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(54) Title : FLEXIBLE UNDERWATER PIPE INCLUDING A LAYER INCLUDING A POLYETHYLENE HAVING ENHANCED HEAT RESISTANCE

(54) Titre : CONDUITE FLEXIBLE SOUS MARINE COMPRENANT UNE COUCHE COMPRENANT UN POLYÉTHYLÈNE À RÉSISTANCE THERMIQUE ACCRUE

(57) Abstract : The invention relates to a flexible underwater pipe for transporting hydrocarbons, including a plurality of layers, at least one of which includes a polyethylene having enhanced heat resistance. The invention further relates to the method for producing same and to the use thereof for transporting hydrocarbons.

(57) Abrégé : L'invention concerne une conduite flexible sous marine destinée au transport de d'hydrocarbures, comprenant une pluralité de couches dont au moins une couche comprend un polyéthylène à résistance thermique accrue, son procédé de préparation et son utilisation pour le transport d'hydrocarbures.

Flexible underwater pipe including a layer including a polyethylene having enhanced heat resistance

5 The present invention relates to a flexible underwater pipe intended for transport of hydrocarbons in deep water.

Flexible pipes for transporting hydrocarbons generally include from the outside towards the inside of the pipe:

- 10 - an external polymeric sealing sheath for protecting the whole of the pipe and notably for preventing seawater from penetrating into its thickness,
- plies of tensile armors,
- a pressure vault,
- an internal polymeric sealing sheath, and
- optionally a metal carcass (figure).

15

If the pipe comprises a metal carcass, it is said to be a rough-bore pipe. If the conduit is free from metal carcass, it is said to be a smooth-bore pipe. Generally for transporting hydrocarbons, a pipe including a carcass is preferred, while a pipe free from carcass will be suitable for transporting water and/or pressurized steam.

20

The metal carcass and the pressure vault consist of longitudinal elements wound with a short pitch, and they give the pipe its resistance to radial forces while the plies of tensile armors consist of metal wires wound according to long pitches in order to spread the load of the axial forces.

25

The nature, the number, the dimensioning and the organization of the layers making up the flexible pipes are essentially related to their conditions of use and installation. The pipes may comprise layers in addition to the aforementioned ones, for example one or several intermediate polymeric layers (a so called "intermediate polymeric sheath") which are located between two aforementioned adjacent layers and which participate in isolating the flexible pipe.

30

In the present application, the notion of winding with a short pitch refers to any helical winding according to a helix angle close to 90°, typically comprised between 75° and 90°. The notion of a winding with a long pitch, as for it, covers helix angles of less than 55°, typically comprised between 25° and 55° for armor plies.

35

These flexible pipes are notably suitable for transporting fluids, notably hydrocarbons in sea beds and this, at great depths. More specifically, they are said to be of the unbonded type and they are thus described in normative documents published by

the American Petroleum Institute (API), API 17J (3rd edition – January 1st 2009) and API RP 17B (3rd edition – March 2002).

5 The flexible pipes may be used at a great depth, typically down to 2,500 meters of depth and advantageously down to 3,000 meters. They allow transport of fluids, notably of hydrocarbons, having a temperature typically attaining 130°C and which may even exceed 150°C and at an internal pressure which may attain 1,000 bars, or even 1,500 bars.

10 The constitutive material of the polymeric sealing sheath has to be chemically stable and capable of mechanically withstanding the transported fluid and its characteristics (composition, temperature and pressure). The material should combine characteristics of ductility, of resistance over time (generally the pipe should have a lifetime of at least 20 years), of mechanical strength to heat and pressure. The material should notably be chemically inert towards chemical compounds forming the transported fluid. Typically, the transported hydrocarbons comprise crude oil, water and pressurized
15 gases.

Various polymeric materials are used as an internal, intermediate or external sealed polymeric sheath, in particular polyethylene (PE), either cross-linked or not. The polyethylene may notably be high density polyethylene (HDPE).

20 For example, patent application CA 2,064,226 (COFLEXIP) describes a flexible tubular pipe for transporting hydrocarbons comprising an internal sealing sheath comprising a silane-grafted polyethylene and cross-linked by hydrolysis and coupling of the silanes. Application WO 03/078134 (NKT FLEXIBLES) describes a flexible tubular pipe for transporting hydrocarbons comprising a sealing sheath comprising a cross-linked
25 polyethylene by treatment of peroxides with electromagnetic radiations. Application WO 2004/065092 (WELLSTREAM INTERNATIONAL LIMITED) describes a flexible tubular pipe for transporting hydrocarbons comprising a sealing sheath comprising a cross-linked polyethylene by irradiation with electron beams.

30 Nevertheless, a sheath based on polyethylene may be subject to the blistering phenomenon. In a flexible pipe, the sealing sheath in polymeric material is used for transporting fluids consisting of crude oil, water and pressurized gas and at a temperature. Under these conditions of use, the polymeric material of the sealing sheath absorbs the gases contained in the petroleum fluid depending on their chemical nature (via their solubility coefficient) and on the partial pressure of each of them. The saturation time of
35 the polymer, equilibration of the system, as for it depends on the diffusion coefficients and therefore essentially on the temperature. If the pressure in the flexible pipe were to be

reduced, the absorbed gases would tend to be extracted from the polymer in order to maintain the equilibrium between the internal and external concentrations. If the breaking of the equilibrium is very rapid, more rapid than the diffusion rate of the gases out of the polymer (like in the case of a production shutdown), the system is no longer at equilibrium.

5 Oversaturation of gas in the polymeric sheath leads to gas concentration and temperature gradients which may generate a more or less significant sudden expansion of gases (rapid gas decompression) which may generate irreversible damage such as the occurrence of blisters or cracks or even the formation of microporosity uniformly distributed in the thickness of the material. Thus, the occurrence of blisters is due to trapping of soluble gases within the sheath or to the too rapid decompression of the pipe not allowing the gas to diffuse out of the sheath. This blistering phenomenon may be a catastrophe for the sealing sheath, and therefore for the flexible pipe which contains it, since it may lead to the loss of its sealing function.

15 Typically, the blistering phenomenon is observed for a sealing sheath based on polyethylene, either cross-linked or not, in contact with a petroleum fluid including corrosive gases which may diffuse within the sheath, under a high pressure (greater than 200 bars) at a temperature of the order of 60°C for non-cross-linked polyethylenes, and 90°C for cross-linked polyethylenes. Thus, in order to guarantee a lifetime of at least 20 years of the flexible pipe, for a pressure of 200 bars, a flexible pipe for which one sealing sheath is in non-cross-linked or cross-linked polyethylene cannot be used at temperatures greater than 60°C and 90°C respectively.

Therefore, alternative polymeric materials to polyethylene were developed for internal, intermediate or external polymeric sealing sheaths, notably:

25 - polyamide (PA), notably polyamide 11. Unlike polyethylene, polyamide has good resistance to blistering, as well as a low tendency to swell when it is in contact with petroleum fluid. The polyamide is generally used for hydrocarbon transport conditions for which the pressure is high and where the temperature may be rise up to 110°C.

30 On the other hand, one of the drawbacks of polyamide is that it tends to hydrolyze in the presence of water (often contained in production crudes). Hydrolysis is rapid when it is subject to temperatures (of the order of 110°C and more) and to high pH values (pH greater than 7). Another drawback is its purchase cost which is substantially greater than that of polyethylene.

35 - polyvinylidene fluoride (PVDF) (which contains more or less plasticizer depending on the grade used) has very good chemical inertia. Sheaths based on PVDF may support high operating pressures as well as temperatures which may attain 130 to 150°C.

Its major drawback remains its price, much higher than that of polyethylene or polyamide.

Thus, the internal, intermediate or external polymeric sealing sheaths based on polyamide or polyvinylidene fluoride are less subject to a blistering phenomenon than sheaths based on polyethylene, either cross-linked or not, but they are more expensive and more subject to degradation by hydrolysis in the case of a sheath based on polyamide.

One of the objects of the present invention is to provide a flexible underwater pipe for transporting hydrocarbons, for which the internal, intermediate and/or external polymeric sealing sheath(s) is(are) less subject, or even not at all, to a blistering phenomenon, and for higher temperatures and/or pressures than pipes comprising sheaths based on polyethylene, either cross-linked or not, while retaining the mechanical properties of the sheath(s).

For this purpose, according to a first object, the invention relates to a flexible underwater pipe intended for transporting hydrocarbons, comprising a plurality of layers, at least one layer of which comprises a polyethylene with enhanced heat resistance (PE-RT).

The inventor actually discovered that a layer comprising a polyethylene with enhanced heat resistance is less subject, or even not at all, to a blistering phenomenon than a layer based on polyethylene, either cross-linked or not, presently used as a sealing sheath of a flexible pipe, and this even at higher temperatures and/or pressures. Such a layer is therefore particularly suitable for being used a sealing sheath in a flexible pipe.

Polyethylenes with enhanced heat resistance or polyethylenes of raised temperature resistance ("polyethylene raised temperature" or "polyethylene of raised temperature" or "polyethylene of raised temperature resistance" PE-RT) are defined in the standards: ASTM F2769-10 revised in 2010, ASTM F2623 revised in 2008 or the ISO 1043-1 standards revised in 2011, ISO 24033 standard revised in 2009 and ISO 22391 standard revised in 2009 and the ISO 15494 standard revised in 2003 for applications.

Polyethylenes with enhanced heat resistance of type I or of type II may be used in the layer of the pipe, those of type II (with higher density) being preferred because they generally better withstand high pressures and/or temperatures.

Polyethylenes with enhanced heat resistance are high density polyethylenes (HDPE) obtained by polymerization in the presence of specific catalysts of ethylene and of one or several α -olefin co-monomers including at least three carbon atoms, generally from 3 to 14 carbon atoms, preferentially from 4 to 12 carbon atoms, more preferentially from 6 to 10 carbon atoms and even more preferentially from 6 to 8 carbon atoms (which leads to polyethylenes with enhanced heat resistance, the side chains of which generally have 1 to 12 carbon atoms, preferably from 2 to 10 carbon atoms, more preferentially from 4 to 8 carbon atoms and even more preferentially from 4 to 6 carbon atoms). Thus, the co-monomers polymerized in the presence of ethylene may be propylene, 1-butene, isobutylene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene. The layer of the flexible pipe according to the invention typically comprises a polyethylene with enhanced heat resistance obtained by polymerization of ethylene and of an α -olefin selected from 1-butene, 1-hexene and 1-octene, preferably 1-hexene and 1-octene. Such polyethylenes with enhanced heat resistance therefore have ethyl, n-butyl or n-hexyl, preferably n-butyl or n-hexyl side chains.

The polyethylenes with enhanced heat resistance are not cross-linked polyethylenes.

Methods for preparing polyethylene with enhanced heat resistance applying specific catalysts, are known from the literature, and are for example described in patent applications EP 0 416 815, WO 94/03509, EP 0 100 879. By using dedicated catalysts it is possible to obtain copolymers derived from ethylene/ α -olefin monomers and the molecular structures of which (controlled distribution of the co-monomer) and crystalline structures give them high performances in terms of resistance to hydrostatic pressure up to high temperatures for non-cross-linked polyolefins. These performances ensure that the polyethylenes with enhanced heat resistance are mainly used in pipes for transporting pressurized cold and hot water, both for domestic applications and industrial applications.

Typically, the polyethylenes with enhanced heat resistance used in the layer of the flexible pipe according to the invention have:

- a density (according to ASTM D1505 revised in 2010 or ISO 1183 revised in 2012) comprised between 0.930 g/cm^3 and 0.965 g/cm^3 , preferentially between 0.935 g/cm^3 and 0.960 g/cm^3 and even more preferentially between 0.940 g/cm^3 and 0.955 g/cm^3 ,
- a melt index (according to ASTM D1238 revised in 2010 or ISO 1133 revised in 2011) measured at 190°C under a mass of 2.16 kg comprised between 0.1 g/10 minutes and 15 g/10 minutes, preferentially between 0.1 g/10 minutes and 5 g/10 minutes and even more preferentially between 0.1 g/10 minutes and 1.5 g/10 minutes,

- a tensile yield strength (according to ASTM D638 revised in 2010 or ISO 527-2 revised in 2012) comprised between 15 and 35 MPa, preferentially between 20 and 30 MPa and even more preferentially between 25 and 30 MPa,
- an elongation at break (according to ASTM D638 revised in 2010 or ISO 527-2 revised in 2012) at least greater than 50%, preferentially greater than 300% and even more preferentially greater than or equal to 500%.

The polyethylenes with enhanced heat resistance which may be used in the layer of the flexible pipe according to the invention are notably marketed by Dow Chemical (Dowlex 2377, Dowlex 2388, Dowlex 2344, DGDA-2399), by Total Petrochemical (XSene XRT70), by Chevron Phillips (Marlex HP076, HHM4903), by Exxon Mobil (HD6704) and by Lyondellbasell (Hostalen 4731 B).

The polyethylenes with enhanced heat resistance used in the layer of the flexible pipe according to the invention, for which:

- the melt index (according to ASTM D1238 revised in 2010 or ISO 1133 revised in 2011) measured at 190°C under the mass of 5.0 kg is less than 2.0 g/10 min, and
- the density (according to ASTM D1505 revised in 2010 or ISO 1183 revised in 2012) is greater than 0.945 g/cm³,

are particularly preferred, since the layer comprising such a polyethylene with enhanced heat resistance particularly well withstands the blistering phenomenon, and this even at high pressures and temperatures encountered during the use of a flexible pipe comprising such a layer for underwater transport of hydrocarbons. Typically, such a layer may actually withstand the blistering phenomenon at pressures greater than 400 bars and at temperatures above 90°C. The inventors have shown that blisters generally appear at lower temperatures and pressures when a layer comprising a polyethylene with enhanced heat resistance which does not have these density and/or melt index characteristics, is used.

Preferably, the tensile yield strengths and the elongations at break of these polyethylenes with enhanced heat resistance are compliant with those described above.

Among polyethylenes with enhanced heat resistance with a density of more than 0.945 g/cm³, those are preferred for which the melt index (according to ASTM D1238 revised in 2010 or ISO 1133 revised in 2011) measured at 190°C under a mass of 5.0 kg is less than 1.0 g/10 min since the resistance to the blistering phenomenon of a layer comprising them is enhanced. Generally, the melt index measured at 190°C under a mass

of 2.16 kg is then less than 0.25 g/10 min and/or the melt index measured at 190°C under a mass of 21.6 kg is less than 20 g/10 min.

These polyethylenes with enhanced heat resistance are notably marketed by Dow Chemical (DGDA-2399), by Total Petrochemical (XSene XRT70), by Chevron Phillips (HHM-TR457) and by Lyondellbasell (Hostalen 4731 B).

The layer comprising a polyethylene with enhanced heat resistance of the pipe according to the invention typically comprises:

- a polymeric matrix, and
- optionally discontinuously dispersed components in the polymeric matrix.

By "polymeric matrix", is meant the continuous polymeric phase which forms the layer. The polymeric matrix is a continuous matrix. The layer may optionally comprise discontinuously dispersed components in the polymeric matrix, but which are not part of the polymeric matrix. Such components may for example be fillers such as fibers.

The polymeric matrix of the layer is generally obtained by extrusion of one or several polymers (which will form the polymeric matrix) and optionally of additives (master mixture). During extrusion, certain additives are incorporated into the polymeric matrix, while others do not mix with the polymers forming the polymeric matrix and are discontinuously dispersed in the polymeric matrix, in order to form discontinuously dispersed components in the polymeric matrix.

According to a first alternative, the pipe according to the invention comprises at least one layer for which the polymeric matrix comprises a polyethylene with enhanced heat resistance.

According to this alternative, the layer, the polymeric matrix of which comprises a polyethylene with enhanced heat resistance is generally obtained by extrusion of one or several polymers (which will form the polymeric matrix), one of them being polyethylene with enhanced heat resistance, and optionally in the presence of additives.

The discontinuously dispersed components in the polymeric matrix may optionally comprise polymers, for example polyethylene with enhanced heat resistance. However, a flexible pipe:

- comprising a layer comprising a discontinuously dispersed component in the polymeric matrix (notably fillers such as fibers) comprising or consisting of polyethylene with enhanced heat resistance,
- but the polymeric matrix of which is free from polyethylene with enhanced heat resistance,

does not fit the definition of a pipe comprising at least one layer, the polymeric matrix of which comprises a polyethylene with enhanced heat resistance, as defined in this first alternative.

5 According to a second alternative, the pipe according to the invention comprises at least one layer comprising a discontinuously dispersed component in the polymeric matrix, said component comprising a polyethylene with enhanced heat resistance.

 According to this second alternative, a discontinuously dispersed component in the polymeric matrix of the layer comprises a polyethylene with enhanced heat resistance.
10 The component may be a filler such as a fiber. This component comprising the polyethylene with enhanced heat resistance may optionally be used as a catalyst support. As an illustration, when the polymeric matrix of the layer comprises a cross-linked polymer, the component comprising the polyethylene with enhanced heat resistance may be used as a support of the cross-linking catalyst of this polymer. The component
15 comprising the polyethylene with enhanced heat resistance is generally one of the additives of the master mixture used during the extrusion. According to this second alternative, the polymeric matrix of the layer may be free from polyethylene with enhanced heat resistance.

20 According to a third alternative, the pipe according to the invention comprises at least one layer comprising a discontinuously dispersed component in the polymeric matrix, said component comprising a polyethylene with enhanced heat resistance and the polymeric matrix of which comprises a polyethylene with enhanced heat resistance.

 According to this third alternative, the polyethylene with enhanced heat resistance
25 is therefore present both in the polymeric matrix and in a discontinuously dispersed component in the polymeric matrix.

 In an embodiment, in the flexible pipe according to the invention, the layer comprises, in addition to the polyethylene with enhanced heat resistance, another
30 polyolefin. Typically, this is the polymeric matrix of the layer which comprises, in addition to the polyethylene with enhanced heat resistance, at least one other polyolefin. By "other polyolefin", is meant that the polyolefin is not a polyethylene with enhanced heat resistance. The polyethylene with enhanced heat resistance may then be the majority polymer (in the layer of the pipe, the mass ratio between the polyethylene with enhanced
35 heat resistance and the sum of the polyethylene with enhanced heat resistance and of the polyolefin then being greater than 50%) or the minority polymer (in the layer of the pipe,

the mass ratio between the polyethylene with enhanced heat resistance and the sum of the polyethylene with enhanced heat resistance and of the polyolefin then being less than 50%).

The other polyolefin of the layer is notably a high molecular weight polyethylene, typically a very high molecular weight polyethylene, preferably a ultra high molecular weight polyethylene.

In the sense of the present application:

- a high molecular weight polyethylene ("high molecular weight polyethylene" (HMWPE or HMwPE)) has a weight average molecular weight (Mw) greater than 400,000 g/mol,
- a very high molecular weight polyethylene ("very high molecular weight polyethylene" (VHMWPE or VHMwPE)) has a weight average molecular weight (Mw) greater than 500,000 g/mol (for example the high density polyethylene GHR8110 from Ticona, for which the weight average molecular weight (Mw) is of the order of 600,000 g/mol), preferably greater than 1,000,000 g/mol,
- an ultra high molecular weight polyethylene ("ultra high molecular weight polyethylene" (UHMWPE or UHMwPE)) has a weight average molecular weight (Mw) greater than 3,000,000 g/mol.

These high molecular weight /very high molecular weight /ultra high molecular weight polyethylenes are available commercially.

Generally, in the flexible pipe, the layer comprising a polyethylene with enhanced heat resistance comprises additives, such as antioxidants, anti-UV agents, lubricants and other fillers usually used in thermoplastics.

The flexible pipe according to the invention may comprise a layer consisting of:

- a polyethylene with enhanced heat resistance,
- optionally a high molecular weight polyethylene, and
- optionally additives, such as antioxidants, anti-UV agents, lubricants and fillers.

A flexible pipe comprising a layer comprising a polyethylene with enhanced heat resistance has the following advantages:

- the layer comprising a polyethylene with enhanced heat resistance better withstands blistering than a layer comprising a conventional polyethylene, either cross-linked or not.

Therefore, a flexible pipe comprising a layer comprising a polyethylene with enhanced heat resistance may be used at temperatures and/or pressures greater than those used for a flexible pipe comprising a layer based on non-cross-linked polyethylene or based on cross-linked polyethylene.

- 5 - For example, the inventor showed that at a temperature of 60°C, a flexible pipe comprising a layer comprising a polyethylene with enhanced heat resistance may be used at higher pressures than a flexible pipe comprising a layer comprising a non-cross-linked polyethylene. Further, a flexible pipe comprising a layer comprising a polyethylene with enhanced heat resistance may be used at
- 10 temperatures above 60°C, which is generally not the case of a flexible pipe comprising a layer comprising a non-cross-linked polyethylene for which the blistering phenomenon is observed at 60°C at 105 bars for the transport of liquid hydrocarbons and at 60°C at 210 bars in the case of dry gas transport.
- Also, the inventor showed that at a temperature of 90°C, a flexible pipe comprising
- 15 a layer comprising a polyethylene with enhanced heat resistance may be used at higher pressures than a flexible pipe comprising a layer comprising a cross-linked polyethylene.
- The layer comprising a polyethylene with enhanced heat resistance is less expensive than a layer based on PVDF;
- 20 - The layer comprising a polyethylene with enhanced heat resistance has better resistance to abrasion than a layer based on polyethylene or on a thermoplastic polymer. The resistances to abrasion of a layer comprising a polyethylene with enhanced heat resistance and of a layer based on polyamide 11 are comparable, but the cost of the layer comprising a polyethylene with enhanced heat resistance is lower.

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The flexible underwater pipe according to the invention comprises a plurality of layers, i.e. at least two layers. Typically, the flexible underwater pipe according to the invention comprises from the outside to the inside:

- an external polymeric sealing sheath,
- 30 - at least one ply of tensile armors (generally two),
- a pressure vault,
- an internal polymeric sealing sheath,
- optionally a metal carcass,

and optionally one or several intermediate polymeric sealing sheaths between two

35 adjacent layers,

provided that at least one of these layers comprises a polyethylene with enhanced heat resistance.

The layer comprising a polyethylene with enhanced heat resistance is at least one of the layers (generally a polymeric sheath) of the flexible pipe.

5 The flexible underwater pipe according to the invention may comprise other layers in addition to the aforementioned ones. For example, it may comprise:

- a holding layer between the external polymeric sheath 10 and the tensile armor plies 12 and 14, or between two tensile armor plies,
- and optionally one or several anti-wear layers in polymeric material either in contact with the internal face of the aforementioned holding layer, or with its external face, or with both faces, this anti-wear layer giving the possibility of avoiding wear of the holding layer on contact with metal armors. The anti-wear layers, which are well known to one skilled in the art, are generally made by helically winding one or several ribbons obtained by extrusion of a polymeric material based on polyamide, on polyolefins, or on PVDF ("polyvinylidene fluoride"). It is also possible to refer to document WO 2006/120320 which describes anti-wear layers consisting of polysulfone (PSU), polyethersulfone (PES), polyphenylsulfone (PPSU), polyetherimide (PEI), polytetrafluoroethylene (PTFE), polyetheretherketone (PEEK) or polyphenylene sulfide (PPS) ribbons.

20 In a flexible underwater pipe according to the invention, the layer(s) comprising a polyethylene with enhanced heat resistance may notably be:

- the internal polymeric sealing sheath, and/or
- one or several intermediate polymeric sealing sheaths located between two other adjacent layers, and/or
- 25 - the external polymeric sealing sheath.

In an embodiment, the intermediate polymeric sealing sheath located between two other adjacent layers and comprising a polyethylene with enhanced heat resistance is an anti-wear layer.

30 Indeed, as explained above, the layer comprising a polyethylene with enhanced heat resistance is less subject to the blistering phenomenon, is therefore particularly suitable for being used as a polymeric sealing sheath (in order to avoid leaking of hydrocarbons through the formed cracks or blisters into the sea on the one hand and the inflow of seawater into the pipe on the other hand).

35 Further, as explained above, a layer comprising a polyethylene with enhanced heat resistance has good resistance to abrasion, notably better than that of a layer in polyolefin, and comparable with that of a layer in polyamide (more expensive than

PE-RT). As resistance to abrasion is a sought property for an external sheath, the layer comprising a polyethylene with enhanced heat resistance is particularly suitable for being used as an external sealing sheath.

5 Moreover, when the pipe is used at temperatures below 60°C, its intermediate polymeric sealing sheath is generally in polyethylene, but for higher temperatures, it is generally in PVDF, clearly more expensive. Thus, when the pipe has to be used at temperatures above 60°C, it is therefore advantageous to use as an intermediate polymeric sheath, a layer comprising a polyethylene with enhanced heat resistance (less expensive than PVDF, but the performances of which in resistance to temperature are
10 considerably greater than a polyethylene).

For example, the flexible pipe according to the invention may comprise from the outside to the inside:

- an external polymeric sealing sheath,
- 15 - at least one ply of tensile armors,
- a pressure vault,
- an internal polymeric sealing sheath comprising a polyethylene with enhanced heat resistance,
- possibly a metal carcass.

20 In a second example, the flexible pipe according to the invention may comprise, from the outside to the inside:

- an external polymeric sealing sheath comprising a polyethylene with enhanced heat resistance,
- at least one ply of tensile armors,
- 25 - a pressure vault,
- an internal polymeric sealing sheath,
- optionally a metal carcass.

In a third example, the flexible pipe according to the invention may comprise from the outside to the inside:

- 30 - an external polymeric sealing sheath,
- at least one ply of tensile armors,
- a pressure vault,
- an internal polymeric sealing sheath,
- optionally a metal carcass,

35 and one or several intermediate polymeric sealing sheaths comprising a polyethylene with enhanced heat resistance between two adjacent layers.

The flexible pipe according to the invention may also comprise several layers (typically two or three) comprising a polyethylene with enhanced heat resistance. For example, the flexible pipe according to the invention may comprise from the outside to the inside:

- 5 - an external polymeric sealing sheath comprising a polyethylene with enhanced heat resistance,
- at least one ply of tensile armors,
- a pressure vault,
- an internal polymeric sealing sheath comprising a polyethylene with enhanced heat
- 10 resistance,
- optionally a metal carcass.

According to a second object, the invention relates to a method for preparing the aforementioned flexible underwater pipe, comprising the following steps:

- 15 a) extrusion for forming a layer comprising a polyethylene with enhanced heat resistance, the extrusion being optionally carried out on another layer,
- b) optionally assembling the layer obtained in step a) with at least one other layer.

The extrusion of a layer comprising a polyethylene with enhanced heat resistance is easy to apply, while extrusion of a layer in cross-linked polyethylene is generally difficult. Thus, the method for preparing a flexible pipe comprising a layer comprising a polyethylene with enhanced heat resistance is simpler than the method for preparing a flexible pipe comprising a layer comprising a cross-linked polyethylene.

The extrusion step a) may be carried out with any method known to one skilled in the art, for example by using a single screw or twin screw extruder. Polyethylene with enhanced heat resistance may easily be co-extruded, unlike cross-linked polyethylene.

The preparation of the layer comprising a polyethylene with enhanced heat resistance does not require any cross-linking step (and no expensive cross-linking device is required), unlike the preparation of a layer in cross-linked polyethylene. Thus, the method for preparing a flexible pipe comprising a layer comprising a polyethylene with enhanced heat resistance is faster, simpler and less expensive than the method for preparing a flexible pipe comprising a layer comprising a cross-linked polyethylene.

When the layer comprises several polymers (for example a polyethylene with enhanced heat resistance and a polyethylene of high molecular weight) the mixing of both polymers may be carried out before or during the extrusion.

The layer obtained at the end of step a) is typically tubular, generally has a diameter from 50 mm to 600 mm, preferably from 50 to 400 mm, a thickness of 1 mm to 150 mm, preferentially from 40 to 100 mm and a length from 1 m to 10 km.

5 The method optionally comprises the step b) for assembling the layer obtained during step a) with at least one other layer in order to form the flexible underwater pipe, notably one of the aforementioned layers.

10 The layers are thus assembled in order to form a flexible underwater pipe of the unbonded type, as described in the normative documents published by the American Petroleum Institute (API), API 17J and API RP 17B.

15 According to a first alternative, the extrusion of step a) is not carried out on another layer of the flexible pipe, but independently, and the layer obtained at the end of the extrusion is then added and calendered with at least one other layer during step b). The method for preparing the flexible pipe then comprises the steps for:

- a) extrusion in order to form a layer comprising a polyethylene with enhanced heat resistance,
- b) assembling the obtained layer in step a) with at least one other layer.

20 For example, when the layer comprises a polyethylene with enhanced heat resistance is the internal polymeric sealing sheath, the layer obtained at the end of step a) is then added and typically calendered with a pressure vault, at least one ply of tensile armors (generally two plies of armors) and an external polymeric sheath. With this example, it is notably possible to make flexible pipes with a smooth bore.

25 According to a second alternative, the extrusion of step a) is carried out on another layer of the flexible pipe. The method for preparing the flexible pipe then comprises the steps for:

- a) extrusion in order to form a layer comprising a polyethylene with enhanced heat resistance, the extrusion being carried out on another layer,
- 30 b) optionally assembling the layer obtained in step a) with at least one other layer.

In a first embodiment of this second alternative, the method for preparing the flexible pipe comprises the steps for:

- 35 a) extrusion in order to form a layer comprising a polyethylene with enhanced heat resistance, the extrusion being carried out on another layer,
- b) assembling the layer obtained in step a) with at least one other layer.

For example, when the layer comprising a polyethylene with enhanced heat resistance is the internal polymeric sealing sheath, the extrusion is typically carried out on the carcass, in order to obtain an assembly (carcass/layer comprising polyethylene with enhanced heat resistance) which will then be added and calendered with at least one other layer during step b), typically a pressure vault, at least one ply of tensile armors (generally two armor plies) and an external polymeric sheath. With this example it is notably possible to make rough-bore flexible pipes.

Also, when the layer comprising a polyethylene with enhanced heat resistance is an intermediate polymeric sheath, the extrusion of the layer is typically carried out on the whole of the layers of the pipe which are more internal than said intermediate polymeric sheath in the flexible pipe obtained by the method, in order to obtain an assembly (intermediate polymeric sheath comprising a polyethylene with enhanced heat resistance/layers of the pipe which are more internal than said intermediate polymeric sheath in the flexible pipe obtained by the method) which will then be added and calendered with the other layer(s) of the pipe which is(are) more external in the flexible pipe obtained by the method.

As an illustration, if the layer comprising a polyethylene with enhanced heat resistance is an intermediate polymeric sheath between the pressure vault and a ply of tensile armors, the extrusion of the layer will be typically carried out on the pressure vault/internal polymeric sealing sheath/optional carcass assembly (the layers being listed from the outside to the inside, the extrusion being carried out on the outer layer of this assembly, i.e. on the pressure vault), in order to obtain an assembly (intermediate polymeric sheath comprising a polyethylene with enhanced heat resistance/pressure vault/internal polymeric sealing sheath/optional carcass) which will then be added and calendered with at least one ply of tensile armors (generally two armor plies) and an external polymeric sheath.

According to another example, if the layer comprising a polyethylene with enhanced heat resistance is an intermediate polymeric sheath between the armor ply(ies) and a polymeric layer (for example an anti-wear layer), the extrusion of the layer would be typically achieved on the assembly of at least one tensile armor ply/pressure vault/internal polymeric sealing sheath/optional carcass (the layers being listed from the outside to the inside, the extrusion being achieved on the exterior layer of this assembly, i.e. on the pressure vault), in order to obtain an (intermediate polymeric sheath comprising a polyethylene with enhanced heat resistance/at least one ply of tensile armors/pressure vault/internal polymeric sealing sheath/optional carcass) assembly which will then be added and calendered with an external polymeric sheath.

In a second embodiment of this second alternative, the method for preparing the flexible pipe comprises the step for:

5 a) extrusion in order to form a layer comprising a polyethylene with enhanced heat resistance, the extrusion being carried out on another layer.

10 For example, when the layer comprising a polyethylene with enhanced heat resistance is the external polymeric sealing sheath, the extrusion is typically carried out on an assembly of layers: at least one ply of tensile armors (generally two armor plies)/pressure vault/internal polymeric sealing sheath/optionally carcass (the layers being listed from the outside to the inside, the extrusion being carried out on the outer layer of this assembly, i.e. on a ply of tensile armors).

15 According to a third object, the object of the invention is a flexible underwater pipe which may be obtained with the aforementioned method.

According to a fourth object, the object of the invention is the use of the aforementioned flexible underwater pipe for transporting hydrocarbons.

20 According to a fifth object, the object of the invention is the use of a polyethylene with enhanced heat resistance as defined above in a layer of a flexible underwater pipe intended for transporting hydrocarbons in order to increase the resistance of said layer to blistering.

25 Other particularities and advantages of the invention will become apparent upon reading the description made hereafter of particular embodiments of the invention, given as an indication but not as a limitation, with reference to the figure.

30 The figure is a partial schematic perspective view of a flexible pipe according to the invention. It illustrates a pipe according to the invention comprising, from the outside to the inside:

- an external polymeric sealing sheath 10,
- an external ply of tensile armors 12,
- an internal ply of tensile armors 14 wound in the direction opposite to the external ply 12,
- 35 - a pressure vault 18 for spread-loading the radial forces generated by the pressure of the transported hydrocarbons,

- an internal polymeric sealing sheath 20, and
- an internal carcass 22 for spread-loading the crushing radial forces.

No intermediate polymeric sheath is illustrated in the figure. As explained above, there would be no departure from the field of the present invention if the pipe comprised one or several intermediate polymeric sheaths. When no intermediate polymeric sheath is present in the pipe, like the one illustrated in the figure, it is the external polymeric sealing sheath 10 and/or the internal polymeric sealing sheath 20 which comprise(s) a polyethylene with enhanced heat resistance.

Because of the presence of the internal carcass 22, this pipe is said to be a rough-bore pipe. The invention may also be applied to a smooth-bore pipe not including any internal carcass.

Also, there would be no departure from the field of the present invention by suppressing the pressure vault 18, provided that the helical angles of the wires making up the armor plies 12, 14 are close to 55° and in the opposite direction.

The armor plies 12, 14 are obtained by winding with a long pitch a set of wires in a metal or composite material, with a generally substantially rectangular section. The invention would also apply if these wires had a circular or complex geometrical section, for example of the self-stapled T type. In the figure, only two armor plies 12 and 14 are illustrated, but the pipe may also include one or several additional pairs of armors. The armor ply 12 is said to be external since it is the last here, starting from the inside of the conduit, before the external seal sheath 10.

The flexible pipe may also comprise layers not illustrated in the figure, such as:

- a holding layer between the external polymeric sheath 10 and the tensile armor plies 12 and 14, or between two tensile armor plies,
- one or several anti-wear layers in a polymeric material in contact either with the internal face of the aforementioned holding layer or with its external face, or with both faces.

EXAMPLE: Blistering resistance test

Blistering resistance tests according to the API17J standard were conducted on PE-RT samples as mentioned earlier (Dow 2377, RT70) 20 times subject to a temperature of 90°C under a pressure of 250 bars while having been saturated in diesel (reference liquid for the tests) without exhibiting any blistering (observation with the naked eye and then with an optical microscope (a binocular microscope LEICA MZ 125)).

As a comparison, the limits of the polyethylene materials (Finathene[®] 3802 (Petrofina)) and cross-linked polyethylene (Crossflex[®] (Technip)) materials used in applications of flexible pipes because of the blistering phenomenon are respectively:

- a temperature of 60°C and a pressure of 105 bars in the presence of liquid hydrocarbons, or 210 bars in the presence of only dry gas, or
- a temperature of 90°C and a pressure of 175 bars in the presence of liquid hydrocarbons.

Thus, the use of a polyethylene with enhanced resistance as a sealing sheath gives the possibility:

- for a temperature of 60°C, of increasing the pressure use range as compared with polyethylene presently used,
- for temperatures above 60°C, i.e. in temperature ranges reserved up to now for cross-linked polyethylene, of increasing the pressure use range as compared with cross-linked polyethylene.

Other blistering resistance tests according to the API17J standard were conducted on PE-RT samples with a thickness of 7 mm as mentioned earlier (Total Petrochemical XSene XRT70) 20 times subject to a temperature of 90°C under a pressure of 300 bars without exhibiting any blistering (observation with the naked eye and then with an optical microscope (binocular microscope LEICA MZ 125)).

A cross-linked polyethylene material (Crossflex[®] (Technip)) was subject to the same conditions. Many blisters appeared.

Other blistering resistance tests according to the API17J standard were conducted on PE-RT samples with a thickness of 7 mm of different natures, 20 times subject to a given temperature and pressure. The characteristics of the PE-RTs and the results of the blistering phenomenon resistance are provided in the following table.

Grade	Dowlex 2344	Dowlex 2388	XRT 70
Provider	Dow Chemical	Dow Chemical	Total Petrochem
Co-monomer	Octene C8	Octene C8	Hexene C6
Type according to ISO 15494-1	I	II	II
Density (g/cm ³)	0.933	0.941	0.947
Melt index (190°C)	0.7 g/10 min (2.16 kg) 2.2 g/10 min (5 kg)	0.54 g/10min (2.16 kg) 1.9 g/10 min (5 kg)	0.7 g/10 min (5 kg)
Tensile yield strength (MPa)	16.5	20	23
Tensile breaking strength (MPa)	34	37	
Elongation at break (%)	>800	780	350
Flexure modulus (MPa)	550 (580 rigid)	660	750 850 (rigid)
Blistering phenomenon	Occurrence of blisters at a pressure of 250 bars and at a temperature of 90°C	Occurrence of blisters at a pressure of 300 bars and at a temperature of 90°C	No blisters observed at a temperature of 400 bars and at a temperature of 90°C

Table: Characteristics of the PE-RTs used and results of the blistering resistance tests.

5 These results show that a PE-RT for which the density is greater than 0.945 g/cm³ and for which the melt index measured at 190°C under a mass of 5.0 kg is less than 2.0 g/10 min (PE-RT XRT 70) better withstands the blistering phenomenon than a PE-RT not having these characteristics (PE-RT Dowlex with densities of less than 0.945 g/cm³).

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1.- A flexible underwater pipe intended for transporting hydrocarbons, comprising a plurality of layers, at least one layer of which comprises a polyethylene with enhanced heat resistance for which the melt index measured at 190°C under a mass of 5.0 kg is less than 2.0 g/10 min and for which the density is greater than 0.945 g/cm³.

2.- The flexible underwater pipe according to claim 1, wherein the melt index measured at 190°C of the polyethylene with enhanced heat resistance is:

- less than 1.0 g/10 min under a mass of 5.0 kg, and/or
- less than 0.25 g/10 min under a mass of 2.16 kg, and/or
- less than 20 g/10 min under a mass of 21.6 kg.

3.- The flexible underwater pipe according to claim 1 or 2, wherein the polyethylene with enhanced heat resistance is obtained by polymerization of ethylene and of an α -olefin selected from 1-butene, 1-hexene and 1-octene.

4.- The flexible underwater pipe according to any of claims 1 to 3, wherein the polyethylene with enhanced heat resistance has:

- a threshold yield strength comprised between 15 and 35 MPa,
- an elongation at break at least greater than 50%.

5.- The flexible underwater pipe according to any of claims 1 to 4, at least one layer of which comprises a polyethylene with enhanced heat resistance and another polyolefin.

6.- The flexible underwater pipe according to claim 5, wherein, in the layer comprising a polyethylene with enhanced heat resistance and another polyolefin, the mass ratio between the polyethylene with enhanced heat resistance and the

sum of the polyethylene with enhanced heat resistance and of the polyolefin is greater than 50%.

5 7.- The flexible underwater pipe according to claim 5, wherein, in the layer comprising a polyethylene with enhanced heat resistance and another polyolefin, the mass ratio between the polyethylene with enhanced heat resistance and the sum of the polyethylene with enhanced heat resistance and of the polyolefin is less than 50%.

10 8.- The flexible underwater pipe according to any of claims 5 to 7, wherein the other polyolefin is a high molecular weight polyethylene.

9.- The flexible underwater pipe according to any of claims 1 to 8, comprising, from the outside to the inside:

15 - an external polymeric sealing sheath,
- at least one ply of tensile armors,
- a pressure vault,
- an internal polymeric sealing sheath,
- optionally a metal carcass,

20 and optionally one or several intermediate polymeric sealing sheaths between two adjacent layers,
provided that at least one of these layers comprises a polyethylene with enhanced heat resistance.

25 10.- The flexible underwater pipe according to any of claims 1 to 9, wherein said layer(s) comprising a polyethylene with enhanced heat resistance is(are):

- the internal polymeric sealing sheath, and/or
- one or several intermediate polymeric sealing sheaths located between two adjacent layers, and/or

30 - the external polymeric sealing sheath.

11.- A method for preparing the flexible underwater pipe according to any of claims 1 to 10, comprising the following steps:

- a) extrusion for forming a layer comprising a polyethylene with enhanced heat resistance, the extrusion being optionally carried out on another layer,
- 5 b) optionally assembling the layer obtained in step a) with at least one other layer.

12.- The use of a flexible underwater pipe according to any of claims 1 to 10 for transporting hydrocarbons.

10 13.- The use of a polyethylene with enhanced heat resistance, for which the melt index measured at 190°C under a mass of 5.0 kg is less than 2.0 g/10 min and for which the density is greater than 0.945 g/cm³ in a layer of a flexible underwater pipe intended for transporting hydrocarbons in order to increase the resistance of said layer to blistering.

15

14.- The flexible underwater pipe according to claim 3, wherein the polyethylene with enhanced heat resistance is obtained by polymerization of ethylene and of an α -olefin selected from 1-hexene and 1-octene.

20

15.- The flexible underwater pipe according to claim 4, wherein the polyethylene with enhanced heat resistance has a threshold yield strength comprised between 20 and 30 MPa.

25

16.- The flexible underwater pipe according to claim 15, wherein the polyethylene with enhanced heat resistance has a threshold yield strength comprised between 25 and 30 MPa.

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17.- The flexible underwater pipe according to claim 4, wherein the polyethylene with enhanced heat resistance has an elongation at break at least greater than 300%.

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18.- The flexible underwater pipe according to claim 17, wherein the polyethylene with enhanced heat resistance has an elongation at break at least greater than or equal to 500%.

5 19.- The flexible underwater pipe according to claim 8, wherein the other polyolefin is a very high molecular weight polyethylene.

20.- The flexible underwater pipe according to claim 19, wherein the other polyolefin is an ultra high molecular weight polyethylene.

