

Title of the invention: Polyurethane/polyisocyanurate foam block of a thermal insulation body of a tank and its preparation process

[0001] A subject-matter of the invention is blocks of fibre-reinforced polyurethane (PUR) and/or polyisocyanurate (PIR) foams fitted into a thermal insulation body which have to exhibit, given their specific applications, very particular mechanical and thermal characteristics, while being as economical as possible to produce, said blocks of foams being used within a tank, integrated in a membrane structure (also called integrated tank) or self-supporting/semi-supporting of type A, B or C, serving to accommodate extremely cold fluids, called cryogenic fluids, such as in particular Liquefied Natural Gas (LNG) or Liquefied Petroleum Gas (LPG).

[0002] The present invention relates more particularly to a sealed and thermally insulating tank using such foams, to a ship equipped with at least one such tank, to a process of loading/unloading such a ship and to a transfer system for a liquid product contained in such a ship.

[0003] The present invention also relates to a process for the preparation of these blocks of foams from at least one polyisocyanate and at least one polyol.

[0004] Polyurethane PUR foam is a cellular insulator, composed of fine cells storing a gas which can have low thermal conductivity. PUR foam is used in a very large number of applications, such as the automotive industry, as flexible PUR foam, or in thermal insulation, as rigid PUR foam. The formation of polyurethane-type foams is well known to a person skilled in the art. Its formation involves a multicomponent reaction between a polyol (compound carrying at least two hydroxyl groups), a polyisocyanate (compound carrying at least two isocyanate —NCO functional groups) and an expanding agent, also designated by the expression "blowing agent". This condensation reaction is in particular catalysed by compounds having basic and/or nucleophilic natures, such as tertiary amines or metal-carboxylate coordination complexes, such as tin or bismuth salts. The polyols commonly used in the manufacture of PUR foams are polyether polyols

or polyester polyols. Thus, a large number of compounds are necessary for the formation of PUR foam.

[0005] Polyisocyanurate (PIR) and polyurethane/polyisocyanurate (PUR-PIR) foams are also used in the building industry (construction/renovation) and exhibit the advantage of providing better fire-resistant properties as well as a greater compressive strength than PURs. The process for the formation of these foams is similar to the process for the formation of PUR foams. This is because to obtain PUR, PIR and PUR-PIR foams depends on the isocyanate/polyol ratio.

[0006] PUR, PIR and PUR-PIR foams are well known to a person skilled in the art; nevertheless, the addition of fibres involves specific technical problems, such as the need for good impregnation of the fibres, so much so that such foams exhibiting, at least locally, a relatively substantial content of fibres currently do not exist.

[0007] In point of fact, in the technical field specific to the use of such foams for a thermal insulation body of a tank, said body is subjected to very cold temperatures on its face exposed to the internal space of the tank, for example approximately -160°C in the case of LNG, whereas the external space of the tank, conventionally the hull of a ship, often exhibits a much greater environmental temperature, at least equal to, indeed even very much greater than, that of the ambient air or of the sea considered in the vicinity of 20°C .

[0008] Thus, the PUR, PIR and PUR-PIR foam block used in the thermal insulation body of such a tank undergoes, during the loading of the extremely cold fluid, called cryogenic fluid, a very significant temperature gradient in its thickness which causes phenomena of heterogeneous contraction of the foam block. This heterogeneous contraction of the foam block induces a bimetal effect which results in a sagging of the block along its longitudinal axis - the two ends having a tendency to lift up significantly - due to the non-uniform contraction of the block in the thickness. As the foam block is conventionally fixed mechanically or by adhesive bonding, this sagging critically reduces the exploitable mechanical properties of the PUR, PIR and PUR-PIR foam block, indeed even locally the thermal properties of the thermal insulation body (integrating the foam block according to the invention).

[0009] This phenomenon of bimetal effect or of sagging of the foam block has been accentuated in recent years due to the fact that the thickness of the foam blocks forming the thermal insulation has been increased, sometimes very significantly, for such tanks containing a cryogenic liquid. In particular, when these tanks comprise a double layer of thermal insulation, conventionally denoted “primary” and “secondary” layer (this said secondary layer being located furthest from the cryogenic liquid), the thickness E of the secondary thermal insulation has increased very significantly in recent structures, for example of the Mark type. Thus, the thickness E of the secondary thermal insulation layer has changed from 170 mm (millimetres) in a Mark III structure to 300 mm in a Mark III Flex structure and then to 380 mm in a Mark III Flex+ structure.

[0010] This bimetal effect or this sagging of the secondary thermal insulation layer has particularly harmful structural consequences on the thermal insulation body, of a sealed and thermally insulating tank, when the thickness of this secondary layer increases appreciably relative to the thickness of the primary thermal insulation layer.

[0011] Structures such as those described in the documents FR 2 882 756, WO 2017/202667 and JP 2005225945 are known, but none provides a satisfactory solution to the particular technical problems set out above.

[0012] At the present time, there does not exist a polyurethane and/or polyisocyanurate foam block, fibre-reinforced or non-fibre-reinforced, which makes it possible to respond effectively to this problem, in other words a PUR, PIR and PUR-PIR foam block exhibiting a thermomechanical stability between its initial state (in a homogeneous thermal environment) and its service state, namely when it is used in a tank containing a cryogenic liquid.

[0013] To overcome this problem of distortions or of geometric instability between these two states of the foam block, special-shaped foam blocks, in particular integrating notches, or of reduced dimensions, are currently produced, so as to limit the thermal distortion of each of the (small) volume elements or (small) foam blocks within an acceptable range. The need to produce these small foam blocks entails a large number of operations for cutting, positioning and joining them to one another, which represents substantial costs. Furthermore, the presence of

numerous expansion joints very significantly degrades the thermal performance qualities of the tank.

[0014] In addition, in certain embodiments of the bodies for the thermal insulation of tanks, the existing foam blocks are placed in a container, typically a box, made of wood plywood, for example made of fir, birch or beech. In these embodiments, the lower and upper faces of the foam block are adhesively bonded to the internal surface of the container so as to correctly position the blocks. However, during cooling, that is to say when the tank is in condition of use/service (the tank containing a cryogenic liquid), the central part or part at the heart of the foam block then contracts significantly, whereas the upper and lower zones of the block are constrained by their adhesive bonding to the internal walls of the container. Due to the fact that the thermal contraction coefficient of the foam is much higher than that of the plywood, this phenomenon results in a distortion of the shape of the block, when it is in condition of use/service, the side ends of which exhibit a profile substantially in an arc, with the shape of an arc) or counter-arc (, thus creating empty spaces between the foam block and its adjacent neighbours or the side walls of the plywood container. These empty foam spaces can result in the appearance of unwanted phenomena of thermal convection because they damage in proportion the thermal insulation qualities of the insulation body of the tank.

[0015] The present invention also intends to provide a solution to this problem specific to certain modes of use of the polyurethane (PUR) and/or polyisocyanurate (PIR) foam block.

[0016] It is in this context that the Applicant Company has succeeded in developing a process for the production of polyurethane (PUR) and/or polyisocyanurate (PIR) foams containing fibres in significant amount making possible both the production of a fibre-reinforced foam exhibiting excellent mechanical and thermal properties, while retaining, over the entire foam block, the integrity of its shape/structure, when the block is in condition of use, that is to say in a very different thermal environment between its two, upper and lower, faces.

[0017] The present invention thus intends to overcome the shortcomings of the state of the art by providing a particularly effective solution for industrially obtaining a

fibre-reinforced PUR/PIR foam, possibly of (very) large dimensions, the mechanical/thermal properties of which are optimal and at least substantially similar between its initial state - at rest, the foam block being in a substantially homogeneous thermal environment - and its state of use/service in which the foam block is in a very heterogeneous thermal environment, the difference in temperature between its upper face (content side of the tank) and its lower face (side outside the tank), considered along the thickness of the block, being at least equal to 80°C, indeed even at least equal to 100°C.

[0018] There has been discovered by the Applicant Company, after various studies and analyses, a fibre-reinforced polyurethane (PUR) and/or polyisocyanurate (PIR) foam block, and its preparation, capable of solving the technical problems associated with the very significant modification of the thermal environment of the PUR/PIR foam block during its use.

[0019] Advantageously, it is also possible, according to a preferred embodiment, to very significantly reduce the production cost of such a fibre-reinforced foam by very significantly reducing the loss of material from the foam block, conventionally necessary according to the prior art during cutting of the foam block in order to obtain the desired (parallelepipedal) dimensions.

[0020] Thus, the present invention relates to a fibre-reinforced polyurethane/polyisocyanurate foam block of a thermal insulation body of a sealed and thermally insulating tank, the density of the fibre-reinforced foam block being between 30 and 300 kg/m³, the fibre-reinforced polyurethane/polyisocyanurate foam block exhibiting a mean density of fibres T_f of between 1% and 60% by weight of fibres, and exhibiting a width L of at least ten centimetres, advantageously of between 10 and 500 centimetres, and a thickness E, from the lower face of said block up to its upper face, of at least ten centimetres, advantageously of between 10 and 100 centimetres, the fibre-reinforced polyurethane/polyisocyanurate foam block being composed of cells storing a gas, advantageously having low thermal conductivity.

[0021] The fibre-reinforced polyurethane/polyisocyanurate foam block is composed, to at least 95% by weight of said block, of cells storing a gas, advantageously

having low thermal conductivity, of the polyurethane/polyisocyanurate foam and of the fibres.

[0022] The foam block according to the invention is composed (solely) of the polyurethane (PUR) and/or polyisocyanurate (PIR) foam, of the fibres, which are preferably of a single nature, such as glass fibres, and of the gas trapped in the cells, and optionally of a minimal portion, for example, of fillers or of other functional adjuvants, i.e. for the latter a maximum of 5% by weight, indeed even preferably a maximum of 2% or of 1% by weight, of the foam block according to the invention (the fibre-reinforced polyurethane/polyisocyanurate foam block is then composed, to at least 98% or 99% by weight of said block, of cells storing a gas, of the polyurethane/polyisocyanurate foam and of the fibres). This is because the foam block according to the invention is obtained:

- in a single operation for preparation of the foam (mixing of the reaction ingredients, optionally of the fillers/adjuvants, with the fibres), preferably in a double band laminator (DBL);
- in the above operation supplemented by a cutting operation, conventionally of the upper face of the block, for the adhesive bonding of a peripheral zone as described below.

[0023] The foam block according to the invention is characterized in that:

- the foam block comprises, along its thickness E, two peripheral zones, one said to be upper, extending from the upper face of the block, and the other said to be lower, extending from the lower face of the block, these two zones each representing at most 20% along the thickness E of the block and being separated by a zone said to be intermediate; and
- the peripheral zones, upper and lower, respectively exhibit a density of fibres $T_{f \text{ upp.}}$ and $T_{f \text{ low.}}$ such that: $2/3 \leq (T_{f \text{ upp.}} / T_{f \text{ low.}}) \leq 3/2$; and
- the density of fibres $T_{f \text{ int.}}$ of the intermediate zone is less than the densities of the peripheral zones, i.e.: $T_{f \text{ int.}} < T_{f \text{ upp.}}$ and $T_{f \text{ int.}} < T_{f \text{ low.}}$.

[0024] The present invention intends to apply in particular, but not exclusively, to the case where the foam block is installed at the secondary layer, conventionally

designated the "secondary". In this application, preferably, the foam block exhibits a thickness of at least twenty-five (25) centimetres (cm), indeed even more preferably of at least 30 or 35 cm.

[0025] The terms "upper" and "lower" are understood to mean a sense or a direction given to the foam block once the latter is in position in the thermal insulation body of a tank. Thus, the upper part or face of the foam block is that located near or on the side of the container of the tank, when the thermal insulation body is positioned in the tank, whereas the lower part or face of the foam block is that located towards or on the side of the outside of the tank, that is to say in particular towards the hull of a ship in the case where the tank is integrated or mounted in a ship for the transportation and/or storage of cryogenic liquid.

[0026] It is thus understood that, during the manufacture or the preparation of the foam block, these notions or terms of "upper" or "lower" do not yet have a meaning since the foam block is not yet installed in the thermal insulation body of a tank. In other words, it will be perfectly possible to prepare the foam blocks according to the invention so that they are obtained, at the outlet of their preparation/manufacturing line, with a position opposite to that of their final fitting/assembly in the thermal insulation body of a tank.

[0027] The expression "along its thickness E" is understood to mean, with regard to the various peripheral, intermediate, indeed even median/central, zones as described subsequently, the fact that these zones each represent a volume of the fibre-reinforced polyurethane (PUR) and/or polyisocyanurate (PIR) foam block considered by taking a cut along the section of thickness E, as represented in particular in Figures 3 and 4, in order to form a block portion exhibiting the same width L and the same length - only the thickness being different - as the foam block according to the invention.

[0028] The expression "cells storing a gas" is understood to mean the fact that the polyurethane/polyisocyanurate foam exhibits closed cells enclosing a gas, preferably exhibiting a low thermal conductivity, originating from a gas injected during a stage of nucleation of the reaction mixture or originating, directly or indirectly, from the chemical or physical blowing agent.

[0029] The term "fibre(s)" or the expression "fibre reinforcement" is understood to mean the fact that the fibres can be provided in two distinct forms:

- either in the form of at least one fabric of fibres, in which the fibres are perfectly aligned along at least one direction, in other words the fibres exhibit at least one favoured direction of fibres. The expression "fabric of fibres" refers per se to a clear technical definition known to a person skilled in the art,
- or in the form of at least one mat of fibres, in which the fibres do not exhibit a defined orientation, in other words these fibres are oriented isotropically essentially along the main plane of the layer of the mat. Again, the expression "mat of fibres" refers per se to a clear technical definition known to a person skilled in the art.

[0030] According to one embodiment, the expression "a gas (advantageously) having low thermal conductivity" is understood to mean the gas originating from the blowing agent, either by chemical reaction of the latter when this agent is said to be "chemical", conventionally carbon dioxide (CO₂) when the chemical blowing agent consists of water, or by a physical blowing agent, such as, for example, molecular nitrogen (N₂), molecular oxygen (O₂), carbon dioxide, hydrocarbons, chlorofluorocarbons, hydrochlorocarbons, hydrofluorocarbons, hydrochlorofluorocarbons, and their mixtures, and also the corresponding alkyl ethers. The physical blowing agents, such as molecular nitrogen N₂, molecular oxygen O₂ or CO₂, are in the gas form. These gases are dispersed or dissolved in the liquid mass of copolymer, for example under high pressure using a static mixer. By depressurizing the system, the nucleation and the growth of bubbles generate a cellular structure.

[0031] The expression "mean density T_f of fibres" is understood to mean the density of fibres expressed as weight of fibres with respect to the total weight of the fibre-reinforced foam block, without taking into consideration the variable local percentages (within the block) of these fibres.

[0032] Thus, the fibre-reinforced foam block is compatible with use in tanks integrated into a supporting structure but also self-supporting/semi-supporting tanks of type A, B or C according to (IMO) IGC regulations, that is to say as

external insulation associated with self-supporting tanks for the storage and/or transportation of very cold liquid, such as LNG or LPG.

[0033] Finally, the thermal properties of the fibre-reinforced foam block are at least equal to those of the non-fibre-reinforced foam blocks of the state of the art; more precisely, the foam block exhibits, in the thickness E, a thermal conductivity of less than 30 mW/m.K (milliwatt per metre per Kelvin), i.e. 0.03 W/m.K, preferably of less than 25 mW/m.K, more preferably still of less than 23 mW/m.K, measured at 20°C, and a thermal conductivity of less than 20 mW/m.K when the upper face of the block is at -160°C, the foam block then being in condition of use, the tank in which it is housed containing LNG.

[0034] Other advantageous characteristics of the invention are briefly presented below:

[0035] Preferably, the two abovesaid peripheral zones each represent at most 10% along the thickness E of the block.

[0036] According to a preferred embodiment of the invention, the intermediate zone comprises a central zone, surrounded by two median zones, representing at most 20% along the thickness E, preferably at most 10% along the thickness E, the density of fibres $T_{f\text{ cen.}}$ of this central zone being at least one and a half times greater than that of the median zones $T_{f\text{ med.}}$, i.e. $T_{f\text{ cen.}} \geq 1.5 T_{f\text{ med.}}$.

[0037] This embodiment is presented in the appended Figure 4 and makes it possible to address more specifically the problem of the shrinkage of the foam at the heart, that is to say at the central zone, while avoiding the bimetal phenomenon by virtue of the peripheral zones of higher density of fibres.

[0038] According to another characteristic specific to this embodiment, the density of fibres $T_{f\text{ cen.}}$ of the central zone is defined with respect to the density of fibres $T_{f\text{ upp.}}$ and $T_{f\text{ low.}}$ of the peripheral zones, upper and lower, such that $0.5 \leq T_{f\text{ cen.}} / (T_{f\text{ low.}} \text{ or } T_{f\text{ upp.}}) \leq 2$.

[0039] Preferably, the density of the fibre-reinforced foam block is between 50 and 250 kg/m³, preferably between 90 and 210 kg/m³. It should be noted here that, for the foam blocks used in a tank of self-supporting type (types B, C) or semi-supporting type (type A), the density range of the fibre-reinforced foam block is

preferably located between 30 and 90 kg/m³, whereas, in the case of a membrane, the still preferred density range is located between 90 and 210 kg/m³.

[0040] Advantageously, at least 60%, preferably at least 80%, of the abovesaid cells storing a gas, advantageously having low thermal conductivity, exhibit a shape elongated or stretched along an axis parallel to the axis of a thickness E of the fibre-reinforced polyurethane/polyisocyanurate foam block.

[0041] According to one possibility offered by the invention, the fibres consist of glass fibre or of basalt fibre, preferably of glass fibre.

[0042] Preferably, the fibres are long to continuous fibres.

[0043] The expression "the fibres being long to continuous" (or "long to continuous fibres") is understood to mean the fact that the fibres, or if appropriate an agglomeration of an assembly of fibres (fibres adhesively bonded or fixed to one another), all - or at least 90% of the fibres, considered alone or agglomerated forming the equivalent of a single fibre, by total weight of said fibres - exhibit a length of at least five (5) centimetres (cm).

[0044] Preferably, the mean density of fibres T_f is between 2% and 25%, preferably 6% and 20%.

[0045] Preferably, the foam block according to the invention is provided in a parallelepipedal or cubic shape.

[0046] It is clearly understood here that this foam block, exhibiting such a parallelepipedal or cubic shape, can exhibit one or more local protuberances, for example in the form of the anchorings presented in the continuation, or also on the contrary empty or hollow portions, while still being able to be described as of parallelepipedal or cubic shape.

[0047] Advantageously, the lower face and/or the upper face of said block exhibit(s) anchorings capable of engaging with an engaging means of the thermal insulation body (not shown in the appended figures) in order to fix or to anchor the foam block to said body, preferably said anchorings being made of a different material from the foam or from the fibres.

[0048] These anchorings are advantageously metallic elements (these anchorings can also be made of plastic/polymers or composites combining one or more polymers with ceramic and/or metallic materials), for example exhibiting an L-shaped attachment lug, or a slot/opening, for example L-shaped, so as to engage with an element or a part of the thermal insulation body enclosing or housing the fibre-reinforced foam block. This part of the thermal insulation body can consist of a metallic membrane for sealing the container, for example made of stainless steel or based on manganese, in the case of a membrane tank, or of a vapour barrier (having the technical function of ensuring a seal to the surrounding environment outside the tank) in the case of self-supporting or semi-supporting tanks of the type A, B or C. In one possibility offered by the invention, this element or this part of the thermal insulation body (in a membrane tank) exhibits a notch or analogue intended to allow engagement with a portion of an anchoring for the mechanical maintenance or retention of the fibre-reinforced foam block with the other thermal insulation block elements. Of course, these anchorings can also have the function of anchoring the foam block to the hull, in the case of a membrane tank, or to the self-supporting structure, in the case of a self-supporting tank of the type A, B or C, it being understood that these anchorings are then those present on the lower face of the foam block.

[0049] In the context of the present invention, these anchorings are inserted at least in part into the fibre reinforcements, those constituting the lower or upper layer of the fibre reinforcement stack, so as to make it possible to locate them on the faces once the foam block has been prepared/finished, without, however, protruding from said face.

[0050] Advantageously, the fibre-reinforced foam block according to the invention comprises a flame retardant in a proportion of between 0.1% and 5% by weight, of the organophosphorus type, advantageously triethyl phosphate (TEP), tris(2-chloroisopropyl) phosphate (TCPP), tris(1,3-dichloroisopropyl) phosphate (TDCP), tris(2-chloroethyl) phosphate or tris(2,3-dibromopropyl) phosphate, or a mixture of these, or of the inorganic flame retardant type, advantageously red phosphorus, expandable graphite, an aluminium oxide hydrate, an antimony

trioxide, an arsenic oxide, an ammonium polyphosphate, a calcium sulfate or cyanuric acid derivatives, or a mixture of these.

[0051] The invention also relates to a sealed and thermally insulating tank integrated in a supporting structure, said tank consisting of:

- a tank integrated in a supporting structure comprising a sealed and thermally insulating tank comprising at least one sealed metal membrane composed of a plurality of metal strakes or metal plates which can comprise corrugations and a thermally insulating body comprising at least one thermally insulating barrier adjacent to said membrane, or
- a tank of type A, B or C according to the definition given by the IGC Code comprising at least one thermally insulating body.

[0052] The tank according to the invention is characterized in that the thermally insulating body comprises a plurality of fibre-reinforced polyurethane/polyisocyanurate foam blocks as described briefly above.

[0053] The expression "IGC Code" is understood to mean the "International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk", well known to a person skilled in the art, like the types B and C of tanks cited.

[0054] It should be noted that it is possible, in particular in the IGC Code, to use the expression "membrane tank" instead of the expression "integrated tank" to denote one and the same category of tanks, equipping in particular tankers transporting and/or storing at least partly liquefied gas. The "membrane tanks" are integrated in a supporting structure, whereas the tanks of types A, B or C are said to be self-supporting or semi-supporting (type A specifically).

[0055] Finally, the invention also relates to a ship for the transportation of a cold liquid product, the ship comprising at least one hull and one sealed and thermally insulating tank as described briefly above, positioned in the hull or mounted on said ship when said tank is of the type A, B or C according to the definition given by the IGC Code.

[0056] Advantageously, in the case where the tank consists of a tank integrated in a supporting structure (membrane tank), such a ship comprises at least one sealed

and insulating tank as described above, said tank comprising two successive sealing barriers, one, primary, in contact with a product contained in the tank and the other, secondary, positioned between the primary barrier and a supporting structure, preferably formed by at least a part of the walls of the ship, these two sealing barriers being alternated with two thermally insulating barriers or a single thermally insulating barrier being positioned between the primary barrier and the supporting structure.

[0057] Such tanks are conventionally designated as integrated tanks according to the Code of the International Maritime Organization (IMO), such as, for example, tanks of type NO, including types NO 96[®], NO 96L03[®], NO 96L03+ or NO 96 Max, or Mark III[®], Mark III[®] Flex or Flex+, preferably tanks of type NO.

[0058] Preferably, the tank, said to be of membrane type or of type A, B or C, contains a liquefied natural gas (LNG) or a liquefied gas (LG).

[0059] The invention also relates to a transfer system for a cold liquid product, the system comprising a ship as defined above, insulated pipes arranged so as to connect the tank installed in the hull of the ship to a floating or onshore storage unit and a pump for driving a flow of cold liquid product through the insulated pipes from or to the floating or onshore storage unit to or from the ship.

[0060] The invention also relates to a process for loading or unloading a ship as defined above, in which a cold liquid product is conveyed through insulated pipes from or to a floating or onshore storage unit to or from the ship.

[0061] The present invention also relates to the process for the preparation of a fibre-reinforced polyurethane/polyisocyanurate foam block of a thermal insulation body of a sealed and thermally insulating tank as described briefly above, said preparation process being characterized in that it comprises the stages:

- a) of mixing chemical components necessary for obtaining a polyurethane/polyisocyanurate foam, said components comprising reactants for obtaining polyurethane/polyisocyanurate, optionally at least one reaction catalyst, optionally at least one emulsifier, and at least one blowing agent,
- b) of impregnation, by gravitational flow of the abovesaid mixture of chemical components, of a plurality of fibre reinforcements, said fibre reinforcements being

positioned in superimposed layers and exhibiting variable densities of fibres, in which the fibre reinforcements extend essentially along a direction perpendicular to the direction of said gravitational flow,

c) of formation and of expansion of the fibre-reinforced polyurethane/polyisocyanurate foam,

in which the expansion of the fibre-reinforced polyurethane/polyisocyanurate foam is said to be by free expansion, i.e. without the constraint exerted by a volume of closed section on at least one face, preferably the upper face, or

in which the expansion of the fibre-reinforced polyurethane/polyisocyanurate foam is physically constrained by walls of a double belt laminator, preferably is physically constrained by the walls of a double belt laminator forming a tunnel of rectangular section with a distance between the walls positioned laterally equal to L and a distance between the walls positioned horizontally equal to E, thus enclosing the expanding fibre-reinforced foam so as to obtain the abovesaid fibre-reinforced polyurethane/polyisocyanurate foam block.

[0062] The expression "cream time" is understood to mean the time necessary, counting from the mixing of the chemical components, for the latter to begin the polymerization reactions and consequently for the mixture of components to start the expansion and crosslinking stage c) (= formation of the fibre-reinforced PUR/PIR foam). This cream time is a piece of information well known to a person skilled in the art. In other words, the cream time is the time elapsed until the mixture turns white under the action of the nucleation of the bubbles (cells storing a gas) and of the expansion of the foam after mixing of the chemical components at ambient temperature. The cream time can be determined visually or using an ultrasonic sensor detecting a variation in thickness reflecting the formation of foam.

[0063] The expression "the fibre reinforcements extend essentially along a direction perpendicular to the direction of the gravitational flow of the mixture of chemical components" is understood to mean the fact that these fibre reinforcements are provided in the form of a layer of low thickness extending, during the impregnation stage b), along a plane perpendicular to the direction of flow of said

mixture of components. Thus, as can be seen in Figure 1, the plurality of fibre reinforcements, exhibiting a width L and positioned in superimposed layers, are entrained in a longitudinal direction I, while the mixture of chemical components is deposited on the fibre reinforcements from a dispenser allowing/making possible the gravitational flow of the mixture of chemical components. In other words, the mixture of chemical components, optionally exiting under pressure from the dispenser, falls under the effect at least of its own weight onto the stacked layers of fibres, thus impregnating these fibre reinforcements from the upper layer down to the lower layer.

[0064] According to one embodiment of the invention, in the case where the expansion of stage c) is carried out by free expansion, one at least of the peripheral zones, preferably the upper zone, is formed independently and fixed, once a cutout on at least the free expansion face has been carried out, to form said foam block.

[0065] The use, in the composition according to the invention, of a chemical blowing agent can be coupled with that of a physical blowing agent. In this case, the physical blowing agent is preferably mixed in liquid or supercritical form with the foamable (co)polymer composition and then converted to the gas phase during the stage of expansion of the PUR/PIR foam.

[0066] Chemical and physical blowing agents are well known to a person skilled in the art, who chooses all, in the appropriate amounts, depending on the PUR/PIR foam which he wishes to obtain.

[0067] The term polyols is understood to mean any carbon-based structure carrying at least two OH groups.

[0068] As the PUR, PIR and PUR-PIR foams are obtained depending on the isocyanate/polyol ratio, a PUR, PIR or PUR-PIR foam will be obtained according to this ratio. When the ratio of a polyol component to an isocyanate component is:

- between 1:1 and 1:1.3, a polyurethane PUR foam will be obtained,
- between 1:1.3 and 1:1.8, a polyurethane-polyisocyanurate PUR-PIR foam will be obtained,

- between 1:1.8 and 1:2.8, a polyisocyanurate PIR foam will be obtained.

[0069] Polyisocyanates appropriate for the formation of PUR, PIR and PUR-PIR foam are known to a person skilled in the art and comprise, for example, aromatic, aliphatic, cycloaliphatic and arylaliphatic polyisocyanates and their mixtures, advantageously aromatic polyisocyanates.

[0070] Examples of polyisocyanates appropriate within the scope of the present invention include aromatic isocyanates, such as the 4,4'-, 2,4'- and 2,2'- isomers of diphenylmethane diisocyanate (MDI), any compound resulting from the polymerization of these isomers, toluene 2,4- and 2,6-diisocyanate (TDI), m- and p-phenylene diisocyanate, naphthalene 1,5-diisocyanate; aliphatic, cycloaliphatic or arylaliphatic isocyanates, such as 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 4,4'-dicyclohexylmethane diisocyanate (H12MDI), 1,4-cyclohexane diisocyanate (CHDI), bis(isocyanatomethyl)cyclohexane (H6XDI, DDI) and tetramethoxylylene diisocyanate (TMXDI). It is also possible to use any mixtures of these diisocyanates. Advantageously, the polyisocyanates are the 4,4'-, 2,4'- and 2,2'- isomers of diphenylmethane diisocyanate (MDI).

[0071] In general, it is known, during the formation of PUR, PIR or PUR-PIR foams, to add, to the mixture comprising the polyol, the polyisocyanate and blowing agent, a reaction catalyst which can, for example, be chosen from tertiary amines, such as N,N-dimethylcyclohexylamine or N,N-dimethylbenzylamine, or from organometallic compounds based on bismuth, potassium or tin.

[0072] According to a preferred embodiment of the invention, advantageously, the positioning of the walls of the tunnel of the double belt laminator (DBL) is defined so that the constraint on the expansion of the fibre-reinforced polyurethane/polyisocyanurate foam results in a volume of fibre-reinforced polyurethane/polyisocyanurate foam, at the outlet of the double belt laminator, representing between 85% and 99%, preferably between 90% and 99%, of the expansion volume of this same fibre-reinforced polyurethane/polyisocyanurate foam in the case of free expansion, without the constraint of the walls of such a double belt laminator. In this case, a foam is obtained, the cells of which, of ovoid shape, are preferentially oriented along the axis E, resulting in advantageous

properties of resistance to crushing along this direction E (measured according to Standard ISO 844), combined with the properties already described in the plane normal to this axis E. Tests and experiments have been carried out by the Applicant Company to determine the broad and preferred ranges mentioned above but are not presented here for the sake of clarity and conciseness.

[0073] By virtue of the abovesaid specific parametrizing of the constraint on the expansion of the fibre-reinforced PUR/PIR foam in a DBL, on the one hand, a fibre-reinforced PUR/PIR foam block is obtained in which at least 60%, generally more than 80%, indeed even more than 90%, of the cells storing a gas having low thermal conductivity extend longitudinally along an axis parallel to the axis of the thickness E of the foam block and a contribution is made, besides the specific choices related to the characteristics of the fibre reinforcements and to the viscosity of the mixture of chemical components, to a perfect homogeneity of the fibre-reinforced foam block. These two characteristics - orientation of the cells and homogeneity of the content T_f of fibres in the block along the different, peripheral or central, zones - make it possible to obtain a fibre-reinforced foam block exhibiting excellent mechanical properties along the thickness E (compressive strength) and in a plane normal to the direction of the thickness (tensile strength and low coefficient of thermal contraction).

[0074] The elongated or stretched shape can be defined by a shape extended in length, that is to say that it comprises one dimension: its length, which is greater than its other dimensions (width and thickness).

[0075] According to another embodiment offered by the invention, the expansion of the fibre-reinforced polyurethane/polyisocyanurate foam is free, i.e. without the constraint exerted by a volume of closed section.

[0076] In this instance, unlike the embodiment of the preparation according to the invention using a DBL, the preparation of the fibre-reinforced polyurethane/polyisocyanurate foam is said to be by "free expansion" in so far as the expansion of the fibre-reinforced foam is not constrained on at least one side or on at least one face of expansion so that the swelling of the fibre-reinforced foam is free on this side or this face, unlike a mould defining a finite volume. Conventionally, a free expansion is carried out by omitting the (top) cover while

the side walls prevent the foam from overflowing over the sides and the foam naturally swells upward, possibly beyond the upper ends of these side walls.

[0077] Advantageously, following the stage of free expansion of the fibre-reinforced polyurethane/polyisocyanurate foam, said fibre-reinforced foam is cut in order to obtain the abovesaid fibre-reinforced polyurethane/polyisocyanurate foam block.

[0078] According to one possibility offered by the invention, not represented in the appended figures, just after the stage of impregnation of the fibre reinforcements, there is applied, to the mixture of components and of at least the blowing agent impregnating the fibres, a system for application of pressure (which can, for example, be a system of rollers, of the type designated "nip roll") intended to apply a pressure to the upper face of the assembly consisting of the abovesaid mixture and of the fibres. This pressure system makes it possible, on the one hand, to plan the upper face of this assembly and, by the pressure exerted on the assembly, contributes to promoting the impregnation of the fibres in the abovesaid mixture. This pressure system can consist of a single or a double roller, the relative positions of which, above the liquid assembly, and possibly below the foam support, are adjusted in such a way that the liquid assembly is forced to spread out perfectly uniformly. Thus, on doing this, an equivalent amount of the liquid assembly is obtained at any point of the section defined by the spacing between the two rollers or upper roller and conveyor belt. In other words, the main object of this pressure system is to complement the liquid dispensing device in that it contributes to rendering the liquid assembly uniform, in thickness/width, before the main part of its expansion.

[0079] Preferably, the dynamic viscosity η of the abovesaid mixture of components is between 30 mPa.s and 3000 mPa.s (or 0.03 Pa.s and 3 Pa.s), preferably between 50 mPa.s and 1500 mPa.s (or 0.05 Pa.s and 1.5 Pa.s), at ambient temperature (25°C) and atmospheric pressure (1015 mPa).

[0080] The dynamic viscosity of the mixture of components can be determined using a viscometer, for example of Brookfield type, or a rheometer, for example using Standard ISO 2555.

[0081] In general, it is clearly understood that the subject-matter of the present invention uses materials/products accessible or available on the market, so that their properties, in particular those relating to their densities or (dynamic) viscosities, are available in the specifications relating to the materials/products under consideration.

[0082] Advantageously, at least 60% of the abovesaid cells storing a gas, advantageously having low thermal conductivity, exhibit a shape elongated or stretched along an axis parallel to the axis of a thickness E of the fibre-reinforced polyurethane/polyisocyanurate foam block.

[0083] More advantageously still, at least 80%, preferably at least 90%, of the abovesaid cells storing a gas, advantageously having low thermal conductivity, exhibit a shape elongated or stretched along an axis parallel to the axis of a thickness E of the fibre-reinforced polyurethane/polyisocyanurate foam block.

[0084] It is clearly understood here that this characteristic related to the elongated shape of the cells storing a gas, advantageously having low thermal conductivity, and their content/proportion in the block according to the invention, is more particularly directed in the context of the implementation of the preparation process with a DBL, but it is absolutely not limited to this scenario. This is because, in the case of a free expansion, more specifically when there is no upper wall/cover restricting the expansion of the fibre-reinforced foam, such a preferential orientation of the cells storing a gas, advantageously having low thermal conductivity, is also obtained.

[0085] Preferably, the fibres (fibre reinforcements) are positioned over an entire width L and stage b) of impregnation of the fibres by the mixture of components, in order to obtain a fibre-reinforced polyurethane/polyisocyanurate foam, and of a blowing agent is carried out via a controlled liquid dispenser, simultaneously over the entire width L.

[0086] The term "simultaneously" is understood to mean the fact that the liquid mixture (reactants and at least the blowing agent) reaches the fibres, over a section of width L, at the same time all along this section so that the impregnation of the different fibre reinforcements begins or is carried out, along the thickness

(or the height) of the foam block and for one and the same section of width, at the same time or at the same rate.

[0087] Advantageously, the blowing agent consists of a physical and/or chemical blowing agent, preferably a combination of the two types.

[0088] Preferentially, the physical blowing agent is chosen from alkanes and cycloalkanes having at least 4 carbon atoms, dialkyl ethers, esters, ketones, acetals, fluoroalkanes, fluoroolefins having between 1 and 8 carbon atoms and tetraalkylsilanes having between 1 and 3 carbon atoms in the alkyl chain, in particular tetramethylsilane, or a mixture of these.

[0089] Under this assumption, as example of compounds, it may be a matter of propane, n-butane, isobutane, cyclobutane, n-pentane, isopentane, cyclopentane, cyclohexane, dimethyl ether, methyl ethyl ether, methyl butyl ether, methyl formate, acetone and fluoroalkanes; the fluoroalkanes being chosen are those which do not degrade the ozone layer, for example trifluoropropane, 1,1,1,2-tetrafluoroethane, difluoroethane and heptafluoropropane. Examples of fluoroolefins include 1-chloro-3,3,3-trifluoropropene or 1,1,1,4,4,4-hexafluorobutene (for example HFO FEA1100, sold by DuPont).

[0090] According to a preferred embodiment of the invention, the physical blowing agent chosen is 1,1,1,3,3-pentafluoropropane or HFC-245fa (sold by Honeywell), 1,1,1,3,3-pentafluorobutane or 365mfc (for example Solkane® 365mfc, sold by Solvay), 2,3,3,3-tetrafluoroprop-1-ene, 1,1,1,2,3,3,3-heptafluoropropane (also designated internationally as HFC-227ea, for example sold by DuPont), 1,1,1,4,4,4-hexafluorobutene (for example HFO FEA1100, sold by DuPont), trans-1-chloro-3,3,3-trifluoropropene (Solstice LBA - Honeywell) or a mixture of these.

[0091] Advantageously, the chemical blowing agent consists of water.

[0092] Advantageously, during stage a) of mixing chemical components, nucleating gas is incorporated in at least one polyol compound, preferably using a static/dynamic mixer under a pressure between 20 and 250 bar, the nucleating gas representing between 0% and 50% by volume of polyol, preferably between 0.05% and 20% by volume of the volume of polyol.

[0093] Preferably, during stage a) of mixing the chemical components, the temperature of each of the reactants for obtaining polyurethane/polyisocyanurate is between 10°C and 40°C, preferably between 15°C and 30°C.

[0094] Preferably, according to a preferred embodiment of the invention, the final mixing of the streams of polyols, isocyanate and/or blowing agent takes place in a mixing head at low pressure (< 20 bar) or high pressure (> 50 bar) using a dynamic or static mixer.

[0095] According to one possibility offered by the invention, there is additionally added, to the mixture, in stage a), an organophosphorus flame retardant, advantageously triethyl phosphate (TEP), tris(2-chloroisopropyl) phosphate (TCPP), tris(1,3-dichloroisopropyl) phosphate (TDCP), tris(2-chloroethyl) phosphate or tris(2,3-dibromopropyl) phosphate, or a mixture of these, or an inorganic flame retardant, advantageously red phosphorus, expandable graphite, an aluminium oxide hydrate, an antimony trioxide, an arsenic oxide, an ammonium polyphosphate, a calcium sulfate or cyanuric acid derivatives, or a mixture of these.

[0096] It will also be possible to envisage that the flame retardant uses diethyl ethanephosphonate (DEEP), triethyl phosphate (TEP), dimethyl propylphosphonate (DMPP) or diphenyl cresyl phosphate (DPC).

[0097] This flame retardant, when it is present in the composition according to the invention, is found in an amount of between 0.01% and 25% by weight of the PUR/PIR foam.

[0098] The description which will follow is given solely by way of illustration and without limitation, with reference to the appended figures, in which:

[0099] [Fig.1] is a diagrammatic view illustrating the different stages of the process for the preparation of a fibre-reinforced PUR/PIR foam block according to the invention.

[0100] [Fig.2] is a diagrammatic representation of an embodiment of a controlled liquid dispenser according to the invention.

[0101] [Fig.3] is a diagrammatic sectional view of a foam block according to one embodiment of the invention in which the peripheral zones as well as the intermediate zone are visible.

[0102] [Fig.4] is a diagrammatic sectional view of a foam block according to another embodiment of the invention in which the peripheral zones as well as the intermediate zone are visible, the intermediate zone exhibiting two median zones sandwiching a central zone.

[0103] [Fig.5] is a diagrammatic view of two sets of thermal insulation panels, fixed one to the other, respectively forming a primary insulation space and a secondary insulation space for a tank, these panels being formed by a plurality of fibre-reinforced polyurethane/polyisocyanurate foam blocks according to the invention.

[0104] [Fig.6] is a partial view of a foam block according to the invention in which a plurality of anchorings have been placed during its preparation so as to allow the fixing or the anchoring of said foam block.

[0105] [Fig.7] illustrates an embodiment of an anchoring, visible along a diagrammatic section, capable of being inserted into a foam block according to the invention.

[0106] [Fig.8] is a cutaway diagrammatic representation of a tank of an LNG tanker, in which tank are installed the two sets of thermal insulation panels of the type of those represented in Figure 7, and of a loading/unloading terminal for this tank.

[0107] Preferably, the preparation of the fibre-reinforced PUR/PIR according to the invention is carried out in the presence of catalysts making it possible to promote the isocyanate/polyol reaction. Such compounds are described, for example, in the document of the state of the art entitled "Kunststoffhandbuch, Volume 7, Polyurethane", published by Carl Hanser, 3rd edition, 1993, Chapter 3.4.1. These compounds comprise amine-based catalysts and catalysts based on organic compounds.

[0108] Preferably, the preparation of the fibre-reinforced PUR/PIR foam block 20 according to the invention is carried out in the presence of one or more stabilizers intended to promote the formation of regular cellular structures during the formation of the foam. These compounds are well known to a person skilled in

the art and, by way of example, mention may be made of foam stabilizers comprising silicones, such as siloxane-oxyalkylene copolymers and other organopolysiloxanes.

[0109] A person skilled in the art knows the amounts of stabilizers, between 0.5% and 4% by weight of the PUR/PIR foam, to be used depending on the reactants envisaged.

[0110] According to one possibility offered by the invention, during stage a) of the preparation process, the mixture of chemical components can include plasticizers, for example polybasic esters, preferably dibasic esters, carboxylic acids with monohydric alcohols, or can consist of polymeric plasticizers, such as polyesters of adipic, sebacic and/or phthalic acids. A person skilled in the art, depending on the reactants used, knows what envisaged amount of plasticizers, conventionally from 0.05% to 7.5% by weight of the polyurethane/polyisocyanurate foam.

[0111] Organic and/or inorganic fillers, in particular reinforcing fillers, can also be envisaged in the mixture of chemical components, such as siliceous minerals, metal oxides (for example kaolin, titanium or iron oxides) and/or metal salts. The amount of these fillers, if they are present in the mixture, is conventionally between 0.5% and 15% by weight of the PUR/PIR foam.

[0112] It should be noted that the present invention is not intended here to add technical teaching to the formation of a PUR/PIR foam, both in terms of the nature of the essential chemical components and of the optional functional agents and their respective amounts. A person skilled in the art knows how to obtain different types of fibre-reinforced PUR/PIR foam and the present preparation relates, starting from a specific choice of the characteristics of the fibre reinforcements, in particular the density of fibres in the different fibre reinforcements, and from a specific choice of the foam for the impregnation of said reinforcements also.

[0113] Thus, the present invention, as set out here, is not primarily aimed at a new chemical preparation of fibre-reinforced PUR/PIR foam but rather at a novel fibre-reinforced PUR/PIR foam block 20 in which, by virtue of a very specific

distribution of density of fibres along the thickness or the height of the block 20, this fibre-reinforced foam block 20 does not undergo any sagging or any deformation of its general parallelepipedal shape/structure other than a slight contraction of its dimensions by a constant factor along all its directions, and preferably any shrinkage at the heart of the foam block 20 likely to result in possible phenomena of thermal convection.

[0114] Thus, as can be seen in Figure 1, a plurality of fibre reinforcements 10 are unwound and brought along a parallel alignment with one another onto or above a conveyor belt 11 intended to carry these reinforcements 10 and the components forming the PUR/PIR foam. This is because the impregnation of the fibre reinforcements 10 is carried out, in the context of a preferred method of preparation of the fibre-reinforced foam block 20 of the present invention, by gravity, that is to say that the mixture 12 of chemical components, blowing agent(s) and optional other functional agents used to obtain the PUR/PIR foam is poured, from a liquid dispenser located above the fibre reinforcements 10, directly onto the fibres 10.

[0115] Thus, the abovesaid mixture 12 has to impregnate all of the layers of fibre reinforcements 10, whether it concerns, for these reinforcements, several mats or several fabrics, in a very homogeneous manner, during the cream time t_c so that the start of the expansion of the PUR/PIR foam takes place after or at the earliest just at the moment when the fibre reinforcements 10 are definitely all impregnated by the mixture 12. On doing this, the expansion of the PUR/PIR foam is achieved while retaining a perfect specific distribution of the fibres 10 in the volume of the PUR/PIR foam block 20, so as to obtain the desired gradient of density of fibres.

[0116] The object of the present invention is achieved by positioning fibre reinforcements parallel to one another, i.e. in superimposed layers, each of these reinforcements exhibiting a greater or lesser density of fibres compared to the others. Thus, the fibre reinforcements intended for the peripheral zones 21, 22, indeed even the central zone 26, exhibit a higher density of fibres than those of the intermediate zone 23, indeed even of the median zones 24, 25 in the embodiment where a central zone 26 is present.

[0117] More precisely, the peripheral zones 21, 22, as well as optionally the central zone 26, exhibit densities of fibres within comparable ranges or domains, that is having high density of fibres. Thus, it can be defined that the ratio of density of fibres for these zones 21, 22, 26 is comprised in the inequations defined below:

$2/3 \leq T_{f \text{ upp.}} / T_{f \text{ low.}} \leq 3/2$ and $T_{f \text{ int.}} < T_{f \text{ upp.}}, T_{f \text{ low.}}$: in the case of the two peripheral zones 21, 22 and of the intermediate zone 23 represented in Figure 3;

$2/3 \leq T_{f \text{ cen.}} / (T_{f \text{ low.}} \text{ or } T_{f \text{ upp.}}) \leq 3/2$ and $T_{f \text{ med.}} < T_{f \text{ low.}}, T_{f \text{ upp.}}, T_{f \text{ cen.}}$: in the case of the two peripheral zones 21, 22 and of the intermediate zone 23 formed by the central zone 26 and the two median zones 24, 25 represented in Figure 4.

[0118] These zones 21, 22, 26 having high density of fibres exhibit a density of fibres of between 10% and 45% by weight of fibres, with respect to the local weight (considered in said zone 21, 22 or 26) of the foam block 20, preferentially between 12% and 25% by weight of fibres.

[0119] In contrast, the intermediate zone 23 (in the absence of a central zone 26) and the median zones 24, 25 (when a central zone 26 is present) exhibit a relatively lower density of fibres. In these zones 23 or 24, 25, the density of fibres is from 1% to 20% by weight of fibres, with respect to the local weight of the foam block 20, preferably between 4% and 11% by weight of fibres, with respect to the local weight in the PUR/PIR foam block 20.

[0120] If the zones 21, 22, 26 having high density of fibres are compared with the zones 23 or 24, 25 having low density of fibres, the zones 21, 22, 26 having high density of fibres preferably exhibit a density of fibres at least greater than that of the zones 23 or 24, 25 having low density of fibres, indeed even advantageously two to three times greater than that of the zones 23 or 24, 25 having low density of fibres.

[0121] In the context of the invention, the cream time of the components of the mixture 12 in order to form the PUR/PIR foam is known to a person skilled in the art and chosen in such a way that the conveyor belt 11 brings the assembly formed from the mixture 12 of components, blowing agent and fibres 10, for example, up to a double belt laminator, not represented in the appended figures,

while the expansion of the foam has just started, in other words the expansion of the PUR/PIR foam then ends in the double belt laminator.

[0122] In such an embodiment with a double belt laminator (DBL), a pressure system, using one or two rollers, is optionally positioned before the double belt laminator, i.e. between the region for impregnation of the mixture on the fibres and the double belt laminator. In the case of the use of a DBL, the expansion of the volume of the foam is carried out in the laminator when the expansion volume of this foam reaches between 30% and 60% of the expansion volume of this same foam when the expansion is left free, i.e. without any constraint. On doing this, the double belt laminator will be able to constrain the expansion of the PUR/PIR foam in its second expansion phase, when the latter is close or relatively close to its maximum expansion, that is to say when its expansion brings the foam close to all of the walls, forming a tunnel of rectangular or square section, of the double belt laminator. According to a different way of presenting the specific choices of the preparation according to the invention, the gel point of the mixture of components, that is to say the moment when at least 60% of the polymerization of the mixture of components is achieved, in other words 70% to 80% of the maximum volume expansion of the mixture, obligatorily takes place in the double belt laminator, possibly in the second half of the length of the double belt laminator (i.e. closer to the outlet of the laminator than to the inlet of the latter).

[0123] As regards the function of simultaneous dispensing of the mixture 12 of chemical components and of blowing agent over the entire width L of the fibre reinforcements 10, it is provided here by a controlled liquid dispenser 15, visible in Figure 2. Such a dispenser 15 comprises a feed channel 16 for the assembly formed of the mixture 12 of chemical components and at least blowing agent from the reservoir forming a reactant mixer, not represented in the appended figures, in which, on the one hand, all the chemical components and the blowing agent are mixed and, on the other hand, in particular the nucleation, indeed even the heating, of such a mixture is carried out. This liquid assembly formed of the mixture 12 of chemical components and of the blowing agent is then distributed, under pressure, in two channels 17 extending transversely to respectively end in

two identical dispensing plates 18, extending along the width L (each exhibiting a length substantially equal to $L/2$), comprising a plurality of nozzles 19 for the flow of said mixture 12 over the fibre reinforcements 10. These flow nozzles 19 consist of orifices of calibrated section exhibiting a predetermined length. The length of these flow nozzles 19 is thus predetermined so that the liquid leaves with an identical flow rate between all the nozzles 19 in order for the impregnation of the fibre reinforcements 10 to take place at the same time, or simultaneously, over the section of width L of the fibre reinforcements 10, and for the surface density of liquid deposited at right angles with each nozzle to be equal. On doing this, if a section of width L of the fibres 10 is considered, the latter are impregnated concurrently so that the impregnation of the layers of fibres 10 by the mixture 12 is carried out, at all points of this section, in an identical manner, which contributes to obtaining, at the outlet of the double belt laminator, a block of fibre-reinforced foam 20 in which the local density of fibres corresponds precisely to the density of fibres of each of the superimposed layers of the fibre reinforcements, at the moment of the gravitational flow of the mixture 12.

[0124] The controlled liquid dispenser 15 represented in this Figure 2 is an exemplary embodiment in which two identical dispensing plates 18 are used but it will be possible to envisage a different design, in so far as the function of simultaneous dispensing of liquid over the width section of the fibres 10 is achieved. Of course, the main technical characteristic used in this instance lies in the different lengths of the flow nozzles 19, long to a greater or lesser extent depending on the route, or path, of the liquid mixture 12 from the feed duct 16 of the dispenser 15 as far as the flow nozzle 19 under consideration.

[0125] One of the aspects of importance for achieving a good impregnation of the fibre reinforcements 10 just before the cream time t_c of the PUR/PIR foam lies in the choice of a specific viscosity of the liquid (consisting of the mixture 12 of chemical components and of the blowing agent) to be linked with the specific characteristics of the different fibre reinforcements, which can vary as a function of the density of fibres. The viscosity range chosen as well as the permeability characteristics of the fibre reinforcements have to make possible good penetration of the liquid into the first layers of fibres 10, in order to reach the

following ones down to the final layer (the lower layer of fibres 10, i.e. that located lowest in the stack of the fibre reinforcements), so that the impregnation time t_i of the fibres 10 is produced within the time period given by the chemical components corresponding substantially to, but always less than, the cream time t_c . The viscosity of the mixture 12 of components is chosen, for example by heating, additions of plasticizers and/or by a greater or lesser nucleation, so that the impregnation of all the fibres 10 by the mixture 12 of chemical components and of the blowing agent, over a section of width L, is obtained just before the cream time, that is to say before or just before the start of the expansion of the PUR/PIR foam.

[0126] The fibre-reinforced foam block 20 is intended to be used in a very particular environment, and thus has to guarantee specific mechanical and thermal properties. The fibre-reinforced foam block 20 obtained by the preparation according to the present invention thus conventionally forms part of a thermal insulation body 30, i.e., in the example used in Figure 5, in an upper or primary panel 31 and/or a lower or secondary panel 32 of such an insulation body 30 of a tank 71 intended to receive an extremely cold liquid, such as an LNG or an LPG. Such a tank 71 can equip, for example, a ground tank, a floating barge or the like (such as an FSRU "Floating Storage Regasification Unit" or a FLNG "Floating Liquefied Natural Gas") or else a ship, such as an LNG tanker, transporting this energetic liquid between two harbors.

[0127] The foam block according to the invention exhibited in Figure 6 comprises a plurality of anchorings 40, distributed over its different faces, upper 41, and lateral 42, 43. These anchorings 40 are placed so as to be flush with the surface of said faces 41, 42, 43 of the foam block, without exhibiting a thickness of foam (or not significant thickness) covering it and/or protecting it from the outside.

[0128] Figure 7 exhibits, in section, an embodiment of such an anchoring 40. This anchoring 40 exhibits a plate 44 extending along a plane. This plate 44 comprises a plurality of orifices 45 which consist of a mechanical anchoring means, in other words one of the two elements making it possible to fix, when engaged with an element of the thermal insulation body (not represented in the appended figures), the foam block in or to the thermal insulation body of the tank.

The plate 44 also comprises a plurality of identical fixing studs 46 as well as a central fixing stud 47 exhibiting greater dimensions than those of the fixing studs 46. The function of these studs 46, 47 consists in fixing the anchoring 40 as best as possible in the fibre-reinforced foam block according to the invention. The fixing studs 46 are ideally positioned circumferentially to form a circle close to the circumference or the periphery of the anchoring 40.

[0129] The anchoring 40 represented in Figure 7 is advantageously placed on the conveyor belt 11, the studs 46, 47 then being directed upwards and the plate 44 resting on said belt 11.

[0130] However, it will also be possible to envisage placing these anchorings 40 on the upper face 41 of the block, indeed even on the side faces 42, 43, as can be seen on the block represented in Figure 6. In the latter case, provision may advantageously be made to embed the studs 46, 47, at least slightly, in an adjacent/contiguous mat of fibres, before its impregnation by the polymer foam.

[0131] Of course, one of these orifices 45 of the anchoring 40 can as such be used to form the female part of the anchoring but provision may also be made for the anchoring to require the use of a plurality of orifices 45. Furthermore, these orifices 45 consist of an anchoring solution but the invention is in no way limited to this embodiment and it will be possible to envisage one or more anchorings 40 of different shape and different mechanical characteristics.

[0132] With reference to Figure 8, a cutaway view of an LNG tanker 70 shows a sealed and insulating tank 71 of prismatic general shape, mounted in the double hull 72 of the ship. The wall of the tank 71 comprises a primary sealed barrier intended to be in contact with the LNG contained in the tank, a secondary sealed barrier arranged between the primary sealed barrier and the double hull 72 of the ship, and two insulating barriers arranged, respectively, between the primary sealed barrier and the secondary sealed barrier and between the secondary sealed barrier and the double hull 72.

[0133] In a way known per se, loading/unloading pipes 73 positioned on the upper deck of the ship can be connected, by means of appropriate connectors, to a

shipping or harbour terminal, in order to transfer a cargo of LNG from or to the tank 71.

[0134] Figure 8 represents an example of a shipping terminal comprising a loading and unloading station 75, an underwater pipeline 76 and a land-based installation 77. The loading and unloading station 75 is a fixed offshore installation comprising a mobile arm 74 and a tower 78 which supports the mobile arm 74. The mobile arm 74 carries a bundle of insulated flexible hoses 79 which can be connected to the loading/unloading pipes 73. The swivelling mobile arm 74 fits all sizes of LNG tankers. A linking pipeline (not represented) extends inside the tower 78. The loading and unloading station 75 allows the LNG tanker 70 to be loaded and unloaded from or to the land-based installation 77. This installation comprises liquefied gas storage tanks 80 and linking pipelines 81 connected via the underwater pipeline 76 to the loading or unloading station 75. The underwater pipeline 76 allows the transfer of liquefied gas between the loading or unloading station 75 and the land-based installation 77 over a great distance, for example 5 km, which makes it possible to keep the LNG tanker 70 at a great distance from the coast during the loading and unloading operations.

[0135] To generate the pressure required for the transfer of the liquefied gas, on-board pumps in the ship 70 and/or pumps equipping the land-based installation 77 and/or pumps equipping the loading and unloading station 75 are used.

[0136] As was stated above, the use or the application of the subject-matter of the present invention, namely in the case in point the fibre-reinforced polyurethane/polyisocyanurate foam block 20, is not intended to be limited to an integrated tank in a supporting structure but it is also provided for tanks of type A, B and C of the IGC Code in force at the date of filing of the present patent application, but also for the future versions of this Code unless very substantial modifications apply thereto for these tanks of type A, B and C, it being furthermore understood that other types of tanks might, under this assumption of a modification of the IGC Code, become applications which can be envisaged for the fibre-reinforced PUR/PIR foam block 20 according to the present invention.

[0137] In the continuation, a part of the experiments and tests carried out by the Applicant Company to allow it to assess the subject-matter of the invention and

its scope are presented, it being considered that other tests/experiments have been carried out and will be liable to be provided subsequently, if necessary/required.

[0138] A polyisocyanurate foam composition, incorporating fibres in the form of mats, is used to demonstrate the invention, these fibres always being provided as long to continuous; more precisely, the lengths of these fibres are exactly the same in the compositions according to invention and those according to the state of the art. The Applicant Company has in particular tested the subject-matter of the invention with fibres said to be short (in contrast to the definition given above to long to continuous fibres) or provided in the form of fabric and the results obtained are equivalent or virtually similar to those obtained with a mat of long to continuous fibres, as presented below.

[0139] Thus, in order to make quite sure that only the combination of particular characteristics of density of fibres of the fibre reinforcements with the choice of a PIR foam exhibiting especially a particular cream time, or one suited to the characteristics of said fibre reinforcements, no other parameter of the preparation of a PIR foam block is modified or different between the preparations in accordance with the invention and those in accordance with the state of the art. As non-exhaustive examples, mention may be made of the fact that the nucleation, the amounts of blowing agents, the reaction temperatures, nature and amounts of the mixture of chemical components, pouring process, distance between the pouring of the mixture of chemical components and the DBL or the device making possible the free expansion, if appropriate, are strictly identical in the cases according to the invention and the cases according to the state of the art.

[0140] Of course, it has been chosen in this instance to illustrate the invention using a PUR foam for the sake of clarity and conciseness but equivalent or virtually similar results have been obtained with PIR foams as well as PUR/PIR mixtures.

[0141] Likewise, the preparations of fibre-reinforced foam, the results of which are presented below, use the free expansion technique but the Applicant Company has shown that equivalent or virtually similar results, from the viewpoint of fibre-

reinforced foams according to the invention and fibre-reinforced foams according to the state of the art, have been obtained using a DBL.

[0142] Furthermore, it is understood that all the compositions tested in the continuation are considered under conditions of identical density, it being understood that this parameter of the density is involved in the assessment of the performance qualities in compressive strength.

[0143] For the compositions according to the state of the art, the characteristics of the fibre reinforcements and of the PUR foam are as follows:

[0144] [Table 1]

Type of product	Content (relative share of the different components)	Description	Commercial reference of the product
Polyol 1 (mixture of polyol ether based on glycerol and on sorbitol)	60-75	385-415 mg KOH/g	Mixture of polyols based on glycerol and on sorbitol of type Daltolac® R200, R251, R404, R470, R500
Polyol 2 (mixture of polyether and aromatic polyester diol)	25-40	230-250 mg KOH/g	Aromatic polyester polyol of type Stepanpol® PS-1752, PS-2352, PS-3152 and polyether polyol of type alkyl ether: PEG, PPG, pBDO, pHDO, pTMEG, Pluriol
isocyanate	95-135	30-31.5% NCO	Polymeric MDI isocyanate of type Suprasec® S5005
Water (chemical blowing agent)	0.05-1.5		
Physical blowing agent	3-12	365mfc/227ea or 245fa or 123zd	
Surfactant	0.5-1.5	PEO/PPO-grafted silicone	Tegostab® B8404 or B8465

Tin-based reaction catalyst	0.05-0.08	DBTL	Dabco® T12N
Glass mat	22	Continuous-fibre glass mat	Unifilo U809 or CFM1020

[0145] For the compositions according to the invention, the characteristics of the fibre reinforcements and of the PUR foam are as follows:

[0146] [Table 2]

Type of product	Content (relative share of the different components)	Description	Commercial reference of the product
Polyol 1 (mixture of polyol ether based on glycerol and on sorbitol)	60-75	385-415 mg KOH/g	Mixture of polyols based on glycerol and on sorbitol of type Daltolac® R200, R251, R404, R470, R500
Polyol 2 (mixture of polyether and aromatic polyester diol)	25-40	230-250 mg KOH/g	Aromatic polyester polyol of type Stepanpol® PS-1752, PS-2352, PS-3152 and polyether polyol of type alkyl ether: PEG, PPG, pBDO, pHDO, pTMEG, Pluriol
isocyanate	95-135	30-31.5% NCO	Polymeric MDI isocyanate of type Suprasec® S5005
Water (chemical blowing agent)	0.05-1.5		
Physical blowing agent	3-12	365mfc/227ea or 245fa or 123zd	
Surfactant	0.5-1.5	PEO/PPO-grafted silicone	Tegostab® B8404 or B8465
Tin-based reaction catalyst	0.05-0.08	DBTL	Dabco® T12N

Glass mat		Continuous-fibre glass mats of varied TEX and/or varied binder content	CFM 1020 or CFM 1050 or Uniconform or Unifilo U809, U801, U812, U813, U816, U850, U852, U854
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[0147] It is noted that the cream time for the PUR foams used and presented above is logically the same for the compositions according to the state of the art and according to the invention, since the foam used is identical, whatever the case under consideration.

[0148] Subsequent to carrying out the tests, some results are presented below, in a simplified manner, in order to illustrate the discoveries of the Applicant Company, in the case where the fibre reinforcements are provided in the form of at least one mat of glass fibres.

[0149] [Table 3]

Mixture of chemical components and of blowing agents (identical density substantially equal to 130 kg.m⁻³ of the compositions tested) with fibres of the type indicated below	Content of fibres % and Characterization of the distribution of the fibres in the foam (by taking a core in the height/thickness of the block)	Performance with regard to tension, by application of Standard ISO 1926 (tension in the plane of the mat(s))	Coefficient of thermal contraction, by application of Standard ASTM E 228, between +23 and -196°C
8 layers of U809 or U801 for a block with a thickness of 180 mm Approx. 135 kg/m ³	14.4% Uniform	E = 192 MPa	$\alpha = 17 \times 10^{-6} \text{ m/m.K}$
12 layers of U812 or U816 or U822 for a block with a thickness of 180 mm Approx. 137 kg/m ³	21.6% Uniform Presence of air bubbles in the foam	E = 253 MPa	$\alpha = 13 \times 10^{-6} \text{ m/m.K}$
15 layers of U852 or U854 or U850 for a	26.9%	E = 301 MPa	$\alpha = 11.0 \times 10^{-6} \text{ m/m.K}$

block with a thickness of 180 mm Approx. 134 kg/m ³	Uniform Presence of air bubbles in the foam		
For a block with a thickness of 180 mm: 1 layer of U850 2 layers of U809 1 layer of U812 1 layer of U850 1 layer of U812 2 layers of U809 1 layer of U850 (in accordance with the invention) Approx. 135 kg/m ³	23% 10% 15% 23% 15% 9% 22% Presence of air bubbles	E = 255 MPa E = 155 MPa E = 180 MPa E = 260 MPa E = 180 MPa E = 152 MPa E = 245 MPa	$\alpha = 12 \times 10^{-6}$ m/m.K $\alpha = 20 \times 10^{-6}$ m/m.K $\alpha = 18 \times 10^{-6}$ m/m.K $\alpha = 12 \times 10^{-6}$ m/m.K $\alpha = 18 \times 10^{-6}$ m/m.K $\alpha = 20 \times 10^{-6}$ m/m.K $\alpha = 13 \times 10^{-6}$ m/m.K

It will be noted that the first composition (with 8 layers of U809 or U801 for a block with a thickness of 180 mm) of Table 3 above consists of a composition in accordance with the document FR 2 882 756. The results for such a composition according to the document FR 2 882 756 are very significantly inferior to those obtained with a composition according to the present invention (final composition of Table 3).

[0150] As is seen with the results presented in the table above, with regard to the three criteria considered in comparing the fibre-reinforced foams obtained, those in accordance with the invention exhibit results which are very significantly better than those of the fibre-reinforced foams according to the state of the art.

[0151] Furthermore, it should be noted that the fibre-reinforced PUR/PIR foams according to the invention do not exhibit any significant deterioration in their property relating to the (very low) thermal conductivity.

[0152] [Table 4]

Thermal conductivity (mW/m.K)		
at -160°C	at -120°C	at +20°C
10-14	11-16	23-27

[0153] Although the invention has been described in connection with several particular embodiments, it is quite obvious that it is in no way limited thereto and

that it comprises all the technical equivalents of the means described as well as their combinations, if these come within the scope of the invention.

[0154] The use of the verb "to comprise" or "to include" and of its conjugated forms does not exclude the presence of other elements or of other stages than those set out in a claim.

[0155] In the claims, any reference sign in brackets should not be interpreted as a limitation on the claim.

Claims

[Claim 1] Fibre-reinforced polyurethane/polyisocyanurate foam block (20) of a thermal insulation body (30) of a sealed and thermally insulating tank, the density of the fibre-reinforced foam block (20) being between 30 and 300 kg/m³, the fibre-reinforced polyurethane/polyisocyanurate foam block (20) exhibiting a mean density of fibres T_f of between 1% and 60% by weight of fibres (10), and exhibiting a width L of at least ten centimetres, advantageously of between 10 and 500 centimetres, and a thickness E, from the lower face of said block (20) up to its upper face, of at least ten centimetres, advantageously of between 10 and 100 centimetres, the fibre-reinforced polyurethane/polyisocyanurate foam block (20) being composed of cells storing a gas, advantageously having low thermal conductivity, characterized in that:

- the foam block (20) comprises, along its thickness E, two peripheral zones (21, 22), one said to be upper (21), extending from the upper face of the block (20), and the other said to be lower (22), extending from the lower face of the block (20), these two zones (21, 22) each representing at most 20% along the thickness E of the block (20) and being separated by a zone said to be intermediate (23); and
- the peripheral zones (21, 22), upper (21) and lower (22), respectively exhibit a density of fibres $T_{f\text{ upp.}}$ and $T_{f\text{ low.}}$ such that: $2/3 \leq (T_{f\text{ upp.}} / T_{f\text{ low.}}) \leq 3/2$; and
- the density of fibres $T_{f\text{ int.}}$ of the intermediate zone (23) is less than the densities of the peripheral zones (21, 22), i.e.: $T_{f\text{ int.}} < T_{f\text{ upp.}}$ and $T_{f\text{ int.}} < T_{f\text{ low.}}$.

[Claim 2] Fibre-reinforced polyurethane/polyisocyanurate foam block (20) according to Claim 1, in which the two abovesaid peripheral zones (21, 22) each represent at most 10% along the thickness E of the block (20).

[Claim 3] Fibre-reinforced polyurethane/polyisocyanurate foam block (20) according to Claim 1 or 2, in which the intermediate zone (23) comprises a central zone (26), surrounded by two median zones (24, 25), representing at most 20% along the thickness E, preferably at most 10% along the thickness E, the density of fibres $T_{f\text{ cen.}}$ of this central zone (26) being at least one and a half times greater than that of the median zones (24, 25) $T_{f\text{ med.}}$, i.e. $T_{f\text{ cen.}} \geq 1.5 T_{f\text{ med.}}$.

- [Claim 4] Fibre-reinforced polyurethane/polyisocyanurate foam block (20) according to Claim 3, in which the density of fibres $T_{f\text{ cen.}}$ of this central zone (26) is defined with respect to the density of fibres $T_{f\text{ upp.}}$ and $T_{f\text{ low.}}$ of the peripheral zones (21, 22), upper (21) and lower (22), such that $0.5 \leq T_{f\text{ cen.}} / (T_{f\text{ low.}} \text{ or } T_{f\text{ upp.}})$
- [Claim 5] Fibre-reinforced polyurethane/polyisocyanurate foam block (20) according to one of the preceding claims, in which the density of the fibre-reinforced foam block (20) is between 50 and 250 kg/m³, preferably between 90 and 210 kg/m³.
- [Claim 6] Fibre-reinforced polyurethane/polyisocyanurate foam block (20) according to any one of the preceding claims, in which at least 60%, preferably at least 80%, of the abovesaid cells storing a gas, advantageously having low thermal conductivity, exhibit a shape elongated or stretched along an axis parallel to the axis of a thickness E of the fibre-reinforced polyurethane/polyisocyanurate foam block (20).
- [Claim 7] Fibre-reinforced polyurethane/polyisocyanurate foam block (20) according to any one of the preceding claims, in which the fibres consist of glass fibre or of basalt fibre, preferably of glass fibre.
- [Claim 8] Fibre-reinforced polyurethane/polyisocyanurate foam block (20) according to any one of the preceding claims, in which the fibres are long to continuous fibres.
- [Claim 9] Fibre-reinforced polyurethane/polyisocyanurate foam block (20) according to any one of the preceding claims, in which the mean density of fibres T_f is between 2% and 25%, preferably between 6% and 20%.
- [Claim 10] Fibre-reinforced polyurethane/polyisocyanurate foam block (20) according to any one of the preceding claims, in which the lower face and/or the upper face (41), preferably the upper face (41), of said block exhibits(s) anchorings (40) capable of engaging with an engaging means of the thermal insulation body (30) in order to anchor the foam block to said body (30), preferably said anchorings (40) being made of a different material from the foam or from the fibres.
- [Claim 11] Sealed and thermally insulating tank (71), said tank (71) consisting of:

- a tank integrated in a supporting structure comprising a sealed and thermally insulating tank comprising at least one sealed metal membrane composed of a plurality of metal strakes or metal plates which can comprise corrugations and a thermally insulating body (30) comprising at least one thermally insulating barrier adjacent to said membrane, or
- a tank of type A, B or C according to the definition given by the IGC Code comprising at least one thermally insulating body (30), characterized in that the thermally insulating body (30) comprises a plurality of fibre-reinforced polyurethane/polyisocyanurate foam blocks (20) according to any one of the preceding claims.

[Claim 12] Ship (70) for the transportation of a cold liquid product, the ship comprising at least one hull (72) and one sealed and thermally insulating tank (71) according to Claim 11, positioned in the hull or mounted on said ship (70) when said tank (71) is of the type A, B or C according to the definition given by the IGC Code.

[Claim 13] Transfer system for a cold liquid product, the system comprising a ship (70) according to the preceding claim, insulated pipes (73, 76, 79, 81) arranged so as to connect the tank (71) installed in the hull of the ship to a floating or onshore storage unit (77) and a pump for driving a flow of cold liquid product through the insulated pipes from or to the floating or onshore storage unit to or from the ship (70).

[Claim 14] Process for loading or unloading a ship (70) according to Claim 12, in which a cold liquid product is conveyed through insulated pipes (73, 76, 79, 81) from or to a floating or onshore storage unit (77) to or from the ship (71).

[Claim 15] Process for the preparation of a fibre-reinforced polyurethane/polyisocyanurate foam block (20) of a thermal insulation body of a sealed and thermally insulating tank according to one of Claims 1 to 10, characterized in that it comprises the stages:

a) of mixing (12) chemical components necessary for obtaining a polyurethane/polyisocyanurate foam, said components comprising reactants for obtaining polyurethane/polyisocyanurate, optionally at least one reaction catalyst, optionally at least one emulsifier, and at least one blowing agent,

b) of impregnation, by gravitational flow of the abovesaid mixture (12) of chemical components, of a plurality of fibre reinforcements (10), said fibre reinforcements being positioned in superimposed layers and exhibiting variable densities of fibres, in which the fibre reinforcements (10) extend essentially along a direction perpendicular to the direction of said gravitational flow,

c) of formation and of expansion of the fibre-reinforced polyurethane/polyisocyanurate foam,

in which the expansion of the fibre-reinforced polyurethane/polyisocyanurate foam is said to be by free expansion, i.e. without the constraint exerted by a volume of closed section on at least one face, preferably the upper face, or in which the expansion of the fibre-reinforced polyurethane/polyisocyanurate foam is physically constrained by walls of a double belt laminator, preferably is physically constrained by the walls of a double belt laminator forming a tunnel of rectangular section with a distance between the walls positioned laterally equal to L and a distance between the walls positioned horizontally equal to E, thus enclosing the expanding fibre-reinforced foam so as to obtain the abovesaid fibre-reinforced polyurethane/polyisocyanurate foam block (20).

[Claim 16] Process for the preparation of a fibre-reinforced polyurethane/polyisocyanurate foam block (20) according to Claim 15, in which, in the case where the expansion of stage c) is carried out by free expansion, one at least of the peripheral zones (21, 22), preferably the upper zone (21), is formed independently and fixed, once a cutout on at least the free expansion face has been carried out, to form said foam block (20).