Claims

[Claim 1] A process for the preparation of a block of fiber-reinforced polyurethane/polyisocyanurate foam of a thermal insulation slab of a sealed and thermally insulating tank, the block of fiber-reinforced polyurethane/polyisocyanurate foam being composed of cells storing a gas and exhibiting a density of less than 50 $kg.m^{-3}$ with a content of fibers C_f representing at least 4% by weight of the block of fiber-reinforced foam, the preparation process comprising the following stages:

a) a stage 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) a stage of impregnation, by gravitational flow of the abovesaid mixture (12) of chemical components, of a plurality of fiber reinforcements (10) chosen from fabrics of fibers and mats of fibers, said fibers having a length of at least five centimeters (cm), arranged in superimposed layers, in which the fiber reinforcements (10) extend essentially along a direction perpendicular to the direction of said gravitational flow, these fiber reinforcements (10) exhibiting a permeability K_c to the abovesaid mixture (12) of chemical components, expressed in m^2, equal to:

$$K_c = (r_f^2 \times p^3)/(k \times \tau^2 \times 4 \times V_f^2), \text{ with}$$

r_f = radius of the fibers, expressed in meters (m),

p = porosity of the fibers (10) (dimensionless), value between 0 and 1,

k = form factor (dimensionless), dependent on the nature of the fiber reinforcement (10), with k = 1 for a fabric of fibers, k = 6 for a mat of fibers,

τ = tortuosity (dimensionless), dependent on the arrangement of the fibers,

V_f = volume fraction of the fibers (proportion of fibers in a volume of the reinforcement), value between 0 and 1,

c) a stage of formation and of expansion of the fiber-reinforced polyurethane/polyisocyanurate foam,

characterized in that the abovesaid mixture (12) of chemical components exhibits a dynamic viscosity η, during the impregnation stage b), such that an impregnation time of the fibers t_i is less than the cream time t_c of the polyurethane/polyisocyanurate foam, and in which $t_c \leq 2\ t_i$,

the impregnation time of the fibers t_i being equal to:

$$t_i = (\eta \times e_m^2)/(K_c \times \Delta P),$$

$$\Delta P = (M_{sd} \times g_T \times k_p), \text{ with}$$

η = the dynamic viscosity, expressed in pascal.seconds (Pa.s),

e_m = sum of the mean thicknesses of the fiber reinforcements (10), expressed in meters (m), each fiber reinforcement exhibiting a mean thickness corresponding to the mean of the distances between a plurality of pairs of local extremums of said fiber reinforcement (10) spaced out from one another along a direction of thickness of said fiber reinforcement,

ΔP = pressure gradient, expressed in pascals per meter (Pa),

M_{sd} = surface density of the abovesaid mixture (12) of chemical components, expressed as weight per unit area ($kg.m^{-2}$),

g_T = terrestrial gravitational force, regarded here as equal to 9.8 $N.kg^{-1}$,

k_p = mean pressure factor, constant equal to 0.5.

[Claim 2] The process as claimed in claim 1, in which the impregnation time t_i observes the following formula with respect to the cream time t_c of the polyurethane/polyisocyanurate foam:

$$0.50 < {}^{t_i}/_{t_c} < 0.91$$

[Claim 3] The process as claimed in claim 1 or 2, in which the expansion of the fiber-reinforced polyurethane/polyisocyanurate foam is physically constrained by the walls of a double belt laminator forming a tunnel, advantageously 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 fiber-reinforced foam so as to obtain the abovesaid block of fiber-reinforced polyurethane/polyisocyanurate foam.

[Claim 4] The process as claimed in claim 3, in which the positioning of the walls of the tunnel of the double belt laminator is defined so that the constraint on the expansion of the fiber-reinforced polyurethane/polyisocyanurate foam results in a volume of fiber-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 fiber-reinforced polyurethane/polyisocyanurate foam in the case of free expansion, without the constraint of the walls of such a double belt laminator.

[Claim 5] The process as claimed in claim 1 or 2, in which the expansion of the fiber-reinforced polyurethane/polyisocyanurate foam is free, i.e. without the constraint exerted by a volume of closed section.

[Claim 6] The process as claimed in claim 5, in which, following the stage of free expansion of the fiber-reinforced polyurethane/polyisocyanurate foam, said fiber-reinforced foam is cut in order to obtain the abovesaid block of fiber-reinforced polyurethane/polyisocyanurate foam.

[Claim 7] The process as claimed in any one of the preceding claims, in which the dynamic viscosity η of the abovesaid mixture (12) of components is between 30 mPa.s and 3000 mPa.s, preferably between 50 mPa.s and 1500 mPa.s, under standard temperature and pressure conditions.

[Claim 8] The process as claimed in any one of the preceding claims, in which 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 block of fiber-reinforced polyurethane/polyisocyanurate foam.

[Claim 9] The process as claimed in any one of the preceding claims, in which 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 block of fiber-reinforced polyurethane/polyisocyanurate foam.

[Claim 10] The process as claimed in any one of the preceding claims, in which the fibers are long to continuous and the fibers consist of glass fiber, of carbon fiber or any other organic or inorganic material, preferably of glass fiber.

[Claim 11] The process as claimed in any one of the preceding claims, in which the fiber reinforcements (10) are positioned over an entire width L and stage b) of impregnation of the fibers by the mixture (12) of components, in order to obtain a fiber-reinforced polyurethane/polyisocyanurate foam, and of a blowing agent is carried out, via a controlled liquid dispenser (15), simultaneously over the entire width L.

[Claim 12] The process as claimed in any one of the preceding claims, in which the blowing agent consists of a physical and/or chemical expanding agent, preferably a combination of the two types.

[Claim 13] The process as claimed in claim 12, in which the physical expanding 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.

[Claim 14] The process as claimed in claim 12, in which the chemical expanding agent consists of water.

[Claim 15] The process as claimed in claim 13, in which, during stage a) of mixing (12) 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.

[Claim 16] The process as claimed in any one of the preceding claims, in which, during stage a) of mixing (12) 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.

[Claim 17] The process as claimed in any one of the preceding claims, in which 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 these, or an inorganic flame retardant, advantageously red phosphorus, expandable graphite, an aluminum oxide hydrate, an antimony trioxide, an arsenic oxide, an ammonium polyphosphate, a calcium sulfate or cyanuric acid derivatives, or a mixture of these.

[Claim 18] The process as claimed in any one of the preceding claims, in which the content of fibers C_f represents between 7% and 15% by weight of the block of fiber-reinforced foam.

[Claim 19] A block of fiber-reinforced polyurethane/polyisocyanurate foam of a thermal insulation slab (30) of a sealed and thermally insulating tank, directly obtained by virtue of the process as claimed in any one of claims 1 to 18, the block of fiber-reinforced polyurethane/polyisocyanurate foam being composed of cells storing a gas, advantageously having low thermal conductivity, and exhibiting a density of less than 50 $kg.m^{-3}$ with a content of fibers C_f representing at least 4% by weight of the block of fiber-reinforced foam,

characterized in that the fibers are distributed uniformly in the block of fiber-reinforced polyurethane/polyisocyanurate foam, in such a way that the content C_f varies only by +/- 35%, preferably by +/- 20%, in all the zones or portions of said block of fiber-reinforced polyurethane/polyisocyanurate foam.

[Claim 20] A sealed and thermally insulating tank, 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 slab (30) comprising at least one thermally insulating barrier adjacent to said membrane, or
- a tank of type B or C according to the definition given by the IGC Code comprising at least one thermally insulating slab (30),

characterized in that the thermally insulating slab (30) comprises the block of fiber-reinforced polyurethane/polyisocyanurate foam as claimed in claim 19.

[Claim 21] A ship (70) for the transportation of a cold liquid product, the ship comprising at least one hull (72) and a sealed and thermally insulating tank (71) as claimed in claim 20, positioned in the hull.