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The present invention relates to a longitudinal reinforcing profile for a flexible tubular pipe for transporting hydrocarbon fluids, and also to a method for manufacturing this longitudinal reinforcing profile. The present invention also relates to a flexible tubular pipe comprising at least one reinforcing layer produced by helical winding of this longitudinal reinforcing profile.

According to the article “Development of lightweight flexible risers for ultra deep water applications”, published during the Deep Offshore Technology conference of 2000, using carbon as a material to form undersea pipes is known. Indeed, carbon fibres have good mechanical properties of tensile strength and fatigue strength, but also good chemical resistance to ageing in a moist and corrosive environment.

Using composite materials filled with carbon fibres to replace metal woven layers for withstanding tensile forces is also known from the prior art. FR 2776358 discloses the manufacture and integration of composite profiles comprising a high fibre content for flexible pipe weaves used in deep sea conditions. This composite profile comprises longitudinal filamentous strands, for example made of carbon, distributed within a thermoplastic or thermosetting polymer matrix.

However, the choice of materials for producing such composite profiles must be rigorous if it is desired to obtain excellent chemical and thermal resistance properties. This is because the nature of the reinforcing fibres and/or the nature of the polymer matrix influence the processing properties of the composite profiles and also the final properties thereof.

Producing, for example, polymer matrices based on an epoxy resin is known from the prior art. To this end, use is made of an epoxy pre-polymer which is mixed with a curing agent.

When it is sought to obtain a polymer matrix which has good chemical resistance and is resistant to hydrolysis, a person skilled in the art knows that they should choose a curing agent comprising an aromatic amine. By mixing such a curing agent with the epoxy resin, they are able to obtain a polymer matrix (or {epoxy resin/curing agent} system) which lends itself well to the manufacture of structural elements produced by moulding. However, the {epoxy/aromatic amine} system is not suitable for producing elongated structural elements realised by the pultrusion process. This is because this system has very slow polymerisation kinetics requiring the supply of a significant amount of heat, which does not make it possible to continuously obtain reliable production of elongated structural elements.

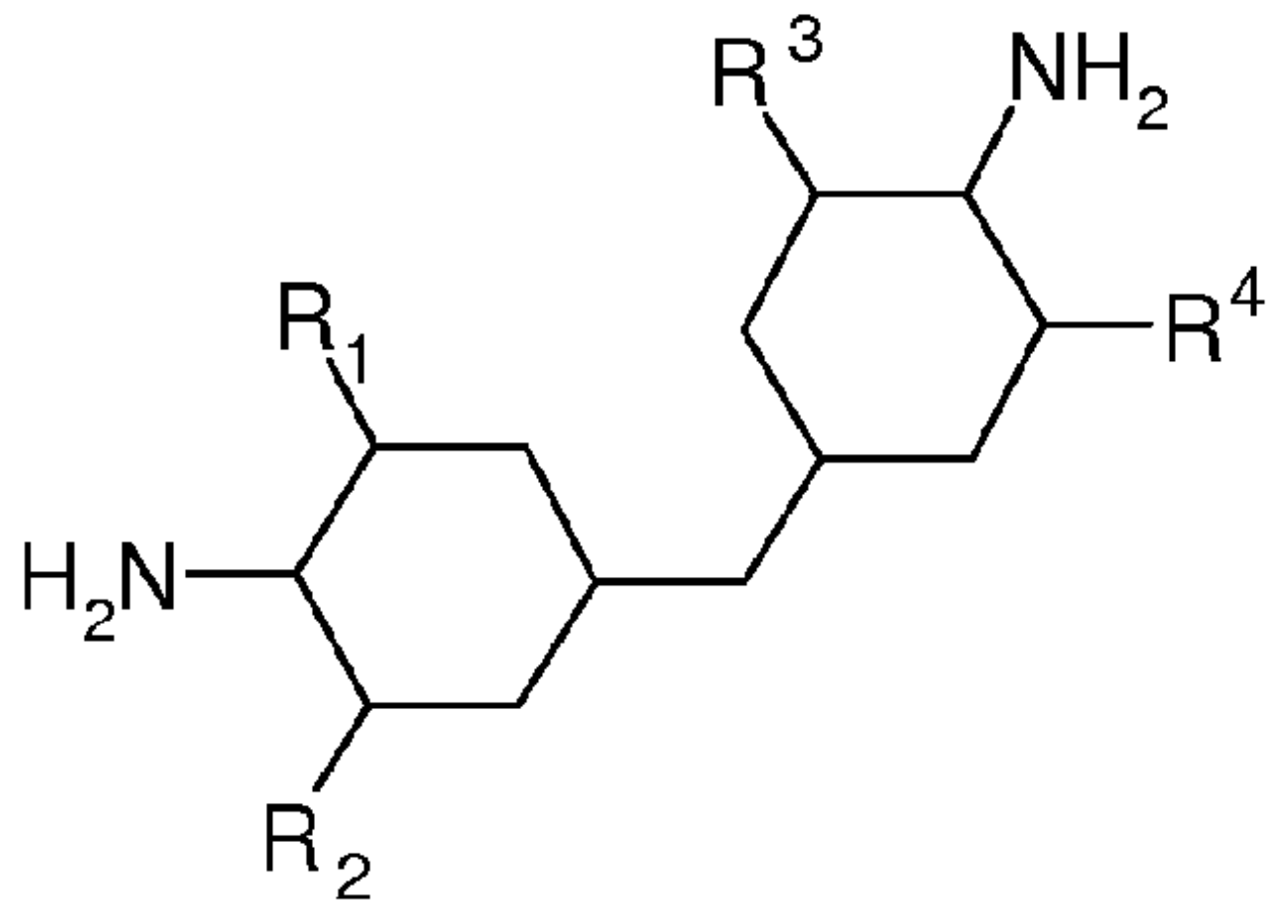
Alternatively, a person skilled in the art may choose to use a curing agent comprising a cycloaliphatic amine. A person skilled in the art knows that this type of curing agent is better suited to producing very long structural elements realised by pultrusion, since it requires a smaller supply of heat to polymerise the system. Nonetheless, the hydrolysis resistance of the final product obtained after pultrusion is poorer than if a curing agent comprising an aromatic amine were used.

Thus, a problem addressed by the present invention, which it aims to solve, is that of providing a composite profile which better withstands high temperatures and also hydrolysis when the flexible tubular pipe is used under severe production conditions.

With a view to solving this problem, the present invention relates to a composite longitudinal reinforcing profile comprising longitudinal carbon fibres embedded in a polyepoxy resinous matrix obtained by polymerisation of a thermosetting blend comprising an epoxy prepolymer (i) and at least one curing agent (ii) and optionally a catalyst, characterised in that:

- the epoxy prepolymer (i) is a DiGlycidyl Ether of Bisphenol A (DGEBA) or a DiGlycidyl Ether of Bisphenol F (DGEBF) or a TetraGlycidyl Methylene DiAniline (TGMDA);
- the at least one curing agent (ii) is a cycloaliphatic amine or an aromatic amine or a blend of a cycloaliphatic amine with an aromatic amine; and the P1/P2 ratio between the proportion by weight Pi of the at least one curing agent (ii) in the thermosetting blend and the proportion by weight P2 of the prepolymer (i) in the thermosetting blend is between 15% and 30% and is preferably equal to 25%.

For the purposes of the application, "cycloaliphatic amine" is intended to mean a compound comprising at least one aliphatic ring and at least one amine function, preferably two aliphatic rings and two amine functions. Saturated aliphatic rings such as cyclohexyl are particularly preferred. The amine function is preferably a primary amine $-NH_2$. The cycloaliphatic amine typically comprises from 5 to 50 carbon atoms and from 1 to 10 nitrogen atoms. A non-exhaustive list of these cycloaliphatic amines is given in the publication "Cycloaliphatic Amines" (Encyclopaedia of Chemical Technology, Kirk-Othmer, 4th Edition (1992), pp. 386-405). They correspond in particular to the following general formula:



in which R^1, R^2, R^3 and R^4 independently represent a group selected from a hydrogen atom or an alkyl having 1 to 6 carbon atoms.

The curing agent based on a cycloaliphatic amine is preferably selected from curing agents of the cycloaliphatic amine type sold by the company Huntsman under the name ARADUR®.

For example, the cycloaliphatic amine is 4,4'-diamino-3,3'-dimethyldicyclohexylmethane, as sold under the name ARADUR® 2954.

For the purposes of the application, “aromatic amine” is intended to mean a compound comprising at least one aromatic ring, typically at least one phenyl, and at least one amine function, preferably two amine functions. The amine function is preferably a primary amine $-NH_2$. The aromatic amine typically comprises from 6 to 50 carbon atoms and from 1 to 10 nitrogen atoms. For example, the aromatic amine is methylenedianiline, m-phenylenediamine or diaminophenylsulfone.

The curing agent based on an aromatic amine is preferably selected from curing agents of the aromatic amine type sold by the company Huntsman under the name ARADUR®, such as ARADUR® 5200.

The curing agent based on a blend of a cycloaliphatic amine and an aromatic amine is for example selected from the curing agents sold by the company Huntsman under the name Ren© HY 5211 or Ren© HY 5212.

These ranges of curing agents enable the longitudinal profile which is a subject of the present invention, obtained by the polymerisation of a thermosetting blend comprising the abovementioned chemical components, to benefit from good thermal, mechanical, electrical and chemical strength properties.

Thus, such a feature according to the invention makes it possible to improve the mechanical properties, and the properties of resistance to hydrolysis (corrosion) of the composite longitudinal reinforcing profiles when they are in contact with a corrosive environment and subjected to high temperatures, for example inside an internal annular space of a flexible undersea pipe.

Carbon fibres have relatively high mechanical properties compared to other types of fibres such as some glass or aramid fibres. Moreover, carbon fibres withstand high temperatures and have good chemical resistance. Thus, they resist corrosion well, as well as hydrogen embrittlement phenomena.

Moreover, the particular polyepoxy resins used to implement the present invention have excellent chemical resistance to corrosion in acid medium, and also a good resistance to high temperatures compared to polyester resins. They also have very good mechanical tensile, compression, shear and elongation properties.

In addition, the combination of carbon fibres with a particular matrix according to the present invention makes it possible to obtain a composite material having high mechanical properties which is able to withstand a high temperature in an extremely corrosive environment.

The composite longitudinal reinforcing profile according to the invention may comprise one or more of the following features, taken alone or in combination:

- preferably, the thermosetting blend has a viscosity measured at 25°C of between 1000 mPa.s and 6000 mPa.s, preferably between 2000 mPa.s and 5000 mPa.s. and advantageously a viscosity measured between 40°C and 80°C of between 100 mPa.s and 1200 mPa.s in order to improve the impregnation of the fibres;
- preferably, the catalyst is chosen from phenolic monomers such as bisphenol A or from amine monomers, for example BenzylDiMethylAmine (BDMA) in order to accelerate the polymerisation reaction of the thermosetting resinous matrix;
- preferably, the P_3/P_2 ratio between the proportion by weight P_3 of bisphenol A in the thermosetting blend and the proportion by weight P_2 of the prepolymer (i) in the thermosetting blend is between 1% and 5% and is preferably equal to 3%;
- advantageously, the maximum continuous usage temperature of the composite longitudinal reinforcing profile is greater than 100°C;
- this longitudinal reinforcing profile is advantageously manufactured by pultrusion.

"Phenolic monomer" is intended to mean a chemical compound comprising at least one phenol, generally at least two phenols, such as a bisphenol, preferably bisphenol A.

Amine monomer is intended to mean a chemical compound comprising at least one amine function, preferably at least one tertiary amine function, for example tris(dimethylaminomethyl)phenol, benzyldiMethylamine (BDMA) or triethanolamine.

Generally, the dimensions of the composite longitudinal reinforcing profile are such that:

- the length thereof is from 500 metres to 5000 metres, and/or
- the width thereof is greater than or equal to 10 millimetres, or even greater than 25 millimetres, and preferably from 10 millimetres to 30 millimetres, and/or
- the thickness thereof is greater than or equal to 0.5 millimetres; it is preferably from 0.5 millimetres to 30 millimetres.

The invention also relates to a method for manufacturing, by pultrusion, a longitudinal reinforcing profile as described above, comprising the successive steps of:

a) pre-heating the longitudinal fibres to a temperature of between 150°C and 180°C;

b) impregnating the longitudinal fibres using a film made of a blend that is thermosetting at a temperature of between 40°C and 80°C, and triggering the polymerisation of the thermosetting blend;

c) preforming or shaping the longitudinal profile and continuing the polymerisation of the thermosetting blend;

d) baking or post-curing the longitudinal profile at a temperature of at least 180°C for at least 1 h.

In addition, advantageously, the manufacturing method according to the invention may comprise one or more of the following features, taken alone or in combination:

- it comprises, between step b) and step c), a step b1) of applying at least one reinforcing web over at least one of the faces of the longitudinal profile;
- it comprises a step of pre-drying and pre-heating the at least one reinforcing web before step b1);
- it comprises, after step e), a step of cutting the longitudinal profile.

Finally, the invention also relates to a flexible tubular pipe for transporting hydrocarbon fluids, comprising an internal leaktight sheath and at least one reinforcing layer comprising a plurality of longitudinal reinforcing profiles according to the invention.

The flexible tubular pipe according to the invention may comprise one or more of the following features, taken alone or in combination:

- the plurality of longitudinal profiles is helically wound;
- the reinforcing layer comprising the plurality of longitudinal profiles is a tensile strength woven ply;
- the reinforcing layer comprising the plurality of longitudinal profiles is a pressure-resistant woven ply;
- the reinforcing layer comprising the plurality of longitudinal profiles is located outside the internal leaktight sheath;
- the flexible tubular pipe comprises a metal casing located inside the internal leaktight sheath;
- the flexible tubular pipe comprises an external leaktight sheath surrounding the reinforcing layer comprising the plurality of longitudinal profiles.

The invention will be better understood in light of the following description and with reference to the appended drawings, in which:

- Fig. 1 is a partial schematic cut-away view of a flexible tubular pipe according to the invention;
- Fig. 2 is a partial schematic sectional view of a longitudinal reinforcing profile in accordance with the invention;
- Fig. 3 is a schematic view of a method for manufacturing a longitudinal reinforcing profile of the type depicted in Fig. 2.

In the following description, the term "internal" denotes any element closest to a longitudinal axis Δ and, conversely, the term "external" denotes any element furthest away from the longitudinal axis Δ.

A flexible tubular pipe 1 according to the invention is schematically depicted in Fig. 1. The pipe 1 is intended for the transport of a hydrocarbon fluid from the seabed to the surface, where said pipe is connected to an offshore installation, such as undersea risers. The distance separating the seabed and the surface is for example between 200 metres and 4000 metres.

The pipe 1 may also be intended for the transfer of hydrocarbon fluids between two floating units, for example between two floating production, storage and offloading (FPSO) units, or between an oil rig or an FPSO and an offloading buoy. This type of pipe is known as an export line.

The structure of the pipe 1 is formed by a superposition of several layers arranged one on top of the other.

The innermost layer of the pipe 1 is generally a metal casing 2 which defines a flow zone 9 for the transport of hydrocarbon fluids extracted from the oil deposit. The casing 2 is produced by winding a profiled strip with a short pitch, i.e. the absolute value of the helical angle between the profiled strip and the axis is between 70° and 90°. The casing 2 makes it possible to absorb radial crushing forces.

Around this casing 2, a first polymer sheath is extruded, also referred to as pressure sheath 3 or internal leaktight sheath, intended to confine the transport of the hydrocarbon fluid to the flow zone 9. The polymer material making it possible to produce the pressure sheath 3 is chosen from families of polymers such as polyolefins, polyamides or fluoropolymers such as PVDF (polyvinylidene fluoride).

A first reinforcing layer referred to as pressure vault is arranged on top of the internal leaktight sheath 3. Said layer is intended to absorb the radial forces generated by the pressurised flow of the hydrocarbon fluid within the flow zone 9 and thereby to prevent the internal leaktight sheath 3 from bursting. The pressure vault comprises one or more pressure-resistant woven plies 4, the weaves of these plies being in the form of longitudinal profiles wound helically with a short pitch, typically at an absolute value of the helical angle of between 70° and 90° relative to the axis Δ. The feature according to which the absolute value of the helical angle is close to 90° gives the woven ply a high resistance to pressure.

Generally, the pipe 1 only comprises a single pressure-resistant woven ply 4 arranged directly on top of the internal leaktight sheath 3 and formed of profiles linked together, for example profiles in the shape of a Z, a T, a U, a K, etc. However, the pipe 1 may also comprise several superposed pressure-resistant woven plies in order to increase the pressure resistance thereof. In this case, the internal ply is generally formed of linked profiles while the external ply is formed of non-linked profiles with a substantially rectangular section.

At least one other reinforcing layer intended to absorb the longitudinal tensile forces exerted on the pipe 1 is arranged on top of the pressure vault. This other reinforcing layer comprises at least one pressure-resistant woven ply 5 ,6, these weaves being in the form of longitudinal profiles wound helically with a long pitch, typically at an absolute value of the helical angle of between 20° and 60° relative to the axis Δ. The feature according to which the absolute value of the helical angle is less than 60° gives the woven ply a high tensile strength.

Generally, the pipe 1 comprises at least one pair of tensile strength woven plies 5, 6 which are superposed and criss-crossed with one another, which makes it possible to torsionally balance the pipe 1. If the tensile strength woven plies 5, 6 are wound with an absolute value of the helical angle close to 55°, the pressure vault is optional since this particular helical angle gives the woven plies 5, 6 the ability to absorb both longitudinal and radial forces.

Finally, and preferably, a second polymer sheath is extruded, also referred to as external leaktight sheath 7, around the reinforcing layers 4; 5, 6. The polymer material making it possible to produce the external leaktight sheath 7 is chosen from the same families as those stated above for the pressure sheath 3. The external leaktight sheath 7 makes it possible in particular to avoid the reinforcing layers being in direct contact with the environment outside the pipe 1, in particular with sea water.

Of course, other intermediate layers formed from a polymeric material or from a metal or composite material can be inserted between the previously described layers.

Thus, the pipe 1 can comprise other polymeric sheaths or polymeric strips inserted between one or more of the previously described layers. The pipe 1 may in particular comprise an intermediate leaktight sheath, or a thermal insulation sheath, or a sheath for neutralising corrosive gases such as H2S and CO2. It may also comprise one or more layers consisting of windings of polymeric strips, for example an anti-wear layer inserted between two reinforcing layers, or a thermal insulation layer.

According to a variant embodiment of the invention, the flexible tubular pipe 1 comprises at least one layer such as a thermal insulation sheath 8 (or a strip) of polymeric foam extruded (or wound) between the pressure-resistant woven ply 4 and the first tensile strength woven ply 5 and/or between the first tensile strength woven ply 5 and the second tensile strength woven ply 6 and/or between the second tensile strength woven ply 6 and the external leaktight sheath 7. The thermal insulation layer is for example produced from a polytetrafluoroethylene (PTFE) strip, a foam based on polyvinyl chloride (PVC) or polypropylene (PP), etc.

The pipe 1 as described previously in Fig. 1 is of the “rough bore” type, i.e. has a non-smooth flow zone 9; that is to say, the innermost layer of its structure is the casing 2. Conversely, when the innermost layer is not the casing 2 but rather the pressure sheath 3, the pipe is of the “smooth bore” type, i.e. has a smooth flow zone 9.

Moreover, the pipe 1 according to the invention is of the unbonded type, i.e. at least two adjacent layers of the pipe 1 can move axially relative to one another when the pipe 1 is subject to bending.

These types of pipes are well known to a person skilled in the art and are also described in the standards API 17J, “Specification for Unbonded Flexible Pipe”, and API RP 17B, “Recommended Practice for Flexible Pipe”, published by the American Petroleum Institute (API).

In the remainder of the text, the term polymerisation is used to denote a chemical reaction between at least two components of low molecular weight with a view to the subsequent formation of a compound with a higher molecular weight. For thermosetting resins, polymerisation (or crosslinking) corresponds to the formation of a three-dimensional network obtained by reaction between a prepolymer, a curing agent (or polymerising/crosslinking agent) and a heating action. A catalyst or accelerator may optionally be added in order to accelerate the crosslinking reaction. The crosslinking reaction thus gives rise to the creation of bonds between the respective macromolecular chains of the prepolymer and of the curing agent.

Fig. 2 shows a cross-sectional view of a shaped wire or composite longitudinal reinforcing profile 50. The longitudinal profile 50 is in the form of a flat tape reinforced with longitudinal carbon fibres 52 embedded in a polymeric matrix 54. The longitudinal fibres 52 are generally arranged in the form of longitudinal strands comprising a plurality of fibres mechanically bonded to one another as described in international application WO 2013/131972. The polymeric matrix 54 is a single-component or dual-component epoxy resin. It is obtained by polymerisation of a thermosetting blend comprising an epoxy prepolymer (i) and at least one curing agent (ii) of the amine type, such as those described previously.

More specifically, the epoxy prepolymer (i) is selected from DiGlycidyl Ether of Bisphenol A (DGEBA), DiGlycidyl Ether of Bisphenol F (DGEBF) or TetraGlycidyl Methylene DiAniline (TGMDA).

The curing agent (ii) is selected from the family of cycloaliphatic amines or aromatic amines, or from a blend of a cycloaliphatic amine and an aromatic amine.

The thermosetting blend comprises the epoxy prepolymer (i) and the at least one curing agent (ii) mixed in variable proportions by weight. Advantageously, the P_1/P_2 ratio between the proportion by weight P_1 of the at least one curing agent (ii) in the thermosetting blend and the proportion by weight P_2 of the prepolymer (i) in the thermosetting blend is between 15% and 30% and is preferably equal to 25%.

A catalyst is optionally added to the thermosetting blend. The catalyst is selected from epoxide monomers, for example bisphenol A or amine monomers, for example BenzylDiMethylAmine (BDMA). The P_3/P_2 ratio between the proportion by weight P_3 of the bisphenol A in the thermosetting blend and the proportion by weight P_2 of the prepolymer (i) in the thermosetting blend is preferably between 1% and 5% and is preferably equal to 3%.

By way of example, if the thermosetting blend comprises 100 grams of epoxy prepolymer (i), 25 grams of at least one curing agent (ii), and 3 grams of a catalyst, the respective proportions by weight of these chemical components in the thermosetting blend are as follows:

- proportion by weight of the epoxy prepolymer (i) in the thermosetting blend:

  $(P_2) = 100\ \text{g}/128\ \text{g} = 0.781 = 78.1\%$;

- proportion by weight of the at least one curing agent (ii) in the thermosetting blend: $(P_1) = 25\ \text{g}/128\ \text{g} = 0.195 = 19.5\%$; and
- proportion by weight of the catalyst in the thermosetting blend: $(P_3) = 3\ \text{g}/128\ \text{g} = 0.024 = 2.4\%$,

giving $P_1P_2 = 25\ \text{g}/100\ \text{g} = 0.25 = 25\%$ and $P_3/P_2 = 3\ \text{g}/100\ \text{g} = 0.03 = 3\%$.

The components of the polyepoxy resinous matrix described above have been selected due to their excellent technical properties and their compatibility with the longitudinal carbon fibres 52 and the sizing thereof. Indeed, the epoxy prepolymer forming part of the composition of the thermosetting blend has high purity and low viscosity. Thus, the viscosity of the thermosetting blend measured at ambient temperature (≈25°C) according to standard EN ISO 12058-1:1997 entitled “Determination of viscosity using a falling-ball viscometer — Part 1: Inclined-tube method” is between 1000 mPa.s and 6000 mPa.s, preferably between 2000 mPa.s and 5000 mPa.s. In addition, in the temperature range for producing the polyepoxy resinous matrix of between 40°C and 80°C, the viscosity of the thermosetting blend drops to reach values of between 100 mPa.s and 1200 mPa.s. This drop in viscosity has the favourable effect of improving the impregnation of the carbon fibres.

According to a first preferred embodiment, the epoxy prepolymer (i) is a DiGlycidyl Ether of Bisphenol A (DGEBA), and the at least one curing agent (ii) is a blend of a cycloaliphatic amine (A) and an aromatic amine (B). Furthermore, advantageously, the proportion by weight (cycloaliphatic amine (A):aromatic amine (B)) varies from (5: 95) to (25: 75), and is preferably equal to (10: 90).

The use of a blend of a cycloaliphatic amine and an aromatic amine as curing agent makes it possible to obtain a composite longitudinal reinforcing profile having excellent chemical resistance and more particularly resistance to hydrolysis, which is in accordance with the prerequisites required in the field of offshore oil. In addition, the realisation by pultrusion of the longitudinal profile is improved compared to the use of a curing agent comprising an aromatic amine or a cycloaliphatic amine.

According to a second preferred embodiment, the epoxy prepolymer (i) is a DiGlycidyl Ether of Bisphenol A (DGEBF), and the at least one curing agent (ii) is a cycloaliphatic amine.

These first and second preferred embodiments make it possible to optimise the viscosity of the matrix before polymerisation for the manufacture by the pultrusion process, and also make it possible to guarantee a glass transition value for the polymerised matrix of greater than 170°C.

Furthermore, the polyepoxy resinous matrix has low water absorption and a very good service resistance to hydrolysis phenomena, including at high temperatures.

In service, within a tensile strength woven ply 5, 6, the longitudinal profile 50 can withstand a high temperature of between 80°C and 180°C, advantageously greater than 100°C, for a duration of several tens of years. Thus, the mechanical properties of the longitudinal profile 50, and in particular the tensile modulus of elasticity thereof and the tensile strength at break thereof remain lastingly stable in this temperature range.

The longitudinal profile 50 may also be subjected to an acid and corrosive environment since it contains gases such as carbon dioxide, hydrogen sulfide, etc. Since this environment is confined, it is favourable to the appearance of hydrolysis and corrosion phenomena.

As described above, the longitudinal profile 50 is manufactured by pultrusion. The method for manufacturing the longitudinal profile 50 is described in Fig. 3 and comprises several successive steps. First of all, by applying a tensile force, the longitudinal reinforcing fibres 52 or filamentous carbon strands, which are stored beforehand on reels 100, are pulled on in order to unwind them and guide them through a first heating device 200, for example a heat-treatment furnace or a radiative furnace (infrared, microwaves, etc.).

According to one variant, the longitudinal fibres 52 wound onto reels 100 have undergone a sizing surface treatment.

Passing through the first heating device 200, the longitudinal fibres 52 are heated to a temperature of between 150°C and 180°C without deteriorating the sizing.

The longitudinal fibres 52 are then conveyed to an impregnation device 300 comprising a heated impregnation means 302 such as a drum, a tank 304 having double walls 305, 306 and heat-regulated by circulating a coolant fluid 307 between the walls, and a circulating means 308, for example a centrifugal pump, to enable the circulation of the coolant fluid 307. The tank 304 is intended to receive the thermosetting blend comprising the epoxy prepolymer (i) contained in a first container 110 with at least one curing agent (ii) of the amine type contained in a second container 120. The epoxy prepolymer (i) and the at least one curing agent (ii) of the amine type are mixed in well- chosen proportions by weight, as described previously. The thermosetting blend thus obtained is kept at a low temperature, around 5°C, so as to retard polymerisation. It is kept in the cooled tank 304 such that its usage time at ambient temperature without adversely affecting its properties (or its “pot life”) is as long as possible.

Passing through the impregnation device 300, the longitudinal fibres 52 are coated with a film of thermosetting blend deposited via the drum 302. The impregnation of the longitudinal fibres 52 is particularly good due to the fact that the drum is heated to a temperature of between 40°C and 80°C, which enables the fluidisation of the thermosetting blend taken from the tank 304. Moreover, the raising of the temperature of the thermosetting blend deposited via the drum 302 makes it possible to trigger the polymerisation of the thermosetting blend.

In parallel, at least one reinforcing web 130 wound on at least one storage reel 100’ is provided. The at least one reinforcing web 130 is unwound, then pre-dried and preheated using at least one second heating device 400-1, 400-2. This at least one second heating device 400-1, 400-2 advantageously comprises at least hot air blowing means.

According to a first variant for implementing the manufacturing method, the at least one reinforcing web 130 is pre-dried and preheated before the longitudinal fibres 52 are preheated by the first heating device 200. According to another implementation variant, the at least one reinforcing web 130 is pre-dried and preheated after the longitudinal fibres 52 have been preheated but before they have been impregnated. Finally, according to yet another implementation variant, the at least one reinforcing web 130 is pre-dried and preheated after the longitudinal fibres 52 have been impregnated but before the longitudinal profile 50 is preformed by a shaping device 500 or shaping die.

The reinforcing web or mat 130 is a nonwoven textile layer consisting of short fibres assembled by mechanical compaction and/or adhesive bonding. It is produced from fibres that are resistant to hydrolysis and/or to the gases contained in the confined environment. These fibres are chosen from carbon fibres, para-aramid fibres such as Technora®, meta-aramid fibres such as Nomex®, basalt fibres, polyester fibres, high-performance fibres such as the liquid-crystal polymers (LCP) sold by Vectran® or glass fibres such as the S-2 fibres sold by AGY. When the longitudinal profile 50 has a substantially rectangular section, the mat 130 may be applied to one or the other of the large lower or upper faces of the longitudinal profile 50 or on both the large faces simultaneously, so as to improve the mechanical properties thereof.

The longitudinal profile 50 is next guided through the preforming device 500 such as a shaping die in order to give it the desired final section.

Finally, the longitudinal profile 50 is wound onto a take-up reel (not shown). The take-up reel and therefore also the longitudinal profile 50 are sent to a baking or post-curing device, for example a heat-treatment furnace, to complete the crosslinking of the thermosetting blend and thus form the polyepoxy resinous matrix 54. The baking is carried out at a temperature of at least 180°C and lasts at least 1 h.

Additionally, and optionally, a final step of cutting said longitudinal profile 50 to the desired dimensions may be carried out.

According to another feature of the invention, a plurality of longitudinal reinforcing profiles 50 are used for the production of at least one reinforcing layer of a flexible tubular pipe 1.

In order to manufacture a tensile strength woven ply, the longitudinal reinforcing profiles 50 are wound with a long pitch at an absolute value of the helical angle of between 20° and 60°, preferably between 25° and 55°, this helical angle being measured relative to the longitudinal axis Δ of the flexible tubular pipe 1.

In order to manufacture a pressure-resistant woven ply, the longitudinal profiles 50 are wound with a short pitch at an absolute value of the helical angle of between 70° and 90° relative to the axis Δ.

The use of longitudinal profiles 50 according to the present invention for producing one or more reinforcing layers 4; 5, 6 of the flexible tubular pipe 1 makes it possible to obtain a flexible pipe 1 which is both light and very mechanically strong, allowing it to be used in particular at great depths.

Moreover, this also allows the flexible pipe 1 to better withstand high temperatures and also hydrolysis when it is utilised in severe production conditions.

Of course, the embodiment described previously and the use made thereof is only given by way of non-limiting examples. Other implementation variants can be produced without departing from the scope of the invention.

Patentkrav

1. Langsgående forstærkningsprofil af komposit (50) der omfatter langsgående carbonfibre (52), som er indlejret i en polyepoxyharpiksmatrix (54) der er opnået ved polymerisering af en termohærdende blanding, som omfatter en epoxypræpolymer og mindst et hærdningsmiddel og eventuelt en katalysator, i hvilken:

- epoxypræpolymeren (i) er en diglycidylether af bisphenol A (DGEBA) eller en diglycidylether af bisphenol F (DGEBF) eller en tetraglycidylmethylen-dianilin (TGMDA);
- det mindst ene hærdningsmiddel (ii) er en cycloalifatisk amin eller en aromatisk amin eller en blanding af en cycloalifatisk amin med en aromatisk amin; og
- P_1/P_2-orholdet mellem vægtandelen P_1 af det mindst ene hærdningsmiddel (ii) i den termohærdende blanding og vægtandelen P_2 af præpolymeren (i) i den termohærdende blanding er mellem 15 % og 30 % og er fortrinsvis lig med 25 %.

2. Langsgående forstærkningsprofil (50) ifølge krav 1, **kendetegnet ved, at** den termohærdende blanding har en viskositet målt ved 25 °C ifølge standarden EN ISO 12058-1:1997 på mellem 1000 mPa.s og 6000 mPa.s, fortrinsvis mellem 2000 mPa.s og 5000 mPa.s og en viskositet målt mellem 40 °C og 80 °C på mellem 100 mPa.s og 1200 mPa.s.

3. Langsgående forstærkningsprofil (50) ifølge et af kravene 1 til 2, **kendetegnet ved, at** katalysatoren er valgt blandt phenolmonomerer, for eksempel bisphenol A, eller blandt aminmonomerer, for eksempel benzyldimethylamin.

4. Langsgående forstærkningsprofil (50) ifølge krav 3, **kendetegnet ved, at** P_3/P_2-forholdet mellem vægtandelen P_3 af bisphenol A i den termohærdende blanding og vægtandelen P_2 af præpolymeren (i) i den termohærdende blanding er mellem 1 % og 5 % og fortrinsvis lig med 3 %.

5. Langsgående forstærkningsprofil (50) ifølge et hvilket som helst af kravene 1 til 4, **kendetegnet ved, at** den maksimale kontinuerlige brugstemperatur deraf er mellem 80 °C og 180 °C, fordelagtigt større end 100 °C.

6. Fremgangsmåde til ved pultrusion at fremstille en langsgående forstærkningsprofil af komposit (50), der omfatter langsgående carbonfibre (52), som er indlejret i en polyepoxyharpiksmatrix (54), der er opnået ved polymerisation af en termohærdende blanding, som omfatter:

- en epoxypræpolymer som er en diglycidylether af bisphenol A (DGEBA) eller en diglycidylether af bisphenol F (DGEBF) eller en tetraglycidylmethylen-dianilin (TGMDA); og
- mindst et hærdningsmiddel der er en cycloalifatisk amin eller en aromatisk amin eller en blanding af en cycloalifatisk amin med en aromatisk amin, og
- eventuelt en katalysator,

kendetegnet ved, at fremgangsmåden omfatter følgende successive trin:

a) at forvarme de langsgående fibre (52) til en temperatur på mellem 150 °C og 180 °C;

b) at imprægnere de langsgående fibre (52) ved anvendelse af en film der er fremstillet af en blanding, som er termohærdende ved en temperatur på mellem 40 °C og 80 °C, og udløser polymeriseringen af den termohærdende blanding;

c) at præforme eller forme længdeprofilen (50) og fortsættelse af polymeriseringen af den termohærdende blanding;

d) at bage eller efterhærde længdeprofilen (50) ved en temperatur på mindst 180 °C i mindst 1 time.

7. Fremstillingsfremgangsmåden ifølge krav 6, **kendetegnet ved, at** den fremstillede langsgående forstærkningsprofil (50) er ifølge et hvilket som helst af kravene 1 til 5.

8. Fremstillingsfremgangsmåde ifølge krav 6 eller 7, **kendetegnet ved, at** den mellem trin (b) og trin (c) omfatter et trin (b1) til påføring af mindst en forstærkningsbane over mindst en af fladerne på den langsgående profil (50).

9. Fremstillingsfremgangsmåden ifølge krav 8, **kendetegnet ved, at** den omfatter et trin med at fortørre og forvarme mindst en armeringsbane før trin (b1).

10. Fremstillingsfremgangsmåde ifølge et hvilket som helst af kravene 6 til 9, **kendetegnet ved, at** den efter trin (d) omfatter et trin til at skære den langsgående profil (50).

11. Undersøisk fleksibel rørledning (1) til transport af fluider af carbonhydrider der omfatter:

- en indvendig lækagetæt kappe (3) og
- mindst et forstærkende lag (4; 5, 6) der omfatter et antal langsgående forstærkningsprofiler af komposit (50), som omfatter langsgående carbonfibre (52), der er indlejret i en polyepoxyharpiksmatrix (54) som er opnået ved polymerisering af en termohærdende blanding, der omfatter:
- en epoxypræpolymer som er en diglycidylether af bisphenol A (DGEBA) eller en diglycidylether af bisphenol F (DGEBF) eller en tetraglycidylmethylen-dianilin (TGMDA); og
- mindst et hærdningsmiddel der er en cycloalifatisk amin eller en aromatisk amin eller en blanding af en cycloalifatisk amin med en aromatisk amin; og
- eventuelt en katalysator.

12. Undersøisk fleksibel rørledning (1) ifølge krav 11, hvor de langsgående forstærkningsprofiler (50) er ifølge et hvilket som helst af kravene 1 til 5.

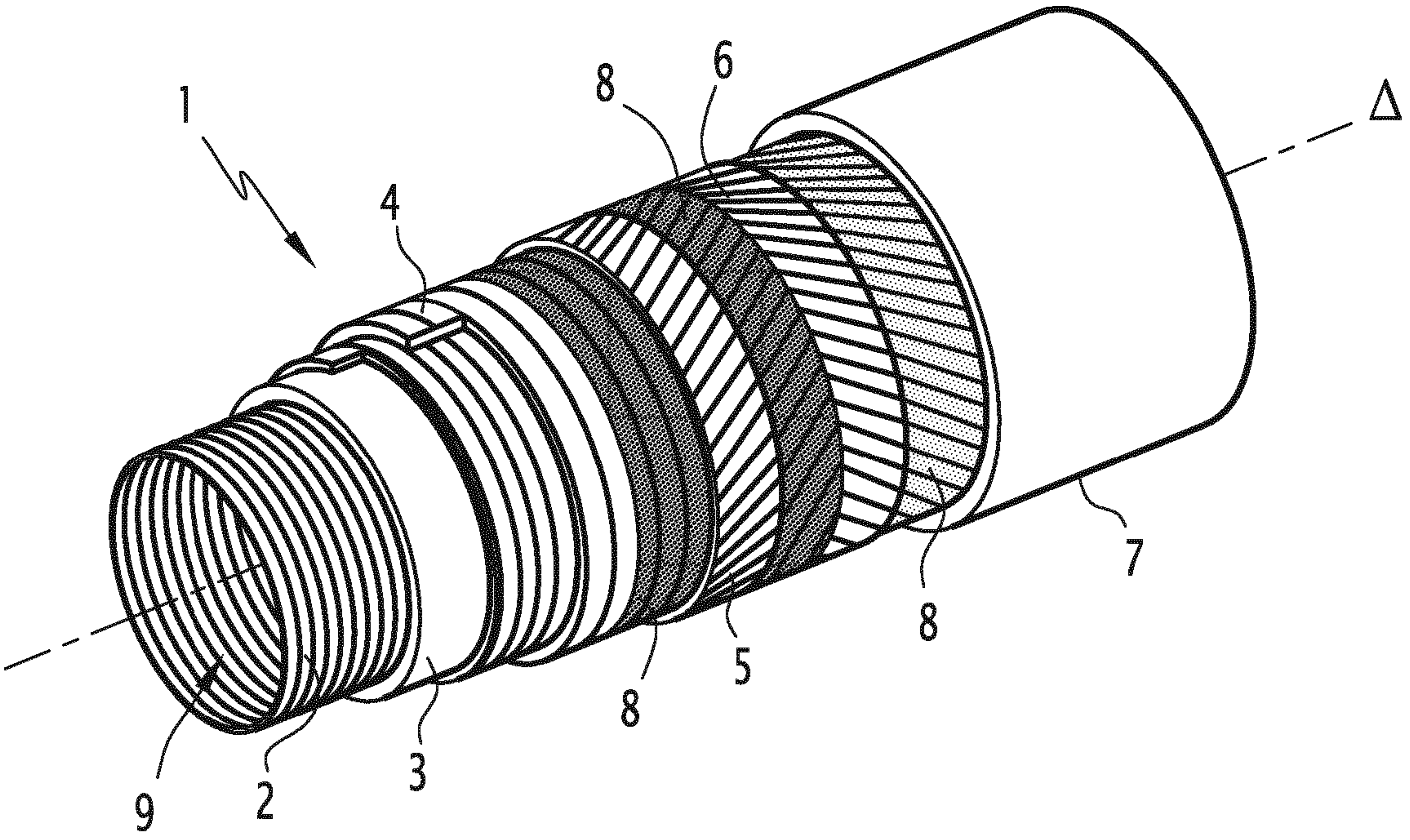


FIG.1

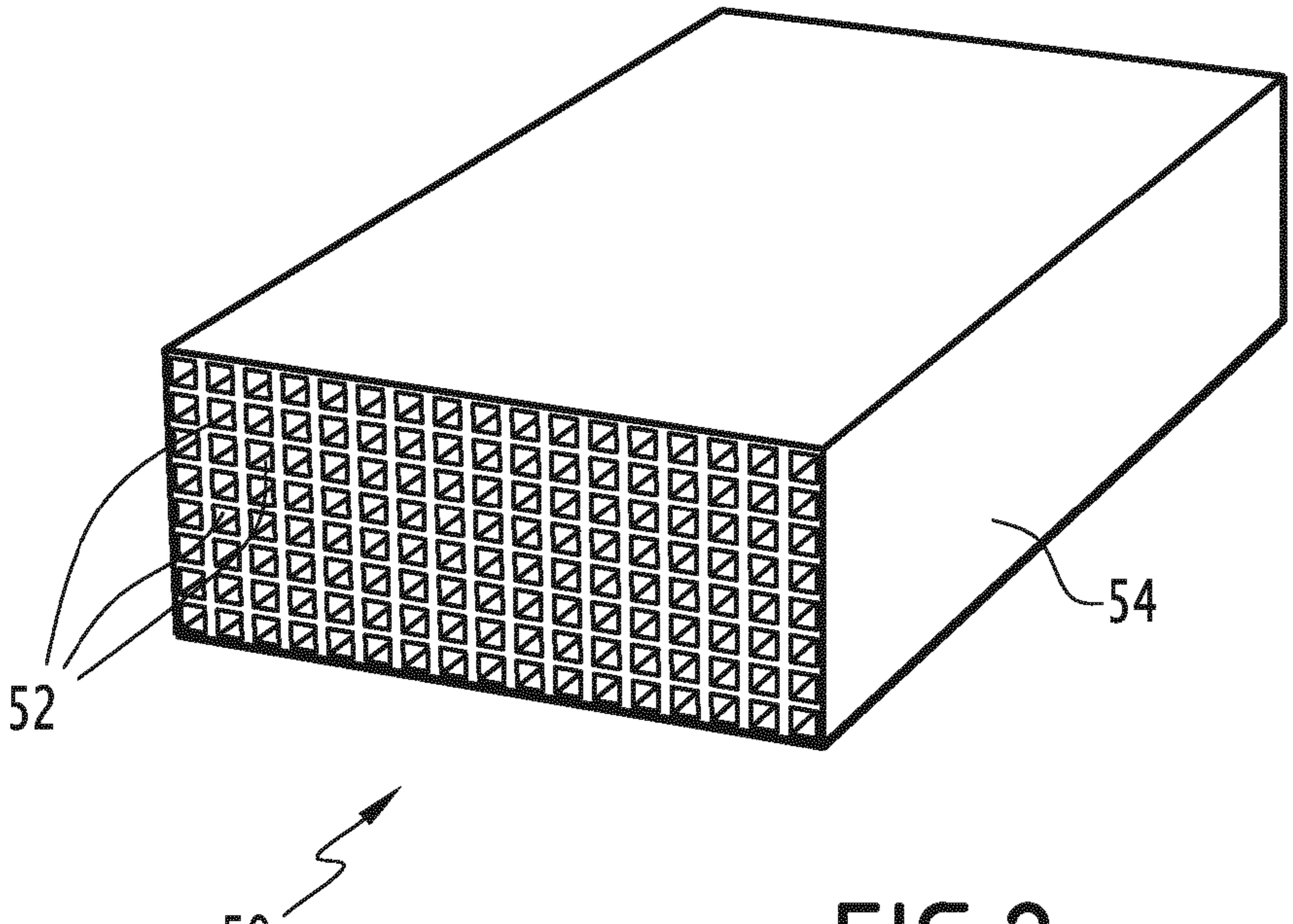


FIG.2

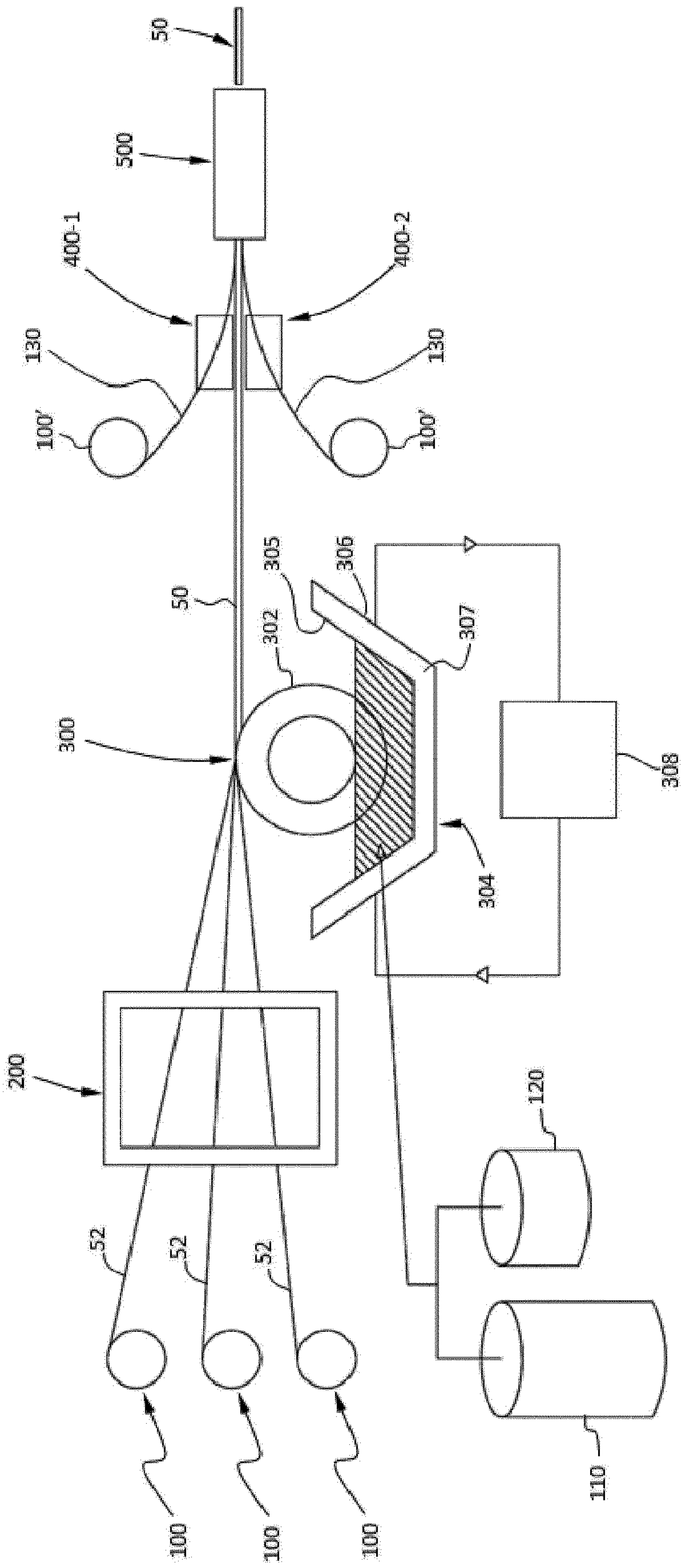

50
500
400-1
400-2
130
130
100'
100'
305
306
50
302
307
300
308
304
200
120
52
52
52
110
100
100
100

FIG.3