A composition and a hose (400) made therefrom having improved fuel vapor barrier layer (10) is provided and the composition comprises a blend of about 20 to 80 weight percent of a first fluorointerpolymer with about 80 to 20 weight percent of a second fluorointerpolymer. The first fluorointerpolymer comprises a copolymer, terpolymer or mixture thereof formed by the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene. The second fluorointerpolymer comprises a copolymer, terpolymer or mixture thereof formed by the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene. The first fluorointerpolymer exhibits elastomer characteristics and second fluorointerpolymer exhibits thermoplastic characteristics.
<table>
<thead>
<tr>
<th>Code</th>
<th>Country</th>
<th>Code</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>Albania</td>
<td>ES</td>
<td>Spain</td>
</tr>
<tr>
<td>AM</td>
<td>Armenia</td>
<td>FI</td>
<td>Finland</td>
</tr>
<tr>
<td>AT</td>
<td>Austria</td>
<td>FR</td>
<td>France</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GA</td>
<td>Gabon</td>
</tr>
<tr>
<td>AZ</td>
<td>Azerbaijan</td>
<td>GB</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>BA</td>
<td>Bosnia and Herzegovina</td>
<td>GE</td>
<td>Georgia</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GH</td>
<td>Ghana</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GN</td>
<td>Guinea</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>GR</td>
<td>Greece</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>HU</td>
<td>Hungary</td>
</tr>
<tr>
<td>BI</td>
<td>Benin</td>
<td>IE</td>
<td>Ireland</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>IL</td>
<td>Israel</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>IS</td>
<td>Iceland</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>IT</td>
<td>Italy</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>JP</td>
<td>Japan</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KE</td>
<td>Kenya</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>KG</td>
<td>Kyrgyzstan</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d'Ivoire</td>
<td>KP</td>
<td>Democratic People's</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>KR</td>
<td>Republic of Korea</td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>KZ</td>
<td>Kazakhstan</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>LC</td>
<td>Saint Lucia</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>LI</td>
<td>Liechtenstein</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>LK</td>
<td>Sri Lanka</td>
</tr>
<tr>
<td>EE</td>
<td>Estonia</td>
<td>LR</td>
<td>Liberia</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>LS</td>
<td>Lesotho</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>LT</td>
<td>Lituania</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td>LU</td>
<td>Luxembourg</td>
</tr>
<tr>
<td>GA</td>
<td>Gabon</td>
<td>LV</td>
<td>Latvia</td>
</tr>
<tr>
<td>GB</td>
<td>United Kingdom</td>
<td>MC</td>
<td>Monaco</td>
</tr>
<tr>
<td>GE</td>
<td>Georgia</td>
<td>MD</td>
<td>Republic of Moldova</td>
</tr>
<tr>
<td>GH</td>
<td>Ghana</td>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>GN</td>
<td>Guinea</td>
<td>MK</td>
<td>The former Yugoslav</td>
</tr>
<tr>
<td>GR</td>
<td>Greece</td>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>HU</td>
<td>Hungary</td>
<td>MN</td>
<td>Mongolia</td>
</tr>
<tr>
<td>IE</td>
<td>Ireland</td>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>IL</td>
<td>Israel</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>IS</td>
<td>Iceland</td>
<td>MX</td>
<td>Mexico</td>
</tr>
<tr>
<td>IT</td>
<td>Italy</td>
<td>NE</td>
<td>Niger</td>
</tr>
<tr>
<td>JP</td>
<td>Japan</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>KE</td>
<td>Kenya</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>KG</td>
<td>Kyrgyzstan</td>
<td>NZ</td>
<td>New Zealand</td>
</tr>
<tr>
<td>KP</td>
<td>Democratic People's</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>KR</td>
<td>Republic of Korea</td>
<td>PT</td>
<td>Portugal</td>
</tr>
<tr>
<td>KZ</td>
<td>Kazakhstan</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>LC</td>
<td>Saint Lucia</td>
<td>RU</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>LI</td>
<td>Liechtenstein</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>LK</td>
<td>Sri Lanka</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>LR</td>
<td>Liberia</td>
<td>SG</td>
<td>Singapore</td>
</tr>
<tr>
<td>SI</td>
<td>Slovenia</td>
<td>SK</td>
<td>Slovakia</td>
</tr>
<tr>
<td>SN</td>
<td>Senegal</td>
<td>SZ</td>
<td>Swaziland</td>
</tr>
<tr>
<td>TG</td>
<td>Chad</td>
<td>TO</td>
<td>Togo</td>
</tr>
<tr>
<td>TJ</td>
<td>Tajikistan</td>
<td>TM</td>
<td>Turkmenistan</td>
</tr>
<tr>
<td>TR</td>
<td>Turkey</td>
<td>TT</td>
<td>Trinidad and Tobago</td>
</tr>
<tr>
<td>UA</td>
<td>Ukraine</td>
<td>UG</td>
<td>Uganda</td>
</tr>
<tr>
<td>US</td>
<td>United States of America</td>
<td>UK</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>UZ</td>
<td>Uzbekistan</td>
<td>VN</td>
<td>Viet Nam</td>
</tr>
<tr>
<td>YU</td>
<td>Yugoslavia</td>
<td>ZW</td>
<td>Zimbabwe</td>
</tr>
</tbody>
</table>
BLENDÖS OF FLUOROElastomer INTERPOLYMERS WITH
THERMO FLUOROPLASTIC INTERPOLYMERS AND THE USE
OF SUCH BLENDS IN HOSES

Technical Field

The present invention relates generally to hoses and
particularly to fuel transport hoses such as fuel filler and fuel filler
neck hoses having reduced permeability to fuel vapors. More
particularly, this invention relates to blends of fluoroelastomer
interpolymers with fluorothermoplastic interpolymers, and to the use
of such blends as a barrier layer for fuel transport hoses to reduce
the permeability of such hoses to fuel vapors.

Background Art

Recent environmental regulations imposed on the
automotive industry severely limit the amount of fuel vapor that can
permeate from the fuel systems of motor vehicles. Choosing the
right polymer to provide high performance, long service life, and
reduced permeability of fuel in the fuel systems of motor vehicles
while maintaining costs at an acceptable level has been more
difficult for automotive designers than ever before. Typically, fuel
transfer and fuel vapor hoses have been made of butadiene-
acrylonitrile rubber as the tube, but such hoses have a high
permeability to fuel. Other hoses have a fluoroelastomer as the
inner wall surface layer of the hose, but such hoses have higher
permeability to fuel vapors. Attempts to produce fuel transfer hoses
with reduced permeability to fuel vapors have included the use of
corrugated polyamide and fluorocarbon thermoplastic tubes.
However, these structures are very expensive.

Other attempts to produce a fuel filler neck hose with
reduced permeability to fuel vapors used a tetrafluoroethylene-
hexafluoropropylene-vinylidene fluoride terpolymer liner and a thicker layer of hexafluoropropylene-vinylidene fluoride copolymer or other suitable elastomer as the conductive inner part of the tube. See, for example, U.S. Patent Nos. 4,606,952 to Sugimoto and 5,430,603 to Albino et al. Such hose structures have a tendency to wrinkle on the inner radius of the forming mandrel or pin causing a cosmetic defect.

Accordingly, there is a need for an improved fuel hose that meets present industry standards.

Disclosure of the Invention

In accordance with the present invention a blend of a first fluorointerpolymer having elastomer characteristics and a second fluorointerpolymer having thermoplastic characteristics unexpectedly provides a composition which not only meets the low permeability standard for fuel vapor, but also is relatively inexpensive to produce, exhibits good service life and, when used in the manufacture of fuel transfer hoses, has a good push-on value, seals well, has good low temperature properties and resists kinking and wrinkling of the hose structure while being formed in conventional molding techniques.

In a first embodiment of the invention, a composition having improved fuel vapor barrier properties is provided. The composition comprises a blend of a first fluorointerpolymer which comprises a copolymer, terpolymer or mixture thereof formed by the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, and a second fluorointerpolymer which comprises a copolymer, terpolymer or mixture thereof formed by the copolymerization of two or more monomers selected from the group
consisting of hexafluoropropylene-vinylidene fluoride and
tetrafluoroethylene, wherein the first fluorointerpolymer exhibits
elastomeric characteristics and the second fluorointerpolymer
exhibits thermoplastic characteristics.

In a second embodiment of the invention, a hose
having improved fuel vapor barrier properties is provided. The hose
comprises a barrier layer comprising a blend of about 20 to 80
weight percent of a first fluorointerpolymer with about 80 to 20
weight percent of a second fluorointerpolymer, the first interpolymer
comprising a copolymer, terpolymer or mixture thereof formed by
the copolymerization of two or more monomers selected from the
group consisting of hexafluoropropylene, vinylidene fluoride and
tetrafluoroethylene, and the second fluorointerpolymer comprising
a copolymer, terpolymer or mixture thereof formed by the
copolymerization of two or more monomers selected from the group
consisting of hexafluoropropylene, vinylidene fluoride and
tetrafluoroethylene, wherein the first fluorointerpolymer exhibits
elastomeric characteristics and the second fluorointerpolymer
exhibits thermoplastic characteristics. The hose not only exhibits
reduced permeability to fuel vapors, but also avoids kinking and
wrinkling in conventional molding techniques, provides extended
service life, and is relatively inexpensive to produce.

In a first manifestation of the hose of the present
invention, the hose structure comprises a conductive or non-
conductive barrier layer comprising a blend of a first
fluorointerpolymer having elastomer characteristics and a second
fluorointerpolymer having thermoplastic characteristics; and a
protective cover adjacent to and surrounding the conductive barrier
layer.
In a second manifestation of the hose of the present invention, the hose structure comprises a conductive or non-conductive barrier layer comprising a blend of a first fluorointerpolymer having elastomeric characteristics and a second fluorointerpolymer having thermoplastic characteristics as a barrier layer forming the interior wall of the hose; an elastomeric layer adjacent to and surrounding the outermost surface of the barrier layer; a reinforcing layer adjacent to and surrounding the outermost surface of the elastomeric layer; and a protective cover layer adjacent to and surrounding the outer surface of the reinforcing layer.

In a third manifestation of the invention, the hose structure comprises a conductive or non-conductive elastomeric layer which forms the interior surface of the hose; a barrier layer comprising a blend of a first fluorointerpolymer having elastomer characteristics and a second fluorointerpolymer having thermoplastic characteristics adjacent to and surrounding the outermost surface of the first elastomeric layer; a reinforcing layer adjacent to and surrounding the elastomeric layer; and a protective cover layer adjacent to and surrounding the reinforcing layer.

In a fourth manifestation of the invention, the hose structure comprises a first conductive or non-conductive elastomer layer which forms the interior surface of the hose; a barrier layer comprising a blend of a first fluorointerpolymer having elastomer characteristics and a second fluorointerpolymer having thermoplastic characteristics adjacent to and surrounding the outermost surface of the first elastomeric layer; a second elastomeric layer adjacent to and surrounding the outermost surface of the barrier layer; a reinforcing layer adjacent to and surrounding
the outermost surface of the second elastomeric layer; and a protective cover layer adjacent to and surrounding the reinforcing layer.

Surprisingly, the hoses of the invention reduce the permeability of hydrocarbon vapors, particularly fuel vapors, from the hose to below proposed industry standards, have good low temperature properties, have good push-on values, exhibit extended service life, and are relatively inexpensive to produce without any wrinkles caused by sharp turns, curves and bends during the formation of the hose on a forming mandrel or pins.

It is an object of the invention to provide a blend of a first fluorointerpolymer having elastomer characteristics and a second fluorointerpolymer having thermoplastic characteristics, wherein the first fluorointerpolymer having elastomeric properties comprises a blend of a first fluorointerpolymer which comprises a copolymer, terpolymer or mixture thereof formed by the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, and a second fluorointerpolymer which comprises a copolymer, terpolymer or mixture thereof formed from the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, wherein the first fluorointerpolymer exhibits elastomeric characteristics and the second fluorointerpolymer exhibits thermoplastic characteristics. The blend, when employed as a barrier layer in fuel transport hoses, provides low permeability to hydrocarbon fuel vapors.

It is another object of the invention to provide a hydrocarbon-resistant hose such as a fuel transfer hose, e.g., fuel
filler hose, that satisfies the industry standards for permeability particularly with respect to fuel vapors, that avoids kinking and wrinkling in conventional molding techniques, that has an extended service life, and that is relatively inexpensive to produce.

Other objects and advantages of the invention will be apparent from the following description and the appended claims.

**Brief Description of the Drawings**

The features of the invention, and its technical advantages, can be seen from the following description of the preferred embodiments together with the claims and the accompanying drawings, in which:

Fig. 1 is perspective cutaway view of a tubular member which illustrates a first manifestation of the present invention;

Fig. 2 is a perspective cutaway view of a tubular member illustrating another manifestation of the present invention;

Fig. 3 is a perspective cutaway view of a tubular member illustrating still another manifestation of the present invention;

Fig. 4 is a perspective cutaway view of a tubular member which illustrates yet another manifestation of the present invention; and

Fig. 5 is a perspective cutaway view of a tubular member which illustrates another manifestation of the present invention.

**Description of Preferred Embodiments**

In accordance with the invention, a blend of a first fluorointerpolymer having elastomer characteristics and a second fluorointerpolymer having thermoplastic characteristics provides a
barrier layer for use in the manufacture of fuel transport hoses such as fuel filler and fuel filler neck hoses, and the like, wherein such barrier layer unexpectedly provides low levels of permeability of fuel vapors from the fuel hose. The permeation rates of fuel vapors from the fuel hose of the present invention satisfies the proposed industry standards.

Fig. 1 is perspective cutaway view of a tubular member which illustrates a first manifestation of the present invention wherein a hose 100 is constructed which comprises a barrier layer 10 and a protective cover layer 18.

Fig. 2 illustrates a second manifestation wherein a hose 200 comprises a barrier layer 10 forming the interior wall of the hose 200; a reinforcing layer 16 adjacent to and surrounding the outermost surface of the barrier layer 10; and an outer cover 18 as the exterior protective surface of the hose 200.

Fig. 3 illustrates a third manifestation wherein a hose 300 comprises a barrier layer 10 forming the interior wall of the hose 300; an elastomeric layer 12 adjacent to and surrounding the outermost surface of the barrier layer 10; a reinforcing layer 16 adjacent to and surrounding the elastomeric layer 12; and an outer cover 18 as the exterior protective surface of the hose 300.

A fourth manifestation of the invention is illustrated in Fig. 4 where the hose 400 comprises an elastomeric layer 12 forming the interior wall surface of the hose; a barrier layer 10 adjacent to and surrounding the outermost surface of the elastomer layer 12; a reinforcing layer 16; and an outer cover 18 as the exterior surface of the hose 400.

Fig 5 illustrates a fifth manifestation of the invention in which hose 500 has a structure similar to the hose 400 shown in
Fig. 4, except that a second elastomeric layer 14 resides between the barrier layer 10 and the reinforcing member 16.

The term fluorointerpolymer as used herein means the polymer produced by the copolymerization of two or more fluoromonomers and, therefore, is meant to encompass copolymers, terpolymers, etc.

The term "hydrocarbon" as used herein is meant to include fuels such as gasoline, oils, air conditioning gases, organic chemicals, and the like.

The barrier layer 10 of the invention is formed from a blend of at least two fluorointerpolymers, wherein at least one of the fluorointerpolymers is characterized as a fluoroelastomer and at least one of the fluorointerpolymers is characterized as a fluoro thermoplastic. Preferably, the barrier layer 10 is a fluoroelastomer which comprises hexafluoropropylene-vinylidene fluoride copolymer or vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene terpolymer, blended with a fluoro thermoplastic such as tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride terpolymer. Most preferably the fluoroelastomer component of the blend has a fluorine content of about 65 to 73% and the fluoro thermoplastic component of the blend has a typical fluorine content of 70 to 75%. The hexafluoropropylene-vinylidene fluoride fluoroelastomer is commercially available from DuPont under the name Viton A, Viton E45 or Viton 60. The vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene fluoroelastomer is commercially available from 3M under the name Fluorel FT2350 or FE583OQD. The tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride fluoroplastic terpolymer is a fluoro thermoplastic such as Dyneon THV, which is commercially available from Dyneon.
Typically, the blend comprises about 20 to 80% by weight fluoroelastomer and about 80 to 20% by weight fluorothermoplastic. Since the permeability of the fuel hose to fuel vapors decreases with an increase in the fluorine content of the blend, a higher ratio of the fluorothermoplastic component which typically contains a higher percentage of fluorine by weight than the fluoroelastomer component may be employed in the blend 10, however, the plastic-like properties of the fluorothermoplastic components are prone to cause kinking of the hose when the fluorothermoplastic component is too high. Typically the fluorine content of the blend is about 70 to 75 weight percent. The barrier layer preferably comprises about 50 to 70% by weight of the elastomeric fluorointerpolymer and about 30 to 50% by weight of the thermoplastic fluorointerpolymer. Blends comprising about 70% by weight of the elastomeric interpolymer and about 30% by weight of the thermoplastic interpolymer have been found to provide a good balance between reduced fuel vapor permeability and good physical properties of the hose. Typically, the thickness of the barrier layer 10 is about 0.127 to 0.635 mm (5 to 25 mils), preferably about 0.330 to 0.356 mm (13 to 14 mils).

The compositions of the present invention are either unvulcanized or vulcanized using any of the art established vulcanizing agents such as peroxides, polyols, polyamines, etc. The peroxide vulcanizing agent includes, for example, dicumylperoxide, 2,5-dimethyl-2,5-di(t-buty)peroxy) hexyne-3, etc. The polyol vulcanizing agent includes, e.g., hexafluoroisopropylidene-bis(4-hydroxyphenyl) hydroquinone, isopropylidene-bis(4-hydroxyphenyl), or the like. The polyamine vulcanizing agent includes, e.g., hexamethylenediamine carbamate,
alicyclic diamine carbamate, etc. The amount of vulcanizing agent employed is generally that which is customarily used in the art. Typically, about 0.5 to 10% vulcanizing agent is employed depending on the vulcanizing agent.

The elastomer layer 12 may be a conductive elastomer such as a conductive acrylonitrile-butadiene rubber, conductive ethylene-acrylate rubber and the like or a conductive fluoroelastomer such as hexafluoropropylene-vinylidene fluoride copolymer or vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene terpolymer.

The elastomer layer 14 is typically a material which has properties causing it to easily adhere to both the outer cover material and the barrier blend, particularly when vulcanized. Preferably the tubular layer 14 is an elastomer which also affords heat resistance, fuel resistance and good flexibility to the hose. Such materials are well known in the art. The elastomeric layer 14 typically is a non-conductive material selected from a group consisting of butadiene-acrylonitrile rubber, epichlorohydrin rubber, ethylene-acrylate rubber, and the like. Preferably, the elastomeric layer 14 is butadiene-acrylonitrile rubber.

The outer cover 18 of the hose is a protective layer of any of the commercially recognized materials for such use such as elastomers, thermoplastic polymers, thermosetting polymers, and the like. Typically, the protective layer is a synthetic elastomer having good heat resistance, oil resistance, weather resistance and flame resistance. Preferably, the outer cover layer is a synthetic elastomer selected from the group consisting of styrene-butadiene rubber (SBR); butadiene-nitrile rubber such as butadiene-acrylonitrile rubber; chlorinated polyethylene; chlorosulfonated...
polyethylene; vinylethylene-acrylic rubber, acrylic rubber; epichlorohydrin rubber such as Hydrin 200, a copolymer of epichlorohydrin and ethylene oxide available from DuPont ECO; polychloroprene rubber (CR); polyvinyl chloride; ethylene-propylene copolymers (EPM); ethylene-propylene-diene terpolymer (EPDM); ultra high molecular weight polyethylene (UHMWPE); high density polyethylene (HDPE) and blends thereof. Preferably, the synthetic elastomer is chloropolyethylene.

The reinforcing member 16 is a material which affords physical strength to the finished hose. Typically, the reinforcing member is selected from a group consisting of glass fibers, cotton fibers, polyamide fibers, polyester fibers, and rayon fibers. Preferably, the reinforcing material is an aromatic polyamide such as Kevlar or Nomex, both of which are manufactured by DuPont. The reinforcing material may be either knitted, braided, or spiraled to form the reinforcing member. In a preferred aspect of the invention, the reinforcing material is spiraled. While the reinforcing layer may be a preferred component of the hose structure, it is not critical and may or may not be used in the manufacture of certain hoses depending upon the requirements of the manufacturer.

As is common practice in the industry, the innermost layer of fuel hoses, whether it is a barrier layer 10 or an elastomer layer 12, is made conductive to prevent the buildup of static electricity generated by the flow of fuel along the inner surface of the hose. Such a buildup of static electricity over time has been known to cause the formation of pin holes in the hose allowing the fuel to leak out through the holes. Typically, the barrier layer 10 or the elastomer layer 12 is made conductive by compounding the layer material with carbon black or other industry recognized
ingredients to provide conductivity to the barrier layer. While the amount of carbon black added is not critical, excess carbon black tends to make the material more difficult to process. In vapor or vent applications, the innermost layer of the hose need not be conductive.

In the first embodiment of the hose of this invention as shown in Fig. 1, the barrier layer 10 is a conductive blend of a fluoroelastomer and a fluorothermoplastic, wherein the fluorine content of the blend is about 70 to 75 weight percent and the ratio of fluoroelastomer to fluorothermoplastic is about 70:30. The blend 10 is made conductive by incorporating carbon black into the composition.

In the embodiments of the invention as shown in Figs. 4 and 5, the elastomeric inner tubular layer 12 which forms the inner tubular wall of the fuel transfer hose is a fluoroelastomer or elastomer having good conductive properties and fuel resistance. Preferably, the conductive fluoroelastomer or elastomer inner tubular layer 12 is selected from the group consisting of nitrile rubber (NBR), thermoplastic fluoroelastomer, such as hexafluoropropylene vinylidene fluoride copolymers or hexafluoropropylene-vinylidene fluoride-tetrafluoroethylene terpolymers, polyvinyl chloride, and blends thereof. Preferably, the elastomeric, inner tubular layer is conductive NBR such as butadiene-acrylonitrile rubber.

The methods of producing the fuel transfer hose of the present invention are known in the art. For example, separate extrusion, tandem extrusion, or coextrusion processes may be used. For versatility and cost reasons, the preferred methods for producing the fuel filler transfer hose of the present invention are
separate extrusion and tandem extrusion.

Production of the preferred embodiment of the present invention is as follows. First, the conductive layer of acrylonitrile-butadiene rubber is extruded into a tube and then immediately fed through another extruder during which the barrier layer comprising a blend of vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene fluoroelastomer with tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride fluorothermoplastic is applied. After the tube has been extruded and the appropriate layers applied, strands of reinforcing fibers such as Kevlar are spiraled onto the tube. A protective cover of chloropolyethylene is then applied to the reinforced tube by a cross-head extruder. The chloropolyethylene is drawn down onto the reinforced tube by use of a vacuum. The covered reinforced tube is then placed on a mandrel and vulcanized. The tube is then manually removed from the mandrel.

Other polymers, e.g., fluorinated ethylene-propylene (FEP) copolymers such as Teflon, which is available from DuPont, may be used as a component in the fluoroelastomer component, the thermoplastic component or as an additional component in the preparation of the blend.

Other additives such as antioxidants, processing aids, etc. can be employed in carrying out the present invention and it is within the scope of this invention to incorporate herein any such additives as commonly used in making fuel line hoses.
The blended fluoroelastomer/fluorothermoplastic barrier layer of the present invention is useful in reducing the permeability of fuel vapors from the fuel transfer hose; however, it is also useful in reducing the permeability of chemical vapors such as in air conditioning hoses, oil hoses, and the like where severe chemical resistance or vapor permeation resistance is required.

The use of the novel blended fluoroelastomer/fluorothermoplastic barrier layer in the fuel transfer hose of the present invention presents a means of unexpectedly achieving almost complete impermeability of fuel filler neck hoses to fuel vapors.

While the fluoroelastomer/fluorothermoplastic blend is particularly useful in hose construction to reduce permeability of fuel vapor, these blends can be used in the manufacture of other articles where reduced fuel or hydrocarbon vapor is desired such as o-rings, gaskets, diaphragms, etc.

Having described the invention in detail and by reference to preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.
CLAIMS:

1. A composition having improved fuel vapor barrier properties, characterized by a blend of about 20 to 80 weight percent of a first fluorointerpolymer with about 80 to 20 weight percent of a second fluorointerpolymer, said first fluorointerpolymer comprising a copolymer, terpolymer or mixture thereof formed by the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, and said second fluorointerpolymer comprising a copolymer, terpolymer or mixture thereof formed by the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, wherein said first fluorointerpolymer exhibits elastomer characteristics and said second fluorointerpolymer exhibits thermoplastic characteristics.

2. The composition of claim 1, characterized in that said first fluorointerpolymer has a fluorine content of about 65 to 73 weight percent and said second fluorointerpolymer has a fluorine content of about 70 to 75 weight percent.

3. The composition of claim 2, characterized in that said first fluorointerpolymer is a vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene terpolymer having elastomeric characteristics, and said second fluorointerpolymer in a hexafluoropropylene-tetrafluoroethylene-vinylidene fluoride terpolymer having thermoplastic characteristics.

4. The composition of claim 1, further characterized by a conductive material, such as carbon black.

5. A fuel hose having improved fuel vapor barrier properties, characterized by:
a barrier layer (10) comprising a blend of about 20 to 80 weight percent of a first fluorointer polymers with about 80 to 20 weight percent of a second fluorointer polymer, said first fluorointer polymer comprising a copolymer, terpolymer or a mixture thereof formed by the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride, and tetrafluoroethylene, and said second fluorointer polymer comprising a copolymer, terpolymer or mixture thereof formed by the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene; and

a protective cover layer (18).

6. The hose of claim 5, further characterized by a reinforcing layer (16) and possibly one or more elastomeric layers (12, 14), wherein one (12, 14) of said one or more elastomeric layers, for example of acrylonitrile-butadiene rubber, resides between said barrier layer (10) and said reinforcing layer (16), and said reinforcing layer (16) resides between said elastomeric layer (12, 14) and said protective cover layer (18).

7. The hose of claim 5, characterized in that said barrier layer is about 0.127 to 0.635 mm thick.

8. The hose of claim 6, characterized in that said reinforcing layer (16) is a layer of fibers selected from the group consisting of polyamide fibers, polyester fibers, rayon fibers, glass fibers and cotton fibers, especially aromatic polyamide fibers which can be knitted, braided or spiraled in the construction of said hose (200-500).

9. The hose of claim 5, characterized in that said protective cover layer (18) is a layer of synthetic elastomer selected
from the group consisting of styrene-butadiene rubber, nitrile-butadiene rubber, chloroprene rubber, chlorinated polyethylene, chlorosulfonated polyethylene, epichlorohydrin ethylene oxide, polyvinyl chloride, and blends thereof.

10. The hose of claim 6, characterized in that said barrier layer (10) or one (12) of said one or more elastomeric layers forms an inner tubular layer of said hose (100-500), and in that said inner tubular layer (10, 12) can further comprise a conductive material, especially carbon black.

11. A hose for transporting fuels, characterized by employing, as a barrier layer (10), a blend of about 20 to 80 weight percent of a first fluorointerpolymer with about 80 to 20 weight percent of a second fluorointerpolymer, said first fluorointerpolymer comprising a copolymer, terpolymer or mixture thereof formed by the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride, and tetrafluoroethylene, and a second fluorointerpolymer comprising a copolymer, terpolymer or mixture thereof formed by the copolymerization of two or more monomers selected from the group consisting of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene, wherein said first fluorointerpolymer exhibits elastomer characteristics and said second fluorointerpolymer exhibits thermoplastic characteristics.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B29D 23/00; B32B 1/08, 27/08
US CL. : 428/36.91, 421; 525/199

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/36.91, 421; 525/199

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>US RE 32,230 A (SATOH et al.) 26 August 1986 (26-08-86), columns 3 and 8.</td>
<td>9, 16-19</td>
</tr>
<tr>
<td>Y</td>
<td>US 5,320,888 A (STEVENS) 14 June 1994 (14-06-94), columns 1-3.</td>
<td>1-20</td>
</tr>
<tr>
<td>Y</td>
<td>US 4,758,455 A (CAMPBELL et al) 19 July 1988 (19-07-88), columns 2-3.</td>
<td>6-19</td>
</tr>
<tr>
<td>Y</td>
<td>US 5,639,528 A (FEIT et al) 17 June 1997 (17-06-97), columns 2 and 4.</td>
<td>9, 16-19</td>
</tr>
<tr>
<td>Y</td>
<td>5,718,957 A (YOKOE et al) 17 February 1998 (17-02-98), columns 4-5 and 7.</td>
<td>1-20</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

"*" Special categories of cited documents:

*A* document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

*P* document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"*" document member of the same patent family

Date of the actual completion of the international search

08 AUGUST 1999

Date of mailing of the international search report

31 AUG 1999

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks

Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SANDRA NOLAN

Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet) (July 1992)