention]

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 talc
having a mean diameter above about 8 μm, said mean diameter being
measured by Laser Mastersizer according to standard ISO 13320-1, the BET of
the talc being in the range 0.5-25 m2/g,
d) carbon black in a proportion sufficient for the foamed material obtained
from the expandable vinyl aromatic polymer to have a thermal conductivity \( \lambda \) of
about 34 mW/m°K or lower,
e) 0-20% by weight, calculated with respect to the polymer (a), of one or
more fillers, other than talc and carbon black, homogeneously distributed in the
polymeric matrix.

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

The thermal conductivity \( \lambda \) 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 \( \lambda \) 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.
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, carbon black, talc and optionally the fillers.

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 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 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 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 expanded beads having in particular a bulk density ranging from 5 to 200 kg/m3, preferably from 5 to 100 kg/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 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).
[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 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 fonctionnalized. These copolymers are described in ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY, fith 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,
  - 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-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 fonctionnalized (see 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-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), 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 Cs-12 vinyl aromatic monomers;

and

ii) from 0 to 40 weight % of one or more monomers selected from the group consisting of C_{4,6} alkyl esters of acrylic or methacrylic acid and acrylonitrile and methacrylonitrile; which polymer may be grafted onto or 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 C_{4,6} conjugated diolefins,

b) copolymers comprising from 60 to 85 weight % of one or more C_{4,6} 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 Cs-12 vinyl aromatic monomers which are unsubstituted or substituted by a C_{4,6} alkyl radical and from 60 to 40, preferably from 60 to 50 weight % of one or more monomers selected from the group consisting of C_{4,6} 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 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. 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 "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.

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 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 methacrylate. The vinyl aromatic polymers of the present invention may be rubber modified.

Advantageously the vinyl aromatic polymer is a monovinylaromatic polymer.

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 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.

Advantageously the first monomer is selected from the group consisting of styrene, alphanethy1 styrene, 1-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 diethylfumarate, and the like; copper diacrylate, copper dimethacrylate, copper divinylacetate, copper di-ethylfumarate, and the like; aluminum triacrylate, aluminum trimethacrylate, aluminum tri-vinylacetate, aluminum triethylfumarate, 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 diethylfumarate, and the like; copper diacrylate, copper dimethacrylate, copper divinylacetate, copper di-ethylfumarate, and the like; aluminum triacrylate, aluminum trimethacrylate, aluminum tri-vinylacetate, aluminum triethylfumarate, and the like; zirconium tetraacrylate, zirconium tetramethacrylate, zirconium tetra-vinylacetate, zirconium tetra-ethylfumarate, and mixtures thereof. Preferably the second ionomer 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, Ci-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, methacrylnitrile, 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 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 way 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 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 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 "Tg" may be affected.
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 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-butyldi-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 the expanding agent,** it is selected from aliphatic or cycloaliphatic 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 7 w%.

As regards talc having a mean diameter, also known as D50, above about 8 \( \mu m \), 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 \( \mu m \) and under 100 \( \mu m \), more advantageously in the range 8-50 \( \mu m \), preferably in the range 8-30 \( \mu m \), more preferably in the range 9-12 \( \mu m \). In an embodiment the talc has a mean diameter above about 9 \( \mu m \) and under 100 \( \mu m \), more advantageously in the range 9-50 \( \mu m \), preferably in the range 9-30 \( \mu m \).

Advantageously the D(95) is around 100 \( \mu m \) or below, more advantageously around 50 \( \mu m \), much more advantageously around 40 \( \mu m \), preferably around 30 \( \mu m \). D(95) means that 95% of particles are smaller than this value. The BET of the talc is in the range 0.5-25 m2/g advantageously in the range 0.5-20 m2/g, more advantageously in the range 0.5-15 m2/g, preferably in the range 0.5-10 m2/g, more preferably in the range 0.5-5m2/g and preferably in the range 3-4 m2/g.

The proportion of talc is advantageously from 0.5 to 2w% and preferably from 0.5 to 1.5w%, more preferably from 0.7 to 1.3w%, still more preferably from 0.8 to 1.2 most preferably around 1%.

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 \( \lambda \) 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-3037/89, ranging from 5 to 1000 m2/g, more advantageously from 5 to 800 m2/g. Preferably said
surface area ranges from 50 to 100m²/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. In an embodiment said area ranges from 50 to 1000m²/g, advantageously from 50 to 800 m²/g.

**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 graphite, mica, silica, titanium dioxide and barium sulfate.

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 hexabromocylohexane, pentabromomonochlorocylohexane 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. They comply with a 10% compression strength (or strain value at 10% deformation) in kPa which is at least [7.14x density of the foam in kg/m3 - 28]. Which means about 50 kPa for a density of 11 kg/m3 and 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, talc carbon black and the fillers.

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 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 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 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 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 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 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]

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

Example 1 (according to the invention, Luzenac® talc and Carbon Black)

A mixture containing 96.5 parts of polystyrene (melt index 6.5, measured following DIN ISO 1133), 1 part of talc from Luzenac®, having a mean diameter of 10.5 μm and BET surface area of 3.8 m²/g, and 2.5 parts of carbon black, characterized by BET surface area of 70 m²/g, are fed in an extruder. 6w% of pentane (80/20 n-/iso pentane) is injected in the extruder through a specific line. The melt 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 board, determined by weighing the board and measuring its dimensions, is 20.8 g/l. After at least 30 ageing days, the measured thermal conductivity of this panel is 0.0305 W/mK according to standard ISO 8301. The sample is also
subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standard, is 125 kPa.

Example 2 (not according to the invention, Luzenac® talc and no Carbon Black)

Expandable beads are produced with the same conditions as described in Example 1, except that the initial mixture contains 99 parts of polystyrene (melt index 11.2, following DIN ISO 1133) and 1 part of talc from Luzenac®, having a mean diameter of 10.5 μm and BET surface area of 3.8 m²/g. The board obtained has a density of 2.14 g/l. After at least 30 ageing days, the measured thermal conductivity of this panel is 0.0355 W/mK according to standard ISO 8301. The sample is also subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standard, is 135 kPa.

Example 3 (according to the invention, Luzenac® talc and Carbon Black)

Expandable beads are produced with the same conditions as described in Example 1, except that the initial mixture contains 96 parts of polystyrene (melt index 11.2, following DIN ISO 1133), 1 part of talc from Luzenac®, having a mean diameter of 10.5 μm and BET surface area of 3.8 m²/g, and 3 parts of carbon black, characterized by BET surface area of 770 m²/g. The board obtained has a density of 19.3 g/l. After at least 30 ageing days, the measured thermal conductivity of this panel is 0.0310 W/mK according to standard ISO 8301. The sample is also subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standard, is 121 kPa.

Example 4 (not according to the invention, Finntalc® and Carbon Black)

Expandable beads are produced with the same conditions as described in Example 1, except that the initial mixture contains 96.5 parts of polystyrene (melt index 11.2, following DIN ISO 1133), 1 part of talc from Finntalc®, having a mean diameter of 5 μm and BET surface area of 6 m²/g, and 2.5 parts of...
carbon black, characterized by BET surface area of 70 m²/g. The board obtained has a density of 21.1 g/l. After at least 30 ageing days, the measured thermal conductivity of this panel is 0.032 W/mK according to standard ISO 8301. The sample is also subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standard, is 117 kPa.

Example 5 (not according to the invention, Finntalc® and Carbon Black)

Expandable beads are produced with the same conditions as described in Example 1, except that the initial mixture contains 94 parts of polystyrene (melt index 11.2, following DIN ISO 1133), 1 part of talc from Finntalc®, having a mean diameter of 5 μm and BET surface area of 6 m²/g, and 5 parts of carbon black, characterized by BET surface area of 70 m²/g. The board obtained has a density of 22.2 g/l. After at least 30 ageing days, the measured thermal conductivity of this panel is 0.0309 W/mK according to standard ISO 8301. The sample is also subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standard, is 110 kPa.

Example 6 (not according to the invention, Jetfine® and Carbon Black)

Expandable beads are produced with the same conditions as described in Example 1, except that the initial mixture contains 96 parts of polystyrene (melt index 11.2, following DIN ISO 1133), 1 part of talc Jetfine®, having a mean diameter of 3.9 μm and BET surface area of 21 m²/g, and 3 parts of carbon black, characterized by BET surface area of 770 m²/g. The board obtained has a density of 20 g/l. After at least 30 ageing days, the measured thermal conductivity of this panel is 0.0330 W/mK according to standard ISO 8301. The sample is also subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standard, is 95 kPa.
Example 7 (not according to the invention, Jetfine® and no Carbon Black)

Expandable beads are produced with the same conditions as described in Example 1, except that the initial mixture contains 99 parts of polystyrene (melt index 11.2, following DIN ISO 1133) and 1 part of talc Jetfine, having a mean diameter of 3.9 µm and BET surface area of 21 m²/g. The board obtained has a density of 22 g/l. After at least 30 ageing days, the measured thermal conductivity of this panel is 0.0358 W/mK according to standart ISO 8301. The sample is also subjected to compression test. The strain value at 10% deformation, evaluated following EN826 standart, is 128kPa.

Comparison between various examples:

<table>
<thead>
<tr>
<th>Example</th>
<th>Talc mean diameter (D50)</th>
<th>Talc D95*</th>
<th>Carbon black spec. surf. Area (m²/g)</th>
<th>Carbon black (wt%)</th>
<th>Board density (g/l)</th>
<th>λ (W/mK)</th>
<th>10% compr. Strength (kPa)</th>
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<tr>
<td>1</td>
<td>10.5</td>
<td>30</td>
<td>70</td>
<td>2.5</td>
<td>20.8</td>
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<td>2</td>
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<td>0</td>
<td>21.4</td>
<td>0.0355</td>
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</tr>
<tr>
<td>3</td>
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<td>4</td>
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<td>0.0330</td>
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<tr>
<td>7</td>
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<td>8</td>
<td>-</td>
<td>0</td>
<td>22</td>
<td>0.0358</td>
<td>128</td>
</tr>
</tbody>
</table>

1 Measured with laser mastersizer according to standart ISO 13320-1.
2 Measured according to ASTM D3037-89.
3 Measurement performed following standart ISO 8301.
4 Measurement performed following standart EN 826.

The data in Table 1 show that the combination of talc, characterized by a mean diameter of 10.5 µm, with 2.5 or 3wt% of carbon black (Examples 1 and 3, respectively) leads to enhanced insulation properties compared to trials where talc of smaller particle size is combined with the same amount of carbon black, as described in Examples 4 and 6. There is thus a synergistic action between
carbon black and the particular talc grade used, i.e. talc with mean particle size above 8μm and D95 below 100μm, which leads to better insulation capability. In fact, the trial of Example 5 shows that with the use of finer talc (mean diameter of 5μm), the amount of carbon black must be doubled to reach similar insulation efficiency than the trial shown in Example 1, where the talc with mean particle size above 8μm and D95 below 100μm is advantageously used. It must also be noted that the use of a higher amount of carbon black (5%) has a detrimental impact on foam compression resistance (see Example 5). It is therefore advantageous to use the synergy between the particular talc grade mentioned and carbon black to avoid such drawback.

The synergy between carbon black and talc with mean particle size above 8μm and D95 below 100μm works either with carbon black grades of low or high specific surface area, as shown is Examples 1 and 3, where similar results are obtained with carbon black of respectively 70 and 770 m³/g specific surface area.
CLAIMS

1 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 talc having a mean diameter above about 8 μm, said mean diameter being measured by Laser Mastersizer according to standard ISO 13320-1, the BET of the talc being in the range 0.5-25 m²/g,
   d) 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,
   e) 0-20% by weight, calculated with respect to the polymer (a), of one or more fillers, other than talc and carbon black, homogeneously distributed in the polymeric matrix.

2 Expandable vinyl aromatic polymer according to claim 1 wherein it is in the form of beads or granules.

3 Expandable vinyl aromatic polymer according to any one of the preceding claims wherein the talc has a mean diameter above about 8 μm and under 100 μm.

4 Expandable vinyl aromatic polymer according to claim 3 wherein the talc has a mean diameter in the range 8-50 μm.

5 Expandable vinyl aromatic polymer according to claim 4 wherein the talc has a mean diameter in the range 8-30 μm.

6 Expandable vinyl aromatic polymer according to any one of claims 3 to 5 wherein the talc has a D(95) around 100 μm.
7 Expandable vinyl aromatic polymer according to claim 6 wherein the talc has a D(95) around 50 μm.

8 Expandable vinyl aromatic polymer according to claim 7 wherein the talc has a D(95) around 40 μm.

9 Expandable vinyl aromatic polymer according to claim 8 wherein the talc has a D(95) around 30 μm.

10 Expandable vinyl aromatic polymer according to any one of the preceding claims wherein the proportion of talc is from 0.5 to 2 wt%.

11 Expandable vinyl aromatic polymer according to any one of the preceding claims wherein the proportion of carbon black is from about 1 to about 5 wt%.

12 Expandable vinyl aromatic polymer according to any one of the preceding claims wherein the BET nitrogen surface area of the carbon black, measured according to ASTM D-3037/89, is ranging from 5 to 1000 m²/g.

13 Expandable vinyl aromatic polymer according to claim 12 wherein the BET nitrogen surface area of the carbon black, measured according to ASTM D-3037/89, is ranging from 50 to 1000 m²/g.

14 Expandable vinyl aromatic polymer according to any one of the preceding claims 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.
15 Expandable vinyl aromatic polymer according to claim 14 wherein the thermal conductivity $\lambda$ of the foamed material obtained from the expandable vinyl aromatic polymer is between about 32 and 33 mW/m°K.

16 Expandable vinyl aromatic polymer according to claim 15 wherein the thermal conductivity $\lambda$ of the foamed material obtained from the expandable vinyl aromatic polymer is between about 30 and 31 mW/m°K.

17 Use of the expandable vinyl aromatic polymer according to any one of the preceding claims to make expanded articles, in particular insulation boards.
A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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

Electronic database consulted during the international search (name of database and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>wo 2006/108672 A2 (POLIMERI EUROPA SPA [IT]; GHIDONI DARIO [IT]; PONTICI ELL0 ANTONIO [IT]) 19 October 2006 (2006-10-19) cited in the application on page 16, lines 13-18 examples 2-4 claims 1,7,8, 11</td>
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<td>EP 0 430 496 AI (CABOT PLASTICS BELGIUM [BE]) 5 June 1991 (1991-06-05) claims</td>
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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 document 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

*I* 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

*A* document member of the same patent family

Date of the actual completion of the international search: 23 September 2011
Date of mailing of the international search report: 29/09/2011

Authorized officer: Oudot, Rene

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
INTERNATIONAL SEARCH REPORT

International application No.
PCT/ EP2011/065347

Box No. I  Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claims Nos. 15, 16
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
   see FURTHER INFORMATION sheet PCT/ISA/210

3. [ ] Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [X] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. [X] As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. [X] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant’s protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[ ] No protest accompanied the payment of additional search fees.
Claims Nos.: 15, 16

The subject-matter described in claim 15 does not fall within the scope of claim 14 from which it depends. This inconsistency between claims 14 and 15 leads to doubt concerning the matter for which protection is sought, thereby rendering the claims unclear (Article 6 PCT). The same inconsistency also occurs between claims 15 and 16. As a consequence, claims 15 and 16 have not been searched.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter I procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.
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