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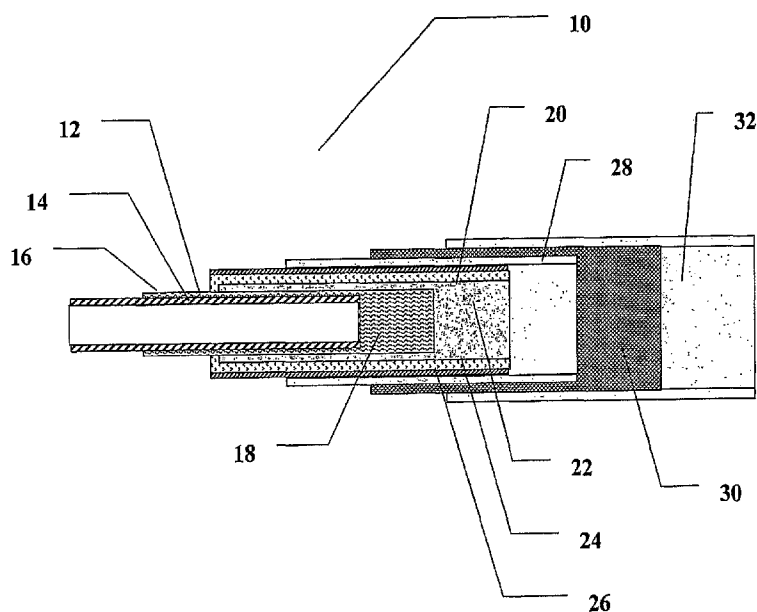
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(54) Title: HIGH PRESSURE BARRIER HOSE AND METHOD OF MANUFACTURE



(57) Abstract: Novel flexible hoses are disclosed that are capable of handling high pressure fluids and providing high barrier against permeation loss. The hoses comprise (from innermost to outermost layer) a thermoplastic veneer; a tie layer; a metal-polymer laminate; a braid under-layer of a thermoplastic or thermosetting elastomer; a reinforcing braid layer; and an outer layer of an elastomeric material. The hoses are suitable for use in air conditioning, refrigeration, fuel handling, hydraulic and similar systems requiring the transport of high pressure fluids.

WO 2008/013829 A2

High Pressure Barrier Hose and Method of Manufacture

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FIELD OF THE INVENTION

The present invention relates to flexible hoses capable of handling high pressure fluids and providing high barrier against permeation loss, and the manufacture thereof. More particularly the present invention relates to such flexible hoses for use in air conditioning, refrigeration, fuel handling, hydraulic and similar systems requiring the transport of high pressure fluids.

BACKGROUND OF THE INVENTION

Many systems require the transport of fluids under high pressure. Examples of these are air conditioning and refrigeration systems where the refrigerant needs to be transported through and/or among various components of the system such as the compressor, condenser and evaporator. Hydraulic systems require transport of the hydraulic fluid from a pump to an actuator.

Hoses used for these and similar purposes need to be flexible for ease of installation and use, and often must be shaped into curves and bends for connecting components already installed into fixed positions. They must also be able to contain the fluid pressure. These hoses are often made of elastomeric materials such as natural or synthetic rubber or thermoplastic elastomers, and are typically reinforced with braiding to impart high pressure capability.

An additional requirement especially in air-conditioning, refrigeration and fuel transport applications is high barrier to permeation of the contained fluid through the wall of the hose construction. It is desired that the hose wall also

provides high barrier to ingress of external fluids, such as air or moisture, into the contained fluid.

5 In order to meet barrier requirements, hoses are often provided with a suitable thermoplastic barrier layer on the inside. A typical high pressure barrier hose may thus consist of multiple layers – an inner thermoplastic barrier layer made of a polyamide, a polyester or a suitable thermoplastic material; an over-
10 layer of an elastomeric material to provide flexibility; and a braid layer over the elastomeric layer to provide pressure capability and an outer protective cover layer of an elastomeric material.

 While such hoses provide pressure capability and flexibility, their barrier properties are limited. With the drive for reduced emissions, this becomes an
15 issue in highly demanding applications such as refrigeration and air conditioning. As systems with new non-halogen based refrigerants are being developed such as those based on CO₂ and hydrocarbons, barrier requirements become significantly more stringent. Conventional hoses are inadequate in such applications.

20 Attempts to make flexible high pressure high barrier hoses often involve first making a corrugated metallic tube and coating the tube with an elastomeric polymer. Such constructions, however, require complex manufacturing processes, and are expensive for large scale uses. US patent 7,055,553
25 describes a fluid transfer hose incorporating a metal barrier layer. The metal barrier layer is bonded using techniques that require use of aggressive chemicals. Also, expensive fluoropolymer layers are incorporated in the hose construction.

30 It is an object of the present invention to provide a flexible hose that offers superior barrier properties. A feature of the invention is its simple and straightforward construction, for example as described by the method of assembly and example provided herein. It is an advantage of the present

invention to provide hoses and hosing materials that are suitable for the various applications enumerated herein. These and other objects, features and advantages of the present invention will become better understood upon having
5 reference to the description of the invention herein.

SUMMARY OF THE INVENTION

There is disclosed and claimed herein a hose including a series of layers arranged from the innermost to the outermost surface, comprising:

- 10 (a) an innermost layer of a thermoplastic veneer having an inner surface and an outer surface;
- (b) a tie layer positioned over the innermost layer;
- (c) a metal-polymer laminate positioned over the tie layer and
15 consisting of a layer of polymer compatible with or bondable to the outer surface of the veneer, a thin layer of metallic foil, and another layer of a polymer protecting the metallic foil;
- (d) a braid under-layer positioned over the metal-polymer laminate and consisting of an elastomeric material;
- (e) a reinforcing braid layer positioned over the braid under-layer;
20 and
- (f) an outer layer of an elastomeric material positioned over the reinforcing braid layer.

Optionally, additional braid layers and outer (or cover) layers may be provided
25 for even higher pressure capability. Therefore the user has latitude to select a tube construction of a sufficient number of layers to meet or exceed the intended applications.

There is also provided a method of manufacture of the above hose
30 construction.

IN THE DRAWING

FIGURE 1 is a cross sectional view of a tube of the instant invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention offers hoses constructed in multiple layers such as described below from the innermost to the outermost surface:

- an layer of a thermoplastic veneer;
- a tie layer;
- a metal-polymer laminate consisting of a layer of polymer compatible with the tie layer, a thin layer of metallic foil, and another layer of a polymer protecting the metallic foil;
- a braid under-layer of a thermoplastic or thermosetting elastomer;
- a braid layer providing reinforcement; and
- an outer layer of an elastomeric material.

Having reference to Figure 1, there is shown generally at 10 each of the layers of the invention, numbered and described from the innermost layer to the outermost layer. Hence, there is first depicted closest to the core (where the mandrel is inserted and then later withdrawn) an innermost layer of a thermoplastic veneer 12 having an inner surface 14 and an outer surface 16. The veneer may incorporate a tie layer 18 positioned at its outer surface 16. A metal-polymer laminate 20 is positioned over the tie layer and consisting of a layer 22 of polymer compatible with or bondable to the outer surface of the veneer, a thin layer 24 of metallic foil, and another layer 26 of a polymer protecting the metallic foil. Thereafter, a braid under-layer 28 is positioned over the metal-polymer laminate 20 and consisting of an elastomeric material. A reinforcing braid layer 30 is then positioned over the braid under-layer 28. Finally, an outer layer 32 of an elastomeric material positioned over the reinforcing braid layer 30.

The hose of the present invention is manufactured in multiple steps, sequenced as provided below.

Step 1 - First a mandrel or a solid rod or other suitable structure is provided that serves as a support through the subsequent manufacturing steps. Such mandrels are commonly used in the manufacture of hoses made out of thermosetting materials that need to be supported during the extrusion and curing steps. They are made of a variety of thermoplastic or thermosetting materials such as copolyester ethers, copolyamides, polyolefins, TPVs, EPDMs, synthetic rubbers etc. It is desirable to ensure that the mandrel has sufficient flexibility to be spoolable in long lengths.

Step 2 - A thermoplastic veneer is extruded over the mandrel. The veneer can be in the form of a monolayer or a two layer tube depending on the type of metal foil and polymer laminate to be used in step 3 as explained below. It should not develop adhesion to the mandrel surface so that mandrel can be extracted at the end of hose fabrication. As appropriate, one of skill in the field can apply suitable release agents to the mandrel to facilitate the nonadhesive properties of the mandrel in relation to the inner layer of the veneer and lubricate its extraction at the end of hose fabrication.

A monolayer veneer or the inner layer of the two-layer veneer can be made of a polyamide, copolyamide, polyphthalamide, polyester or copolyester that provides chemical and thermal resistance to the contained fluid it is in contact with.

When a monolayer veneer is used, the laminate used in step 3 is provided with an adhesive that can bond to the surface of the veneer. Examples of such laminates are those where metallic foil is laminated with a pressure sensitive adhesive (PSA) that can adhere to the surface of the veneer. Such laminates are available commercially with variety of adhesives such as acrylics, rubber, silicones etc.

In a two-layer veneer construction, the outer layer is made of a functionalized polymer to function as a tie layer between the inner thermoplastic veneer and the metal-polymer laminate to be provided over it. It can be made of a functionalized polyolefin or copolyolefin such as those made by grafting or copolymerizing functional monomers with olefins and copolyolefins. Some examples of functional monomers include those with acid, anhydride, acrylate, epoxy functionality.

When a two-layer veneer is used, the laminate used in step 3 does not need to have an adhesive surface. It is rather sufficient to have a polymeric layer at the surface that is compatible or otherwise bondable to the functionalized tie layer of the veneer.

Step 3 - A metal foil and polymer laminate consisting of a first polymer layer compatible or bondable to the surface of the veneer, a thin metallic foil and a second polymer layer (which may be identical to or different from the first polymer layer) is then applied over the assembly prepared in step 2.

Adhesion can be further promoted by application of heat and/or pressure as warranted. Heating may not be necessary if the first polymer layer of the laminate is a room temperature pressure sensitive adhesive (PSA) type. When a two-layer veneer is used along with a functionalized polyolefin as the tie layer, application of both heat and pressure are needed. In one embodiment, the assembly of Step 2 is covered by the metal foil laminate and passed through a heated die designed to apply pressure on to the assembly to form the bonding. In another embodiment, the veneer supported by the mandrel is first passed through a heating tunnel so as to raise the surface temperature of the veneer. The metal foil laminate is then applied over the veneer, and the assembly is passed through another heated die designed to apply pressure and affect bonding.

The laminate is applied over the veneer lengthwise so that it circumferentially wraps around it. The two edges of the foil positioned lengthwise along the tube are bonded tightly together and any excess foil is then trimmed to provide a fully covered assembly. This form of wrapping is preferred over the so-called helical wrap formed by winding a tape over the veneer in a helical fashion at an angle to the axis of the hose because it results in only one seam running along the length of the hose. From barrier perspective, a seam can provide potential site for permeation leak. Hence, it is desirable to minimize it's occurrence in the construction. Lengthwise wrap described above is also easier to apply especially on a small diameter tubing such as that encountered in flexible high pressure hoses.

In cases where extremely high barrier is desired, it may be advantageous to provide multiple layers of the laminate in a manner that seams do not overlap thus providing higher level of permeation barrier.

Metallic foil is thin enough to provide flexibility while resist fracture during handling. For example, it can be aluminum foil, in 1-10 micron thickness range to provide very high level of barrier while retaining flexibility. Note that this approach provides a continuous layer of metal over the tube surface unlike vapor deposition techniques which leave gaps in metal coverage resulting in inferior barrier properties.

The second layer of polymer over the metallic foil is selected to protect the surface of the metal foil and provide compatibility with the braid under-layer to be provided over it. It can be a polyamide, polyester or a polyolefin, and is selected so as to be compatible with the type of braid underlayer to be used in the next step.

Step 4 – A braid underlayer is extruded over the assembly of Step 3. The underlayer is an elastomeric material such as a natural or synthetic rubber or a thermoplastic elastomer such as thermoplastic olefin (TPO), thermoplastic ester

elastomer (TEE) or a thermoplastic vulcanizate (such as ETPV or TPV, common selections in this field). Its purpose is to provide cushioning and protection against forces imposed during braiding.

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It is preferable if this braid underlayer bonds to the surface of the laminate applied in step 3. This may be accomplished by several means such as ensuring that the braide underlayer material is compatible with the surface layer of the laminate, extruding a two-layer braid underlayer such that its inner layer acts as a tie layer to bond to the surface of the laminate or sequentially extruding a tie layer over the laminate first and then the braid underlayer.

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A functionalized polymer such as that used for forming the tie layer of the two-layer veneer of step 2 may be used for this purpose, the functionalization chosen to be compatible with the two layers to be bonded.

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Step 5 – A braided reinforcement layer is provided over the assembly of Step 4.

Depending on the desired pressure capability, braiding can be made of metallic or polymeric filaments or high performance filaments such as Kevlar® or

Nomex®, both commercially available from E.I. DuPont de Nemours & Co Inc. of Wilmington, Delaware. Braid density is determined according to desired pressure capability and filament material selection. Multiple layers of braid and hybrid braids of multiple types of filaments are often used in practice to maximize the degree of reinforcement while optimizing the cost.

20

Step 6 – An outer protective layer is extruded over the braided reinforcement layer. This layer can again be made of an elastomeric material such as TPO, TEE or a thermoplastic vulcanizate (ETPV or TPV).

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Step 7 – If any of the layers in the hose construction are made of a thermosetting material, then the assembly of Step 6 needs to be cured. If all the layers are made of thermoplastic materials, then curing is not necessary. Note that one or more outer protective layers can be added at this time as well.

30

Step 8 – Finally, the mandrel is extracted from the assembly of Step 6 or Step 7 to produce the finished hose. The mandrel can be extracted by applying hydraulic pressure to one end of the hose or by mechanical means.

Hose made this way can be cut to desired length and fittings can be applied as desired. The hose made this way provides flexibility, high pressure capability and very high barrier capability.

It is readily apparent to those having skill in the art to which this invention pertains that in addition to the materials mentioned herein, a variety of other materials are suitable for each layer as is well known and understood. Likewise, representative thicknesses of each layer and techniques for braiding are already well appreciated by those having skill in the field, and are selected according to the intended application.

Example

A hose was constructed according to this invention in the following manner. A mandrel was first made in the form of a solid rod with a diameter of 6.4 mm. A veneer consisting of an inner layer of 0.65 mm thick Zytel® 42 (a high MWA 66 commercially available from E.I. DuPont de Nemours & Co., Inc.) and 0.1 mm thick outer tie layer of Bynel® 4206 (a maleic anhydride grafted polyethylene commercially available from E.I. DuPont de Nemours & Co., Inc.) was extruded over the mandrel. The assembly was then laminated with a metal-polymer laminate available as BFW 46 and obtained from James Dawson Enterprises Ltd of Lachine, Quebec, Canada. The laminate consisted of an inner layer of low density polyethylene, a tie layer of EEA, an aluminum foil (10 micron thick) and an outer layer of polyethylene terephthalate (PET) with a total thickness of 0.1 mm. Lamination was carried out using a heated die with a passage way of appropriate size to pass the assembly through. The assembly of the previous step was uncoiled from a spool and a strip of metal-polymer laminate was wrapped around it such that two long edges of the strip met against each other. The assembly was passed through the die heated to 140 C to affect the bonding. Excess laminate edge was trimmed off carefully so as not to

damage the seal and avoid exposing underlying layer. A layer of TPV was
extruded over the assembly. Following that, a braid of PET filaments was applied,
and outer protective layer of ETPV was extruded over the top. The mandrel was
5 subsequently extracted to prepare the multi-layer hose.

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IN THE CLAIMS

1. A hose including a series of layers arranged from the innermost to the outermost surface, comprising:

- 10 (a) an innermost layer of a thermoplastic veneer having an inner surface and an outer surface;
- (b) a tie layer positioned over said innermost layer;
- (c) a metal-polymer laminate positioned over said tie layer and consisting of a layer of polymer compatible with or bondable to said outer surface of said veneer, a thin layer of metallic foil, and another
- 15 layer of a polymer protecting the metallic foil;
- (d) a braid under-layer positioned over said metal-polymer laminate and consisting of an elastomeric material;
- (e) a reinforcing braid layer positioned over said braid under-layer; and
- (f) an outer layer of an elastomeric material positioned over said
- 20 reinforcing braid layer.

2. The hose of Claim 1 further comprising one or more additional braid layers (e) and/or one or more additional outer layers (f).

25 3. A method of manufacturing a tube exhibiting superior barrier resistance and flexibility, the method comprising:

- (a) Providing a mandrel;
- 30 (b) Extruding over the mandrel a thermoplastic veneer having an inner surface and an outer surface;

(c) Applying over said veneer a metal foil and polymer laminate consisting of a first polymer layer compatible with or bondable to said outer surface of said veneer, a thin metallic foil and a second polymer layer;

5

(d) Extruding over said metal foil and polymer laminate an elastomeric braid underlayer;

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(e) Providing over said elastomeric braid underlayer a braided reinforcement layer;

(f) Extruding over said braided reinforcement layer an outer protective layer;

15

(g) If any of said layers are made of a thermosetting material, then the curing the assembly of step (f); and

(h) Extracting the assembly of either step (f) or step (g) from the mandrel.

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4. The method of Claim 3 wherein in step (b) said thermoplastic veneer is a monolayer and in step (c) said laminate is provided with an adhesive that bonds to said outer surface of said thermoplastic veneer.

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5. The method of Claim 4 wherein said adhesive is a pressure sensitive adhesive.

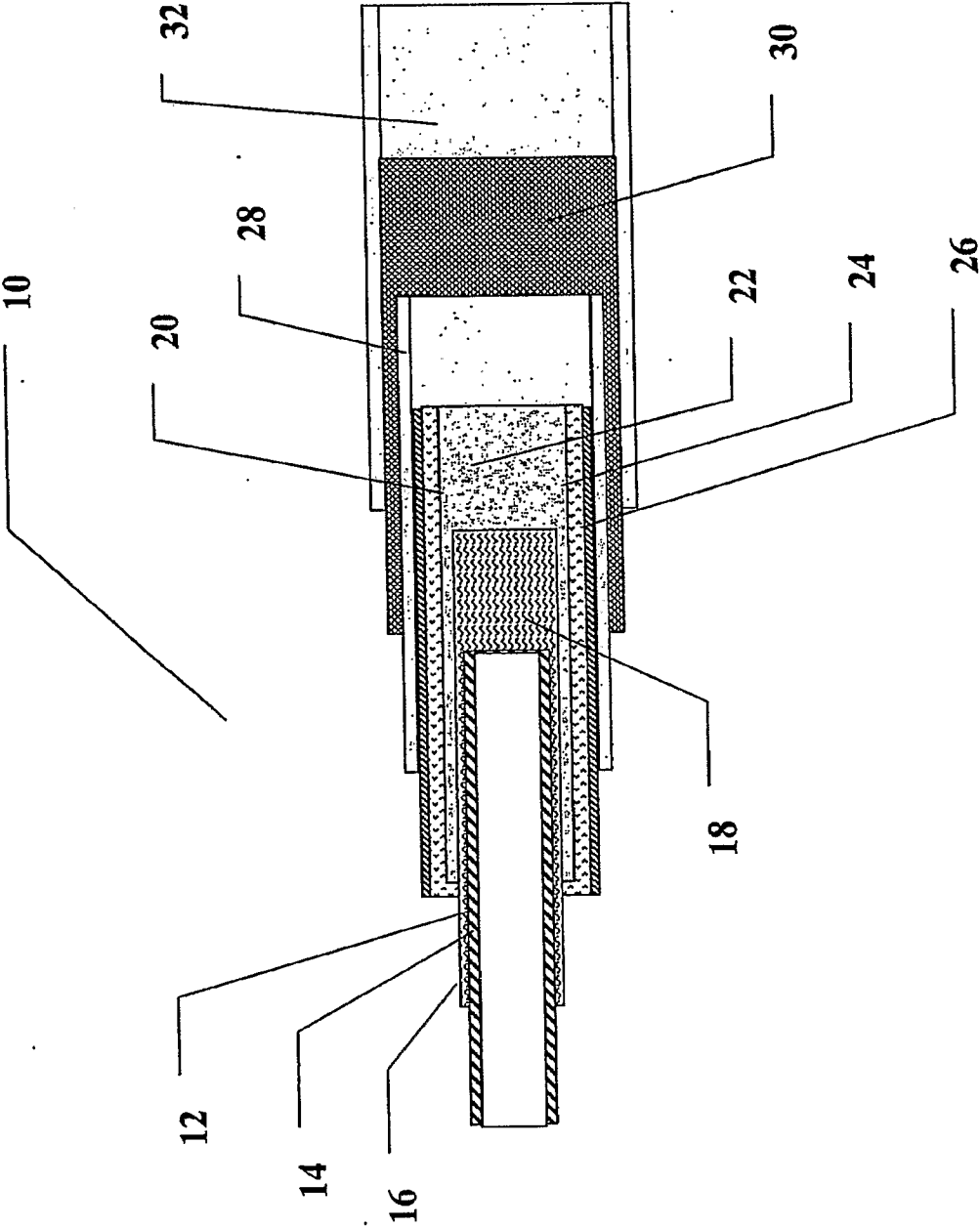


Figure 1

