

FORCED DIFFUSION TREATMENT FOR AN INSULATING PART MADE FROM EXPANDED SYNTHETIC FOAM

Technical field

The invention relates to the field of use of expanded synthetic foams for
5 producing thermal insulation parts and more particularly closed-cell thermoplastic or
thermosetting foams.

Technological background

Closed-cell porous materials consist of a solid matrix in which numerous
gas bubbles, of greater or smaller sizes, are trapped. Various synthetic
10 thermoplastic and thermosetting materials can be employed as matrices, for
example polyurethane (PU), polyethylene terephthalate (PET), polyvinyl chloride
(PVC), polystyrene (PS), polyetherimide, polyethylene (PE), polypropylene (PP) or
polyimide. This list is not exhaustive.

In processes for synthesis by expansion, a foaming agent is used. Two
15 main families of blowing agents can be used depending in particular on the process
for synthesis of the matrix: the blowing agents resulting from a chemical reaction,
known as chemical agents, and the blowing agents resulting from the evaporation of
a liquid under a rise in temperature or a decrease in the pressure, known as
physical agents. Some synthetic foams can contain exclusively physical agents, for
20 example pentane-expanded polypropylene foam, and others exclusively chemical
agents, for example the PU foam expanded with carbon dioxide (CO₂), and yet
others can employ both types of blowing agents, for example the polyurethane
foams expanded with several agents, including pentane and the blowing gases
141b, 365 and 245fa. In all cases, the blowing agent is or gives rise to a blowing gas
25 which develops and occupies the cells of the foam.

The blowing gases are generally selected according to their processing
properties and their prices but also according to their thermal conductivity. They are
generally chosen in order to limit as much as possible transfers of heat by
conduction in the gas phase of the insulating material, on the one hand, and to
30 exhibit low coefficients of diffusion into the matrix selected.

Once the expanded foam part has been manufactured, the cells thus
contain a starting gas or a starting gas mixture. Throughout the lifetime of the foam

under consideration, the latter is the site of diffusion phenomena which gradually change the composition of the gas phase in the cells of the foam, in particular the partial pressures of the blowing gases and of the gases of the surroundings. Thus, the chemical entities, the partial pressure of which is weaker in the ambient medium
5 than the foam, tend to escape from the foam, whereas those, the partial pressure of which is weaker in the foam than in the surrounding media, tend to penetrate into the foam by diffusion.

Thus, under conditions of storage in the open air, the majority of the blowing agents tend to leave the foam, whereas the nitrogen and the oxygen of the
10 air tend to diffuse inside the insulating material. Given that the blowing gases generally exhibit lower thermal conductivities than those of the gases of the ambient medium, the insulating quality of the foams under consideration thus tends to deteriorate over a long period of time. These phenomena are described as aging of the foam.

15 This point is illustrated in figure 1, which represents the change in the thermal conductivity at 20°C, expressed in W/mK, on the axis of the ordinates, as a function of the time of exposure to the ambient atmosphere, expressed in days, on the axis of the abscissae, for two parts of polyurethane foam expanded with CO₂ with a density of 130 kg/m³. Curve 1 and the diamonds relate to a part with a
20 thickness of 25 mm. Curve 2 and the squares relate to a part with a thickness of 50 mm.

Summary

One idea at the basis of the invention is to prevent and/or overcome the phenomena of aging of the foam which are described above.

25 For this, according to one embodiment, the invention provides a process for the forced diffusion treatment of a thermally insulating part made of expanded synthetic foam, comprising:

during a discharge stage, heating the insulating part to a discharge temperature greater than ambient temperature and simultaneously exposing the insulating part to
30 a gas atmosphere exhibiting low partial pressures, at least for molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen,

terminating the discharge stage when the accumulated partial pressures of molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen in the insulating part is less than a predetermined threshold.

In other words, during the discharge stage, the insulating part is exposed to a gas atmosphere exhibiting partial pressures for molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen which are lower than partial pressures of these substances in air at standard pressure.

In addition, the discharge stage is terminated when the accumulated partial pressures of molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen in the insulating part is less than a predetermined threshold, when a physical property of the insulating part related to said accumulated partial pressures reaches a predetermined threshold or after a predetermined time.

Furthermore, the thermally insulating part is positioned in a leaktight and thermally insulating vessel wall and forms an insulating barrier of the vessel wall. Consequently, during the discharge stage, all or part of the vessel wall is heated.

Such a discharge stage makes it possible to discharge gases unfavorable to the thermal properties of the foam, in particular molecular nitrogen, molecular oxygen, carbon dioxide, helium, dihydrogen, argon and others.

According to one embodiment, the invention also provides a process for the forced diffusion treatment of a thermally insulating part made of expanded synthetic thermosetting polyurethane foam comprising at least 80% of closed cells, said process comprising:

during a discharge stage, heating the insulating part to a discharge temperature greater than ambient temperature and simultaneously exposing the insulating part to a gas atmosphere exhibiting partial pressures for molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen

which are lower than their partial pressure in air at standard pressure, terminating the discharge stage when the accumulated partial pressures of molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen in the insulating part is less than a predetermined threshold or when a physical property of the insulating part related to said accumulated partial pressures reaches a predetermined threshold or after a predetermined time.

According to one embodiment, the invention also provides a leaktight and thermally insulating vessel intended to contain a liquefied fuel gas at low temperature, in which a wall of the vessel comprises a multilayer structure fitted to a carrier wall, the multilayer structure comprising a primary leaktightness membrane in contact with the liquefied fuel gas present in the vessel, a secondary leaktightness membrane positioned between the primary leaktightness membrane and the carrier wall, a primary thermally insulating barrier positioned between the primary leaktightness membrane and the secondary leaktightness membrane, and a secondary thermally insulating barrier positioned between the secondary leaktightness membrane and the carrier wall, and in which one or each thermally insulating barrier comprises thermally insulating parts made of expanded synthetic foam.

According to one embodiment, the vessel is equipped with a forced diffusion treatment device comprising:

- a heating device capable of heating the primary leaktightness membrane and/or the carrier wall and/or the thermally insulating barriers in order to raise the temperature of the thermally insulated parts, for example by circulation of hot gas,
- a pumping device connected to the or each thermally insulating barrier comprising the thermally insulating parts made of expanded synthetic foam and capable of reducing the total pressure of a gas phase in the or each thermally insulating barrier below standard pressure, preferably below 10 mbar,
- and a control unit capable of:
- controlling the heating device and the pumping device in order to simultaneously heat the thermally insulating parts to a discharge temperature greater than ambient temperature and exposing the thermally insulating parts to the total pressure lower than standard pressure during a discharge stage, and
- terminating the discharge stage when the accumulated partial pressures of

molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen in the insulating part is less than a predetermined threshold.

5 **Brief description of the figures**

A better understanding of the invention will be obtained and other aims, details, characteristics and advantages of the invention will become more clearly apparent during the following description of several specific embodiments of the invention, given solely by way of illustration and without limitation, with reference to
10 the appended drawings.

- figure 1 is a graph of the change in the thermal conductivity of an expanded synthetic foam as a function of the time of exposure to the ambient atmosphere.
- 15 • figure 2 is a graph analogous to figure 1 showing the influence of the aging temperature of the expanded synthetic foam.
- figure 3 is a diagrammatic view in section of a leaktight and insulating vessel in which processes according to the invention can be carried out.
- figure 4 is a diagrammatic side view of an insulating panel which
20 can be employed in the vessel of figure 3.
- figure 5 is a cutaway diagrammatic representation of a vessel of a liquid natural gas tanker and of a terminal for loading/unloading this vessel.

Detailed description of embodiments

25 In the description and the claims, the term "standard pressure" will be used as synonym for atmospheric pressure.

Processes for the treatment of an insulating part made of synthetic foam which make it possible to prevent or overcome the phenomena of aging of the foam, indeed even to improve the quality of thermal insulation of the insulating part, will
30 now be described.

For this, during the first stage, known as discharge stage, the treatment process consists in heating the insulating part to a discharge temperature greater than ambient temperature and simultaneously exposing the insulating part to a gas atmosphere exhibiting low partial pressures for molecular nitrogen and molecular oxygen, that is to say lower than their partial pressure in air at atmospheric pressure.

This stages makes it possible to accelerate the diffusion of the gases present in the foam toward the ambient medium. The foam is placed under high temperature conditions in order for the diffusion coefficients of gases present in the matrix to be increased. Furthermore, the foam is placed at reduced pressure, at least for the main gases constituting the air, in order to accelerate the diffusion of the gases present in the foam, at least molecular nitrogen and molecular oxygen, toward the external gas atmosphere.

This process can be applied to numerous varieties of expanded synthetic foams and of blowing agents. Preferably, the expanded synthetic foam comprises at least 80% of closed cells. The materials of the matrix and the blowing agents can be chosen from the polymers and agents mentioned in the introduction. By way of example, the expanded synthetic foam is in particular a thermosetting polyurethane foam comprising at least 80% of closed cells.

The discharge temperature is chosen so as not to damage the expanded synthetic foam. For this, a discharge temperature of less than 100°C is preferably chosen.

A temperature up to 100°C can be acceptable for certain polymers, such as polypropylene or polyethylene. For many synthetic polymers, the discharge temperature is preferably less than 80°C. This threshold of 80°C is, for example, preferred for a polyurethane foam, a PVC foam or a polystyrene foam, in particular in order to prevent sublimation of the polystyrene. The choice of the discharge temperature may also take into account the resistance to heat of other materials which are assembled with the insulation part, according to the characteristics of the targeted application.

Any rise in temperature is liable to increase the coefficient of diffusion of the gases. By measure of effectiveness, the discharge temperature preferably

corresponds to a substantial rise in temperature. According to one embodiment, the discharge temperature is greater than 50°C, and even greater than 60°C.

The insulating part can be heated by various heating means, for example by radiation, conduction, for example bringing into contact with a hot solid, or
5 conduction/convection, that is to say bringing into contact with a hot fluid.

According to one embodiment, the gas atmosphere of the discharge stage additionally exhibits a low partial pressure for a blowing gas used for the manufacture of the expanded synthetic foam. By virtue of these characteristics, it is also possible to decrease the concentration of the blowing gas during the discharge
10 stage, in order to reduce the thermal conductivity of the expanded foam.

It is advantageous for the implementation of this discharge stage for the insulating foam to be expanded with one or more blowing agents exhibiting a coefficient of diffusion which is as high as possible.

According to one embodiment, the blowing gas used for the manufacture of
15 the expanded synthetic foam is essentially composed of carbon dioxide. For example, the rigid polyurethane foam can be expanded with CO₂. The coefficient of diffusion of CO₂ is greater than that of the other known blowing agents, in particular blowing gases 141b, 245fa, 365, or pentane. A foam expanded with CO₂ additionally exhibits the twofold advantage of not employing gases liable to contribute strongly to
20 global warming or to the hole in the ozone layer, on the one hand, and of exhibiting the lowest production costs, on the other hand. This is because the foam expanded with CO₂ is expanded by chemical reaction of water.

For illustration, table 1 gives orders of magnitude of the coefficients of diffusion measured at ambient temperature on various polyurethane foams having a
25 density of 120 to 135 kg/m³.

Gas considered	Coefficient of diffusion 10 ⁻¹³ m ² /s
N ₂	10 to 100
O ₂	100 to 1000
CO ₂	1000 to 10000
141b	1 to 10
245fa	1 to 10

Table 1: Order of magnitude of the coefficients of diffusion

Table 2 illustrates the change in the coefficients of diffusion as a function of the temperature and shows in particular the increase in coefficient of diffusion with the temperature.

5

Gas	Effective coefficient of diffusion, $D_{eff}(10^{-12} \text{ m}^2 \cdot \text{s}^{-1})$	
	23°C (73°F)	70°C (158°F)
CO ₂	124	712
Air	3.77	71
Cyclopentane	0.128	0.418
Isopentane	0.052	0.159

Table 2: Effective coefficient of diffusion D_{eff} of different gases in a low-density PIR foam

Several techniques can be employed during the discharge stage in order to
 10 create the partial pressure gradients which make it possible to bring about the departure from the foam of the desired chemical entities, in particular molecular oxygen and molecular nitrogen and carbon dioxide.

A first technique consists in subjecting the insulation part to a reduced total pressure. According to a corresponding embodiment, the gas atmosphere of the
 15 discharge stage exhibits a total pressure which is less than standard pressure, preferably less than 10 mbar. By virtue of this reduced pressure, the external atmosphere is depleted in the gas entities liable to diffuse on a large scale into the foam. This reduced pressure can be established and maintained with a vacuum pump or other suction device. The suction makes it possible to remove, from the
 20 ambient medium, the gases which have exited from the foam as they exit from the foam. In this vacuum technique, the heating of the insulating part is advantageously carried out by direct conduction or radiation.

A second technique alternative to the first consists in immersing the insulation part in an atmosphere essentially composed of one or more gases which diffuse very poorly into the foam. According to a corresponding embodiment, the gas atmosphere of the discharge stage is a gas phase of gases having large molecules
 5 in forced convection, that is to say a gas phase of gases exhibiting a molar mass of greater than or equal to 70 g/mol.

The gas phase of gases having large molecules, insofar as it exhibits extremely low contents of molecular nitrogen and molecular oxygen, also creates a partial pressure gradient which promotes the migration of molecular nitrogen and
 10 molecular oxygen toward the outside of the insulating part. Furthermore, the convection movement makes it possible to remove, from the ambient medium, the gases which have exited from the foam as they exit from the foam.

Such a flushing with a gas, the coefficient of diffusion of which into the foam is very low, can be carried out with gases having a very large molecule, for example
 15 cyclopentane (C_5H_{10}), CF_4 gas, R-23 gas, R-508 B gas, R-134 (CH_2FCF_3) gas, 141b gas, 245fa gas, 365 gas or any other gas with a molar mass of greater than or equal to 70 g/mol.

The molar masses of several gases are represented in the table below, the gases below exhibiting a molar mass of greater than or equal to 70 g/mol being
 20 liable to be used as gas atmosphere in which the insulating part is immersed during the discharge stage.

Gas considered	Molar mass (g/mol)
N_2	28
O_2	32
CO_2	44
cyclopentane (C_5H_{10})	70
CF_4	88
R-23	70
R-508 B	95
R-134 (CH_2FCF_3)	102
141b	104

245	134
365	148

This is because it is observed that, the smaller the molar mass of a gas, the faster the phenomenon of diffusion through the foam.

The discharge stage is terminated after the partial pressures of certain of the gases initially present in the cells have reached a target value. The most important and the most damaging gases for the conductivity of the foam are molecular nitrogen and molecular oxygen, and possibly CO₂, for example if it was employed as blowing agent. It is thus appropriate to terminate the discharge stage when the accumulated partial pressures of at least molecular nitrogen and molecular oxygen in the insulating part is less than a predetermined threshold.

10 According to one embodiment, the predetermined threshold is less than or equal to 30 mbar for the accumulated partial pressures of molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen. This threshold corresponds approximately to a foam containing 3% of air.

15 Such a condition can be detected by direct or indirect experimental measurement and/or by calculation, in particular by numerical modeling. According to an embodiment corresponding to a direct measurement, the molecular nitrogen and molecular oxygen are assayed in the insulating part during the discharge stage and the discharge stage is halted when the concentrations of molecular nitrogen and
20 molecular oxygen measured in the insulating part cross the desired thresholds.

According to an embodiment corresponding to an indirect measurement, one or more physical properties related to the concentration of molecular nitrogen and molecular oxygen in the insulating part, such as the thermal conductivity of the foam, is/are measured and the discharge stage is halted when the property
25 measured reaches a value which has been otherwise determined, experimentally or by modeling, to correspond to the desired concentration.

According to one embodiment, the discharge stage is halted after a predetermined time which has been determined by calculation, in particular by numerical modeling, taking into account the thermodynamic conditions of the

treatment and the physical properties of the foam and of the chemical entities present.

This forced diffusion treatment process can be applied to any type of insulating part made of expanded foam. This forced diffusion treatment process can
5 be carried out either in a dedicated treatment plant, for example in a factory for the manufacture of insulating parts, or directly in the environment in which the insulating part is used.

According to one embodiment, the insulating part comprises projections or holes, small in dimension, which increase the exchange surface area of the
10 insulating part with the gas atmosphere. By virtue of these characteristics, the foam part exhibits a high Volume/Exchange Surface Area ratio, so as to promote the diffusion phenomena during the discharge stage. For this, the foam part exhibits, for example, grooves with a thickness of the order of a millimeter or indents with a small diameter, for example approximately 2 mm, carefully distributed in order to facilitate
15 the diffusion of the gases without the risk of the creation of gas convection regions. These projections or holes can in particular be arranged in the width or the length of a parallelepipedal panel.

According to one embodiment, the insulating part is positioned in a leaktight and thermally insulating vessel wall and forms an insulating barrier of the vessel
20 wall. The insulating part made of expanded foam can in particular form a constituent part of a prefabricated insulating panel installed in the thickness of the wall of the vessel, for example in a liquid natural gas tanker. It should be noted, by way of illustration, that examples of such prefabricated panels are described in the publication FR-A-2781557.

25 According to a corresponding embodiment, the discharge stage comprises the stage of heating all or part of the vessel wall. In the case of a vessel intended to contain a cold product, for example a liquefied gas vessel, this heating of the vessel wall has to be carried out while the vessel is empty. Such a heating can be obtained by numerous means, for example by radiative heating, conductive heating or
30 conductive/convective heating. According to one embodiment, an internal surface and/or an external surface of the vessel wall is exposed to a hot gas atmosphere.

According to a preferred embodiment, the process additionally comprises one or more diffusion-inhibiting actions applied to the insulating part during an

operational stage subsequent to the discharge stage, said or each inhibiting action being effective in slowing down gas diffusion toward the interior of the expanded material part. By virtue of these characteristics, after the discharge stage, the entry or the reentry of the ambient gases into the foam when it is subsequently made use
5 of is prevented or slowed down.

Preferably, the diffusion-inhibiting action or actions are actions which are substantially continuous over time, so as to lastingly prevent or slow down the penetration of air or other ambient gases by diffusion into the synthetic foam. For this, different inhibiting actions can be used alternatively or in combination. Several
10 inhibiting actions can be used in combination by being used simultaneously in time or by being used successively in time during successive periods of the operational stage of the insulating part.

Three embodiments of the inhibiting actions are presented below by way of illustration.

15 According to a first embodiment, the inhibiting action consists in exposing the insulating part to a gas atmosphere, the total pressure of which is kept below standard pressure, preferably below 10 mbar. By virtue of these characteristics, the foam is maintained in a space at reduced pressure. As the ambient gases then have very low partial pressures, their miniscule diffusion no longer impacts the
20 conductivity of the foam.

According to a second embodiment, the inhibiting action consists in maintaining the insulating part at a temperature of less than 0°C, preferably of less than -20°C. By virtue of these characteristics, the foam is maintained under reduced temperature conditions at which the coefficients of diffusion of the ambient gases
25 into the matrix are much lower than they are during the discharge stage. As the diffusion phenomenon is for this reason extremely small, the migration of the ambient gas toward the cells can be greatly slowed down until kinetics are reached, the effect of which on the duration of use of the insulation is negligible.

Figure 2 illustrates the effects of the low temperatures on the change in the
30 thermal conductivity over time. The thermal conductivity, expressed on the axis of the ordinates in W/mK, is plotted as a function of the aging time, expressed on the axis of the abscissae in days. The example relates to a PU foam with a density of 40 kg/m³. On curves 3 and 4, the thermal conductivity is measured at a positive

temperature of +20°C. On the curves 5 and 6, the thermal conductivity is measured at a negative temperature of -120°C, which produces much lower values.

On the curves 3 and 5, the aging of the foam took place at a positive temperature +20°C. On the curves 4 and 6, the aging of the foam took place at a negative temperature of -20°C. Thus, the effect of the cold as retarder of gas diffusion is very substantial over a period of at least 60 days. The aging of a high-density foam produces analogous observations starting from a higher initial thermal conductivity ranging from 0.024 W/mK for a foam, the blowing gases of which are HFC and 141b, to 0.027 W/mK, for a foam expanded with CO₂.

10 According to a third embodiment, the inhibiting action consists in exposing the insulating part to a gas atmosphere essentially composed of a chemical entity having large weakly diffusive molecules. By virtue of these characteristics, the foam is maintained in a non-diffusive gas environment.

It is preferable to choose gases which exhibit the following properties: a very low coefficient of diffusion into the matrix of the foam, a low thermal conductivity, and densities and viscosities which greatly limit thermal convection. Gases which can be employed for this are in particular CF₄, R-23 gas, R-508 B gas, R-134 (CH₂FCF₃) gas, 141b gas, 245fa gas, 365 gas or any other gas with a molar mass greater than or equal to 70 g/mol. The choice among the abovementioned gases can in particular be made as a function of the temperature and pressure conditions in the operating environment. This is because it is advisable for the gas chosen to be in the vapor phase under the temperature and pressure conditions of the operating environment. Consequently, in order to keep these substances in the vapor phase, it may be necessary to simultaneously maintain a relatively low pressure in the operating environment of the insulating part, for example in the primary or secondary insulating barrier of a wall of a vessel for liquefied natural gas. By way of illustration, gases which are particularly appropriate for an operating environment in a primary or secondary insulating barrier of a wall of a vessel for liquefied natural gas are in particular the gases HFC R-508-B and HFC R-23 at a temperature of approximately -100°C to -120°C and CF₄ at a lower temperature.

By way of illustration, the saturated vapor pressure of HFC R23 gas is 60 mbar at -120°C. The saturated vapor pressure of CF₄ gas at -160°C is 30 mbar and at -120°C is 1.15 bar.

Embodiments of the process which are applied to blocks of expanded foam which can be used in the manufacture of a thermal insulation barrier arranged in the thickness of a wall of a vessel for liquefied gas will now be described.

According to an embodiment represented in figure 3, a leaktight and thermally insulating vessel 10 intended to contain a liquefied fuel gas at low temperature exhibits a prismatic shape and is incorporated in a carrier structure formed by the double hull of a tanker. The external wall and the internal wall of the double hull forming the carrier structure are designated by the numbers 11 and 12 in figure 3. A ballast space 13 is defined between the two walls 11 and 12.

As shown diagrammatically in figure 3, a wall of the vessel comprises a multilayer structure fitted to the carrier wall 12. The multilayer structure comprises a primary leaktightness membrane 15 in contact with the liquefied fuel gas present in the vessel, a secondary leaktightness membrane 16 positioned between the primary leaktightness membrane 15 and the carrier wall 12, a primary thermally insulating barrier 17 positioned between the primary leaktightness membrane 15 and the secondary leaktightness membrane 16, and a secondary thermally insulating barrier 18 positioned between the secondary leaktightness membrane 16 and the carrier wall 12.

There exists numerous materials which can be employed in the thermally insulating barriers. In the embodiment under consideration, one or each of the thermally insulating barriers 17 and 18 comprises thermally insulating parts made of expanded synthetic foam.

In one embodiment, the constituent foam of the insulating blocks is treated once installed on board but in a phase preceding the cooling of the vessels of the tanker. For this, the foam blocks are heated to a discharge temperature at which the foam and the optional components used in combination with the foam, for example commonly used materials, such as plywood, glass wool and triplex, are not damaged by the heat. According to a preferred embodiment, this temperature varies from 60 to 80°C approximately. Thus, the coefficients of diffusion of the gases present in the foam are increased in order to reduce the duration of the forced diffusion treatment.

For this, it is possible to reheat the interior space 20 of the vessel and optionally the ballast spaces 13 to the desired temperature using a blowing

installation 21, for example blowing hot air or exhaust gases recovered from an installation for the propulsion of the tanker. Other heating means can also be employed. Figure 3 diagrammatically shows a blowing pipe 22 emerging in the interior space 20 and a blowing pipe 23 emerging in the ballast space 13 for this
5 purpose.

The or one of the insulation spaces 17 and 18 thus reheated are also placed at reduced pressure, for example between 0.1 mbar and 10 mbar, in order to increase the pressure gradient which is the motor of the diffusion of the gases present in the foam, that is to say to ensure that the ambient medium of the foam
10 exhibits partial pressures which are sufficiently low for the gases exiting from the foam to substantially empty the cells of the gas which the cells contain. For this, it is possible to employ a vacuum pump 25 arranged in order to extract the gas phase from the primary thermally insulating barrier 17 and/or from the secondary thermally insulating barrier 18. Figure 3 diagrammatically shows a suction pipe 26 emerging in
15 the primary space and a suction pipe 27 emerging in the secondary space for this purpose.

The diffusion of the gases is forced by the temperature and the concentration gradient until a satisfactory level is obtained. This discharge stage can be automatically guided by an electronic control unit 30 controlling the vacuum
20 pump 25 and the blowing installation 21 by making use of various feedback parameters 31, for example physical measurements taken in the vessel by pressure, temperature, gas analysis or other sensors.

This discharge stage is preferably followed by diffusion-inhibiting actions which make it possible to keep the cells of the foam substantially devoid of gases
25 damaging the thermal conductivity.

One possibility of action is to maintain the gas of the insulation spaces at a reduced pressure throughout the operation of the tanker, in order to reduce the partial pressures of the entities liable to migrate into the foam.

One possibility of action is to cool the vessel so that the insulation foam is
30 placed under reduced temperature conditions. The reduction in these temperatures makes it possible to very greatly lower the coefficients of diffusion of the ambient gases into the foam, even if the insulation spaces 17 and 18 are placed back at atmospheric pressure. Each insulation space can thus be flushed with nitrogen

vapor without risk of damaging the thermal conductivity properties of the foam, as long as the vessels of the tanker are under cold conditions.

One possibility of action when the tanker returns to virtually ambient temperature conditions, that is to say when the vessels are empty, is to again
5 produce the vacuum with the vacuum pump 25, without necessarily simultaneously heating the vessel wall. This makes it possible to prevent diffusion of the ambient gas into the foam and to optionally empty the peripheral layers of the foam of the flushing gas which would have been able to diffuse in a reduced amount.

Another possibility of action is to fill the insulation space with a gas
10 exhibiting a coefficient of diffusion into the matrix of the foam which is as low as possible.

In order to improve the effect of the abovementioned inhibiting actions, it is also possible to apply a facing which is leaktight to the gas or which has a low coefficient of diffusion of the gases to the external surfaces of the foam which are
15 exposed to the ambient gases. Such a facing is put in place before the installation of foam blocks in the vessel wall, for example in a manufacturing plant where the forced diffusion treatment of the foam blocks has been carried out beforehand. The facing can then remain in place throughout the operating life of the insulating part.

According to one embodiment, illustrated in particular in figure 4, the
20 insulating part is a flat parallelepipedal foam block 40, the surface of which exhibits two main faces 43, 44 parallel to directions of length and of width of the block and mutually separated in a direction of thickness of the block, and peripheral faces 41, 42 which are smaller than the main faces and which extend along the direction of thickness of the block between the two main faces. The leaktight coating 45 exhibits
25 here the form of a strip positioned longitudinally on the peripheral faces 41, 42 of the block all around the block and exhibiting a width which is less than the thickness of the block.

According to the embodiment of figure 4, this leaktight coating is positioned solely on the surfaces of the foam block 40 which are exposed to a temperature of
30 greater than -20°C in service, that is to say the portions close to the double hull 11, 12. For example, the width of the strip 45 is between 3 and 6 cm and ideally 4.5 cm for a secondary insulation barrier made of high density PU foam.

The gastight coating can be produced in several ways. For example, the gastight coating comprises a layer of polymer resin and/or of paint positioned on the external surface of the insulating part and/or a metal sheet, for example with a thickness of a few microns, adhesively bonded to the external surface of the
5 insulating part. Such a metal sheet can be made of aluminum or other metals.

In the embodiment of figure 4, the foam block 40 is employed within a prefabricated insulating panel 50, the structure of which is otherwise known and which will now be recalled.

The panel 50 has substantially the shape of a rectangular parallelepiped; it
10 is composed of a first sheet 51 of plywood or of a composite material with a thickness of 9 mm surmounted by the foam block 40, itself surmounted by a leaktight composite material layer 52 intended to form the secondary membrane 16. A second foam block 53 is positioned on the leaktight layer 52, which foam block itself carries a second sheet of plywood 54 with a thickness of 12 mm. The
15 subassembly 53, 54 is intended to constitute an element of the primary insulation barrier 17. It has, seen in plan, a rectangular shape, the sides of which are parallel to those of the subassembly 51, 40, 52. The two subassemblies have, as seen in plan, the shape of two rectangles having the same center. A peripheral rim 57, of constant width, exists all around the subassembly 53, 54 and is composed of the
20 edge of the subassembly 51, 40, 52. The leaktight layer 52 is, for example, made of a multilayer composite composed of one or more metal sheets and of one or more glass fiber mats impregnated with polymer resin.

The technique described above for preventing the aging of the insulation parts can be used in different types of tanks, for example in an LNG tank in an
25 onshore installation or in a floating structure, such as a liquid natural gas tanker or other.

A vessel equipped with a forced diffusion treatment device as illustrated in figure 3 can also be produced in the form of an onshore storage installation, for example for storing LNG, or be installed in an inshore or deep-water floating
30 structure, in particular a liquid natural gas tanker, a floating storage regasification unit (FSRU), a floating production storage and offloading unit (FPSO) and others.

According to one embodiment, a tanker for the transportation of a cold liquid product comprises a double hull and an abovementioned vessel positioned in the double hull.

According to one embodiment, the invention also provides a process for the
 5 loading or unloading of such a tanker, in which a cold liquid product is conveyed through insulated pipes from or to a floating or onshore storage installation to or from the vessel of the tanker.

According to one embodiment, the invention also provides a transfer system for a cold liquid product, the system comprising the abovementioned tanker,
 10 insulated pipes arranged so as to connect the vessel installed in the hull of the tanker to a floating or onshore storage installation and a pump for entraining a stream of cold liquid product through the insulated pipes from or to the floating or onshore storage installation to or from the vessel of the tanker.

With reference to figure 5, a cutaway view of a liquid natural gas tanker
 15 shows a leaktight and insulated vessel 71 of prismatic general shape fitted in the double hull 72 of the tanker. The wall of the vessel 71 comprises a primary leaktight barrier intended to be in contact with the LNG present in the vessel, a secondary leaktight barrier arranged between the primary leaktight barrier and the double hull 72 of the tanker, and two insulating barriers respectively arranged between the
 20 primary leaktight barrier and the secondary leaktight barrier and between the secondary leaktight barrier and the double hull 72.

In a way known per se, loading/unloading pipes 73 positioned on the main deck of the tanker can be connected, by means of appropriate connectors, to a maritime or harbor terminal in order to transfer an LNG cargo from or to the vessel
 25 71.

Figure 5 represents an example of a maritime terminal comprising a loading and unloading station 75, an underwater pipeline 76 and a land-based facility 77. The loading and unloading station 75 is an offshore facility comprising a movable arm 74 and a tower 78 which supports the movable arm 74. The movable arm 74
 30 carries a bundle of insulated hoses 79 which can be connected to the loading/unloading pipes 73. The adjustable movable arm 74 adjust to all liquid natural gas tanker dimensions. A connecting pipeline (not represented) extends inside the tower 78. The loading and unloading station 75 makes possible the

loading and the unloading of the liquid natural gas tanker 70 from or to the land-based facility 77. The latter comprises liquefied gas storage tanks 80 and connecting pipelines 81 linked via the underwater pipeline 76 to the loading or unloading station 75. The underwater pipeline 76 makes it possible to transfer the
5 liquefied gas between the loading or unloading station 75 and the land-based facility 77 over a great distance, for example 5 km, which makes it possible to keep the liquid natural gas tanker 70 at a great distance from the coast during the loading and unloading operations.

In order to generate the pressure necessary for the transfer of the liquefied
10 gas, pumps onboard the tanker 70 and/or pumps equipping the land-based facility 77 and/or pumps equipping the loading and unloading station 75 are employed.

Although the invention has been described in connection with several specific embodiments, it is very obvious that it is in no way limited thereto and that it comprises all the technical equivalents of the means described and also of their
15 combinations, if the latter come within the context of the invention.

The use of the verb "to comprise" or "to include" and of its conjugated forms does not exclude the presence of other elements or other stages than those set out in a claim. The use of the indefinite article "a" or "an" for an element or a stage does not exclude, unless otherwise mentioned, the presence of a plurality of such
20 elements or stages.

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

CLAIMS

1. A process for the forced diffusion treatment of a thermally insulating part (40) made of expanded synthetic foam positioned in a leaktight and thermally insulating vessel wall and forming an insulating barrier of the vessel wall, said process comprising:

during a discharge stage, heating all or part of the vessel wall so as to heat the insulating part to a discharge temperature greater than ambient temperature and simultaneously exposing the insulating part to a gas atmosphere exhibiting low partial pressures for molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen, said low partial pressures being, for each of these substances, lower than the partial pressure of said substance in air at standard pressure,

terminating the discharge stage when the accumulated partial pressures of molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen in the insulating part is less than a predetermined threshold or when a physical property of the insulating part related to said accumulated partial pressures reaches a predetermined threshold or after a predetermined time.

2. The process as claimed in claim 1, in which the expanded synthetic foam comprises at least 80% of closed cells.

3. The process as claimed in claim 1 or 2, in which the expanded synthetic foam is a polyurethane foam.

4. The process as claimed in claim 3, in which the polyurethane foam is a thermosetting foam.

5. The process as claimed in one of claims 1 to 4, in which the discharge temperature is less than 100°C, preferably less than 80°C.

6. The process as claimed in one of claims 1 to 5, in which the discharge temperature is greater than 50°C.

7. The process as claimed in one of claims 1 to 6, in which the blowing gas used for the manufacture of the expanded synthetic foam is essentially composed of carbon dioxide.

8. The process as claimed in one of claims 1 to 7, in which the gas atmosphere of the discharge stage exhibits a total pressure which is less than standard pressure, preferably less than 10 mbar.

9. The process as claimed in one of claims 1 to 7, in which the gas atmosphere of the discharge stage is a gas phase of gases exhibiting a molar mass of greater than or equal to 70 g/mol in forced convection.

10. The process as claimed in one of claims 1 to 9, in which the predetermined threshold is less than or equal to 30 mbar for the accumulated partial pressures of molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen.

11. The process as claimed in one of claims 1 to 10, in which the insulating part comprises projections or holes, small in dimension, which increase the exchange surface area of the insulating part with the gas atmosphere.

12. The process as claimed in one of claims 1 to 11, additionally comprising:
a diffusion-inhibiting action applied to the insulating part during an operational stage subsequent to the discharge stage, said inhibiting action being effective in slowing down gas diffusion toward the interior of the expanded material part.

13. The process as claimed in claim 12, in which the inhibiting action consists in exposing the insulating part to a gas atmosphere, the total pressure of which is kept below standard pressure, preferably below 10 mbar.

14. The process as claimed in claim 12 or 13, in which the inhibiting action consists in exposing the insulating part to a gas atmosphere essentially composed of a chemical entity exhibiting a molecular weight of greater than or equal to 70 g/mol.

15. The process as claimed in one of claims 12 to 14, in which the inhibiting action consists in maintaining the insulating part at a temperature of less than 0°C, preferably of less than -20°C.

16. The process as claimed in any one of claims 1 to 15, in which the insulating part comprises a gastight coating (45) positioned on an external surface of the insulating part.

17. The process as claimed in claim 16, in which the gastight coating comprises a layer of polymer resin and/or a metal sheet positioned on the external surface of the insulating part.

18. The process as claimed in claim 16 or 17, in which the insulating part is a flat parallelepipedal foam block (40), the surface of which exhibits two main faces (43, 44) parallel to directions of length and of width of the block and mutually separated in a direction of thickness of the block, and peripheral faces (41, 42) which are smaller than the main faces and which extend along the direction of thickness of the block between the two main faces, in which the leaktight coating exhibits the form of a strip (45) positioned longitudinally on the peripheral faces (41, 42) of the block all around the block and exhibiting a width which is less than the thickness of the block.

19. A leaktight and thermally insulating vessel (71) intended to contain a liquefied fuel gas at low temperature,
in which a wall of the vessel comprises a multilayer structure fitted to a carrier wall (12), the multilayer structure comprising a primary leaktightness membrane (15) in contact with the liquefied fuel gas present in the vessel, a secondary leaktightness membrane (16) positioned between the primary leaktightness membrane and the carrier wall, a primary thermally insulating barrier (17) positioned between the primary leaktightness membrane and the secondary leaktightness membrane, and a secondary thermally insulating barrier (18) positioned between the secondary leaktightness membrane and the carrier wall, and in which one or each thermally insulating barrier comprises thermally insulating parts made of expanded synthetic foam, characterized in that the vessel is equipped with a forced diffusion treatment device comprising:

a heating device (21, 22, 23) capable of heating the primary leaktightness membrane and/or the carrier wall and/or the thermally insulating barriers in order to raise the temperature of the thermally insulated parts,

a pumping device (25, 26, 27) connected to the or each thermally insulating barrier comprising the thermally insulating parts made of expanded synthetic foam and

capable of reducing the total pressure of a gas phase in the or each thermally insulating barrier below standard pressure, preferably below 10 mbar,

and a control unit (30) capable of:

controlling the heating device and the pumping device in order to simultaneously heat the thermally insulating parts to a discharge temperature greater than ambient temperature and exposing the thermally insulating parts to the total pressure lower than standard pressure during a discharge stage, and

terminating the discharge stage when the accumulated partial pressures of molecular nitrogen, molecular oxygen, carbon dioxide and the gases having a coefficient of diffusion into the expanded synthetic foam which is greater than or equal to that of molecular nitrogen in the insulating parts is less than a predetermined threshold.