(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 May 2001 (25.05.2001)

PCT

(10) International Publication Number
WO 01/36556 A2

(51) International Patent Classification[7]: C09J

(21) International Application Number: PCT/US00/41714

(22) International Filing Date: 31 October 2000 (31.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/439,708 12 November 1999 (12.11.1999) US

(71) Applicant *(for all designated States except US)*: **GOSHEN RUBBER CO., INC.** [US/US]; 1525 South Tenth Street, P.O. Box 517, Goshen, IN 46527 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **BENHAM, Neil, R.** [US/US]; 2045 Barron Lake Road, Niles, MI 49120 (US).

(74) Agents: **MYERS, James, B.** et al.; Woodard, Emhardt, Naughton, Moriarty & McNett, Bank One Center/Tower, Suite 3700, 111 Monument Circle, Indianapolis, IN 46204 (US).

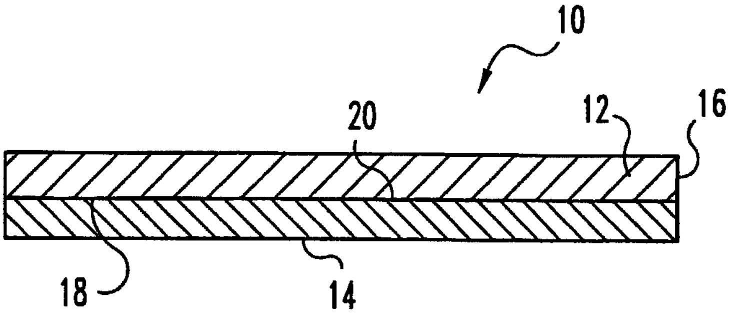
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *Without international search report and to be republished upon receipt of that report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FUEL BARRIER LAMINATE



(57) Abstract: In general, this invention relates to an adhesive rubber blend, preferably a nitrile rubber, a laminate formed from the adhesive rubber blend, and a process for providing the laminate. The adhesive rubber blend includes a curing agent and an adhesion promoter selected from a C_7 to C_{15} azacycloalkyl, a cyclic amidine and a polymer blend comprising monomeric unites derived from maleic anhydride and butadiene. The adhesive rubber blend can be used to provide a laminate (10) wherein a rubber layer (12) is directly bonded to a fluoropolymer layer (14). The laminate (10) can be used to provide a wide variety of seals (20) and gaskets as a barrier to inhibit release of volatile organic compounds (VOC). The process of providing the laminate includes compounding the rubber blend with the curing system and the adhesion promoter; extruding a first layer that comprises the rubber layer; contacting the first layer with a second layer that includes a fluoropolymer; and curing the resulting laminate.

WO 01/36556 A2

FUEL BARRIER LAMINATE

FIELD OF THE INVENTION

Generally the present invention relates to a multirubber or rubber and plastic composition, a laminate formed to include the rubber composition, and methods of manufacturing the laminate. More specifically, the present invention is directed to an adhesive polymer blend, a laminate having a polymeric layer directly bonded to a fluoropolymer layer, and methods of forming the laminate.

BACKGROUND OF THE INVENTION

There is an increased public awareness of the environmental harm associated with the emission of volatile organic compounds from a variety of sources, in particular, the emission of gasoline or oxygenated gasoline from vehicles and their associated fuel systems. This increased awareness is reflected in recent enactment of federal and state regulations mandating the reduction of airborne hydrocarbon emissions allowed per vehicle. One potential source of the emissions is permeation of fuel vapors through rubber hoses and seals interconnecting components in combustion engines and related fuel handling components. This provides an increased incentive for continued development of new and reliable polymeric composites and structures to inhibit and further reduce the emission of volatile organic compounds.

Certain fluoropolymers are known and have been used to provide effective barriers inhibiting release of volatile organic compounds. However, types of fluoropolymers do not exhibit the compressive stress resistance desired in seals and gasket material to provide an effective seal between component parts of fuel handling systems. Therefore, certain fluoropolymers traditionally have been combined with other materials, such as nitrile rubber, which were selected to enhance the compressive resistance of the seal or gasket material. Most fluoropolymers are relatively non-polar and substantially chemically inert. The fluoropolymers resist forming a bond to other polymeric materials. Adhesive often must be introduced between the layers to bond them together. The use of adhesive requires additional manufacturing steps, and increases labor and material costs. This limits the potential advantages that might be realized for seals and gaskets formed from fluoropolymers.

In light of the above-described problems, there is a continuing need for advancements in the relevant fields, including improved polymer compositions and methods for manufacturing seals and gasket materials. The present invention is such an advancement. The present invention meets the needs discussed above, and has a variety of other benefits and advantages.

SUMMARY OF THE INVENTION

The present invention relates to adhesive polymeric compositions, laminates formed to include the adhesive polymeric compositions and the manufacture and use thereof. Various aspects of the invention are novel, nonobvious, and provide various advantages. While the actual nature of the invention covered herein can only be determined with reference to the claims appended hereto, certain forms and features, which are characteristic of the preferred embodiments disclosed herein, are described briefly as follows.

In general, this invention provides an adhesive polymer blend that can be used to bond to a fluoropolymer substrate to provide a laminated structure. The laminated structure can be formed into a wide variety of configurations. The preferred laminate structure provides particular advantages. Gaskets and seals formed from the preferred laminate maintain their structural integrity even under extreme compression that occurs when placed between mating machined components, such as engine components or fuel handling system components, that are subsequently pressed together. Volatile organic chemicals do not significantly permeate the gasket or seals thus, making the laminated seal a highly effective barrier inhibiting release of fuel or vapors. The laminated seals resist delamination that can occur under normal or even extreme use.

In one form, the present invention provides a laminate formed of a first layer having a first composition that includes a polymeric material, a curing agent, and an adhesion promoter. The adhesion promoter can be selected from an azacycloalkyl having between seven and fifteen ring atoms; a cyclic amidine compound and a polymer blend comprising monomeric units derived from maleic anhydride and butadiene, and an amount of a co-agent. The laminate also includes a second layer comprising a fluorinated polymer. The fluorinated polymer is directly bonded to the first layer. The fluorinated polymer can consist of one or more monomers. The fluoropolymer can be selected to include a wide variety of fluorine-containing monomers. In preferred embodiments, the fluorinated polymer can include: at least one monomeric residue derived from the group consisting essentially of vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene, pentafluoropropylene, trifluoroethylene, trifluoro chloro ethylene, vinyl fluoride, perfluoromethyl vinyl ether, perfluoroethyl vinyl ether. The laminate can be formed into a variety of shaped or cut components, including "O" rings, seals, gaskets, hoses, and the like.

In another form, the present invention provides a rubber blend for adhering to a polymeric substrate. The rubber blend comprises a nitrile polymer, a curing system, and adhesion promoter. The curing system comprises a curing agent and an acid acceptor. The adhesion promoter is capable of enhancing adhesion to the polymeric substrate and can be selected from an azacycloalkyl having between seven and fifteen ring atoms; a cyclic amidine compound; and a polymer blend comprising: a polymer formed of monomeric units derived from maleic anhydride and butadiene, and a co-agent. In one embodiment, the adhesion promoter is selected to include azacycloheptane. In alternative embodiments, the adhesion promoter is selected from a variety of cyclic amidines, preferably C_7 to C_9 cyclic amidine. Preferably, the cyclic amidine promoter includes 1,8-diazabicyclo[5.4.0]undecene-7. In still yet another embodiment, the adhesion promoter is selected to include a polymer blend and a co-agent. Preferably, the polymer blend includes a polymer having monomeric units formed from maleic anhydride and butadiene. In preferred forms, the co-agent may be selected from triallyl cyanurate; triallyl isocyanurate; ethylene dimethacrylate; divinylbenzene; diallyl phthalate; tolyl bismaleimide and *m*-phenylene bismaleimide; N,N'-*m*-phenylene bismaleimide; dipropargyl terephthalate; diallyl phthalate; tetraallyl terephthalamide; vinyl-tris(2-methoxyethoxy) silicate; and mixtures thereof. The polymeric blends for this invention can also include a variety of other components including antioxidants, antiozonants, chain transfer agents, plasticizers, and fillers.

In still yet another form, the present invention provides a process of forming a laminate. The process comprises compounding a rubber material with an organic peroxide curing agent and an adhesion promoter capable of enhancing adhesion to a polymeric substrate to provide an adhesive rubber blend; extruding a first layer comprising the adhesive rubber blend; and contacting the first layer with a second layer comprising a fluorinated polymer to provide a green laminate. The adhesion promoter included in the adhesive rubber blend can be selected from an azacycloalkyl having between seven and fifteen ring atoms; a cyclic amidine compound; and a polymer comprising monomeric units derived from maleic anhydride and butadiene; and a co-agent. In preferred embodiments, the green laminate can be further processed by steam curing, injection molding and/or compression.

Therefore it is one object of the present invention to provide a fuel barrier laminate having a rubber layer bonded directed to a fluoropolymer layer.

Further objects, features, aspects, forms, advantages and benefits shall become apparent from the description and drawings contained herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an elevated plan view of one embodiment of a laminate formed according to the present invention.

Figure 2 is a cross-sectional view of one embodiment of a laminated pre-form according to the present invention.

Figure 3 is a perspective view of one embodiment of a cut gasket formed according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to the embodiments illustrated herein and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended. Any alterations and further modifications in the described processes, systems or devices, and any further applications of the principles of the invention as described herein, are contemplated as would normally occur to one skilled in the art to which the invention relates.

In general, this invention provides an adhesive polymer used in a laminate with a fluoropolymer. The term fluoropolymers as used herein includes a wide variety of fluorinated materials, including fluoroelastomers, fluoroplastics, and fluoroset polymers. The rubber blend can be extruded in a variety of conformations to overlay a fluoropolymer layer and provide a laminate structure. The preferred laminated structure provides particular advantages by maintaining its structural integrity even under extreme compressive force, thereby significantly reducing emission of volatile vapors from fuel sources.

Figure 1 is an illustration of one embodiment of a laminate 10 that includes a first layer 12 formed of a nitrile rubber and a second layer 14 formed of a fluoropolymer. At interface 16, surface 18 of first layer 12 is directly bonded to a surface 20 of second layer 14. While only two layers are depicted in laminate 10, it is understood that laminate 10 can include three or more layers. Preferably, but not required, laminate 10 includes alternating layers of a nitrile rubber layer and a fluoropolymer layer. Further, while a substantially flat laminate is depicted in Figure 1, laminate 10 can be formed into a variety of shapes having curved, flat or oblique, beveled surfaces.

Figure 2 is an illustration of one embodiment of a laminated pre-form formed according to this invention. Laminated pre-form 40 includes a first outer layer 42 that includes a rubber material, a second layer 44 which includes a fluoropolymer, and an inner layer 48 that includes a rubber material. In the illustrated embodiment, outer layer 42 is directly bonded to second layer 44 at interface 46. Similarly, inner layer 48 is directly bonded to second layer 44 at interface 50. It will be understood that pre-form 40 can include more than the three layers, 42, 44 and 48, depicted in Figure 2. The pre-form can be lath cut into thin seals.

Figure 3 is an illustration of an alternative embodiment of the present invention that includes a circular cut gasket 20. Gasket 20 is formed of a laminate 21 that includes a first rubber material 22, fluoropolymer layer 24, and second rubber material layer 26. First layer 22 is directly bonded to fluoropolymer layer 24 at an interface 28. Similarly, second rubber layer 26 and fluoropolymer layer 24 directly bond together at interface 30. It is understood that second rubber layer 26 can be the same or can be different from first fluoropolymer layer 22. Furthermore, while only three layers are illustrated in Figure 3, gasket 20 can include additional layers as described for laminate 10 above. Gasket 20 can be cut in a variety of shapes using techniques known in the art, including die cutting.

In one form, the present invention provides an adhesive polymer blend. The adhesive polymer blend can be used to bond directly to polymeric substrates, for example, elastomeric films such as the fluoropolymer films depicted in the embodiments illustrated in Figures 1-3. Preferably, the polymeric blend includes a nitrile polymer or rubber. It should be understood that the polymer blend can include other polymeric materials. Generally, a nitrile rubber (NBR) is a copolymer that includes monomeric units derived from acrylonitrile and butadiene. The ratio of acrylonitrile and butadiene residues in the nitrile polymer can vary widely. Preferably, the amount of the acrylonitrile in the nitrile polymer can range between about 15 weight percent (wt%), based upon the total weight of the nitrile polymer weight, and about 55 wt%. The butadiene content of the nitrile polymer preferably ranges in weight percent from between about 45 wt% and about 85 wt%. The nitrile rubber can also include additional monomeric units. Alternatively, the adhesive polymer blend can be a rubber material that includes unsaturated monomers, for example, but not restricted to, acrylonitrile, butadiene, isoprene, styrene, epichloriohydrin, (methyl) acrylates, (ethyl) acrylates, ethylene, propylene and mixtures thereof. In a preferred embodiment, the adhesive nitrile rubber blend for use in this invention is formulated to provide a thermoplastic or an elastomeric rubber blend. Nitrile polymers are well known in the art and can be obtained from a variety of commercial sources. Examples include: PERBUNAN or KRYNAC from Bayer, PARACRIL from Uniroyal Chemical, and NIPOL from Zeon Chemical.

The adhesive polymer blend includes a curing system. The curing agent can be selected to include known and commonly used curing agents. Preferably the curing agent is a peroxide-based curing agent and includes peroxide compounds useful for curing or providing post-polymerization cure for nitrile polymer. Examples of peroxides useful in the present invention include, but are not limited to: tert-butyl hydroperoxide; cumene hydroperoxide; 1,1-bis(tert-butylperoxy)-3,5,5-trimethylcyclohexane; 2,5-dimethyl-2,5-dihydroxyperoxide; di-tert-butylperoxide; tert-butylcumylperoxide; dicumylperoxide; α,α-bis(tert-butylperoxy)-*p*-diisopropylbenzene; 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane; benzoylperoxide; tert-butylperoxybenzene; *p*-chlorobenzene peroxide; 2,5-dimethyl-2,5-di(benzoylperoxy)hexyne-3; 2,5-dimethyl-2,5-di(benzoylperoxy)hexane; tert-butylperoxymaleic acid; tert-butyl-peroxyisopropyl; and mixtures thereof. The preferred peroxide curing agent includes 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane or dicumylperoxide.

The curing agent included in the adhesive polymer blend is added in an amount sufficient to initiate curing and/or propagate adhesion of the polymer blend to the polymeric substrate. Preferably, the curing agent is included in the nitrile rubber in amounts ranging from between about 0.5 parts per hundred weight of the nitrile rubber (phr) to about 10 phr. More preferably, the peroxide curing agent is included in the adhesive polymer blend in a range between about 1 phr to about 5 phr, still more preferably, between about 1.5 phr to about 3.5 phr.

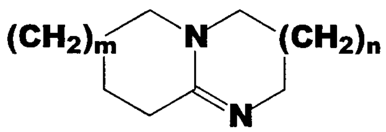
Preferably the adhesive polymer blends include a processing aid. Suitable candidates for use as processing aids in this invention include waxes, low molecular weight polyethylene and fatty acids. Examples of waxes include carnauba and paraffinic waxes. When the processing aids include a fatty acid, the acid can be selected from a variety of carboxylic acids, for example, a C_{10} to C_{25} carboxylic acid, more preferably a C_{15} - C_{20} mono or di carboxylic acid. A still more preferred acid is stearic acid. Preferably, the concentration of the organic acid is maintained sufficiently low. The organic acid is included in the adhesive polymer blend in a range of between about 0.5 phr to about 5 phr. More preferably, the organic acid is included in the polymer blend in a range between about 1 phr and about 3 phr.

Preferred acid acceptors for use with the present invention include metal oxides and metal hydroxides. More preferably, the acid acceptor includes oxides and hydroxides of metals selected from Group I and Group II of the periodic chart. Yet more preferably, the acid acceptor for use in the present invention is selected from magnesium oxide, calcium oxide, calcium hydroxide, and mixtures thereof. The acid acceptor is included in the adhesive polymer blend in amounts ranging between about 0.5 phr to about 10 phr, more preferably, between about 2 phr and about 4 phr.

The adhesive polymer blend also includes an adhesion promoter. The adhesion promoter enhances the bonding between the adhesive polymer blend layer and the polymeric substrate. While not to be bound by any theory, it is thought that the adhesion promoter used in the present invention enhances the bonding between adjacent polymeric layers by crosslinking or initiating crosslinking between one or more of the polymers in the adhesive polymer blend layer and one or more polymers in the fluoropolymer layer. The crosslinking can occur by one functional group in one polymer adding to a double bond on one of the polymers; reacting with a functional group on one of the polymers; or abstraction of an atom or group of atoms from one of the polymers, followed by addition to the resulting reactive site on the polymer. The bonding can be initiated and propagated through a free radical mechanism. A desired amount of the adhesive promoter is added to the adhesive polymer blend sufficient to enhance adhesion between the rubber and the substrate polymer layer. Preferably, the adhesion promoter is included in amounts between about 0.5 phr and about 15 phr. More preferably, the adhesion promoter is included in amounts between about 1 phr and about 10 phr. In one form, the adhesive promoter can be selected from an azacycloalkyl having between seven and fifteen ring atoms; a cyclic amidine compound; or a polymer blend comprising monomeric units derived from maleic anhydride and butadiene.

In one form the adhesive promoter can be selected to include a cyclic amine. It has been unexpectedly determined that when the adhesion promoter is included and maintained as a free amine, the resulting adhesive polymer blend forms strong, adherent bonds to the fluoropolymeric substrate. The free amine can be selected to include a nitrogen containing a heterocycle. Preferred heterocyclic amines include azacycloalkyls having between seven and fifteen ring atoms and cyclic amidine compounds. Azacycloalkyl adhesion promoters for use of the present invention include monocyclic azacycloalkyls having seven and fifteen ring members. The azacycloalkyl ring may be substituted with a variety of ring substituents, including cyclic, branched, and straight chain alkyl groups, as well as halogens. The azacycloalkyl ring may be saturated or unsaturated, with one or more double bonds appearing in the ring. Preferably, the azacycloalkyl ring is unsubstituted and saturated. Preferred azacycloalkyls for use in the present invention include any of the azacycloalkyl compounds having between seven to ten ring members; more preferably, unsubstituted, saturated azacycloalkyl rings having seven to eight ring members. Yet more preferred is azacycloheptane or hexamethyleneimine (HMI) commercially available from DuPont.

The cyclic amine for use as an adhesion promoter can also include a cyclic amidine. A wide variety of reactive cyclic amidines can be used with this invention. Examples of bicyclic amidines for use in the present invention include, but are not limited to: 1,5-diaza-bicyclo(4,2,0)octene-5; 8-diaza-bicyclo(7,2,0)undecene-8; 1,4-diaza-bicyclo(3,3,0)octene-4; 3,6,7,7-tetramethyl-1,4-diaza-bicyclo(3,3,0)octene-4; 7,8,8-trimethyl-1,5-diaza-bicyclo(4,3,0)nonene-5; 1,8-diaza-bicyclo(7,3,0)tridecene-8; 1,5-diaza-bicyclo(4,4,0)decene-5; 1,5-diaza-bicyclo(4,3,0)nonene-5; 1,8-diaza-bicyclo(7,4,0)tridecene-8; 1,8-diaza-bicyclo(7,3,0)dodecene-8; 1,6-diaza-bicyclo(5,5,0)dodecene-6; 1,7-diaza-bicyclo(6,5,0)tridecene-7; 1,8-diaza-bicyclo(7,5,0)tetradecene-8; and mixtures thereof. The preferred cycloamidines for use in this invention are diaza-bicyclo-alkenes having the general formula (1),



(1)

particularly those where m is 1-3 and n is 1-3. Most preferred is 1,8-diaza-bicyclo(5,4,0)undecene-7 (hereinafter referred to as DBU) and commercially available from Air Products.

The adhesion promoter can also be selected to include a polymeric component having monomeric units derived from maleic anhydride and butadiene, commonly referred to as a maleinized rubber or maleinized polybutadiene. A wide variety of maleinized butadiene polymers are commercially available. A preferred maleinized butadiene for use with the present invention includes RICOBOND 1756 available from Ricon Resins Inc. located in Grand Junction, Colorado.

The adhesive polymer blend can include an amount of a co-agent. It has been discovered that inclusion of a co-agent or co-crosslinking aid greatly improves the effectiveness of the maleinized rubber adhesion promoter. Furthermore, the amount of maleinized butadiene polymer in the adhesive nitrile rubber can be significantly reduced by including a co-agent and yet still provide a laminate that resists delamination. However, the inclusion of the co-agent is not intended to be restricted to use with the maleinized rubber adhesion promoter. A wide variety of co-agents or co-crosslinking agents may be effective insofar as they are reactive with a peroxide curing agent. Preferably, the co-agent includes at least one double bond in the molecule. Still more preferable are polyfunctional co-agents having at least one double bond and a second reactive function group. Preferred examples of the co-agents include: triallyl cyanurate; triallyl isocyanurate; ethylene dimethacrylate; divinylbenzene; diallyl phthalate; tolyl bismaleimide and metaphenylene bismaleimide; N,N'-*m*-phenylene bismaleimide; dipropargyl terephthalate; diallyl phthalate; tetraallyl terephthalamide; and vinyl group-containing siloxane oligomers such as polydimethylvinylsiloxane and polymethylphenylvinyl siloxane, etc., that are chemically compatible with the adhesion promoter. By chemically compatible, it is understood that the co-agent or co-crosslinking aid does not react with the adhesion promoter in the adhesive polymer blend to reduce or inhibit the adhesive strength between the polymer blend and the fluoropolymer substrate. An amount of the co-agent or co-crosslinking agent is not limited, but should not be in excess to deteriorate the properties of the polymer blend. Preferably, the amount of the co-agent or co-crosslinking agent that can be used in the polymer blend is from about 0.1 to about 20 phr, more preferably about 0.2 to about 10 phr, still more preferably from about 0.5 phr to about 5 phr of the adhesive polymer blend.

The adhesive polymer blend can include a wide variety of additional components. Such components can include additives such as fillers, reinforcing agents, plasticizers, lubricants, stabilizers, antioxidants, antiozonants, flame retardants, and/or pigments. The fillers can include both reinforcing fillers and inert fillers. Examples of fillers which are suitable for use in the present invention include, for example, but are not limited to: metal oxides (e.g., calcium oxide, titanium oxide, silicon oxide, zinc oxide, lead oxide, aluminum oxide); metal hydroxides (e.g., magnesium hydroxide, aluminum hydroxide, calcium hydroxide, zinc hydroxide, lead hydroxide); carbonates (e.g., magnesium carbonate, aluminum carbonate, calcium carbonate, barium carbonate); silicates (e.g., magnesium silicate, calcium silicate, sodium silicate, aluminum silicate); sulfates (e.g., aluminum sulfate, calcium sulfate, barium sulfate, etc.); sulfides (e.g., molybdenum sulfide, iron sulfide, copper sulfide); diatomaceous earth; asbestos; lithopone, zinc sulfide/barium sulfate; graphite; carbon black; carbon fluoride; calcium fluoride; cokes; wollastonite; mica powder; glass powder; carbon fiber; and quartz powder. These fillers may be used singly or as a combination of two or more.

The filler component can be included in the adhesive polymer blend in amounts between about 20 phr and about 150 phr. Preferably the filler component is included in amounts between about 30 and 80 phr.

Antioxidants and antiozonants can be included in the adhesive polymer blend to enhance the longevity of the rubber and the resulting laminate structure. Examples of antioxidants/antiozonants include, but are not limited to: diphenyl amines; substituted diphenyl amines, dialkyl or alkylaryl or diaryl phenylenediamines, and 2 mercaptotolylimidazole or its zinc salt.

The adhesive polymer blend can be extruded according to the procedures known to those skilled in the art to provide a polymeric structure, e.g., a thin film. The extruded structures are capable of adhering to fluorinated substrates, i.e., fluorinated polymeric substrates when cured in contact with such substrates.

The fluorinated polymers for use with this invention include a wide variety of known and commonly used fluoropolymers. Preferably, the fluoropolymer is selected from a thermoplastic or elastomeric polymer and can include a homopolymer, copolymer or terpolymer, with random or block configurations, and copolymer. The fluoropolymer can also include a polymer alloy that includes two or more polymers. Examples of fluorinated polymers in the alloy include the fluorinated polymers described above as well as: poly(vinylidene fluoride); poly(hexafluoropropylene); poly(tetrafluoroethylene); poly(pentafluoropropylene); poly(trifluoroethylene); poly(trifluoro chloro ethylene); poly(vinyl fluoride); poly(perfluoromethyl vinyl ether), per(fluoroethyl vinyl ether), and mixtures thereof. A wide variety of fluorinated polymers are commercially available.

For example, a fluoroelastomer sold under the trade name VITON is available from DuPont Dow, and a fluoroplastic sold under the trade name THV is available from Dyneon. The fluoropolymers for use in this invention preferably have an average molecular weight of between about 10,000 and 200,000, more preferably between about 50,000 and 100,000. Further, the fluoropolymers preferably exhibit a glass transition temperature (T_g) of at least about -40°C or higher.

The adhesive polymer blend and the fluoropolymer can be processed by any of the methods known in the art for processing the materials selected. For example, the materials can be extruded, flow molded or injected molded. Extrusion is a well-known technique (see, e.g., the descriptions of extrusion and co-extrusion in the Encyclopedia of Polymer Science and Engineering, Vol. 6, John Wiley & Sons, New York (1986), the descriptions of which are incorporated herein by reference). Single or twin screw extruders, ram extruders, and gear pumps can be used. The extrusion-shaping die can be side- or bottom-fed, spiral, or of a cross-head design and can have multiple manifolds for the distribution and formation of the materials into layers. The revolutions per minute (rpm) of the extruder of the polymer metering system can be chosen so that adequate mixing and/or melting of the materials can be achieved without over-shearing or degradation. The rpm and size of the extruder can be selected so that the output rates of each material is sufficient to form the desired thickness of each layer at the intended line speed.

In preferred forms, the adhesive polymer blend is prepared by first mixing a masterbatch. The masterbatch can be mixed in a variety of mixers, including internal mixers, such as Banbury, transfer mixers, or VIC Pomenii mixers. Preferably, the masterbatch of nitrile rubber is prepared by combining the polymer, the acid acceptor, the processing agent, and optionally the adhesion promoter, along with other desired ingredients, such as fillers, co-agents, antioxidants and colorants. These ingredients are mixed to homogeneity at temperatures or about 100°C (212°F) to about 150°C (302°F). After the components are thoroughly blended, the resulting mixture is discharged. When desired, the adhesive polymer blend is prepared by adding either the curing agent or the adhesion promoter to the masterbatch and blending the resulting mixture under conditions similar to the masterbatch preparation at a temperature of about 220°F (100°C). The resulting adhesive polymer blend is extruded. It is desirable, but not required, to cure the resulting adhesive in contact with a fluorinated substrate soon after extrusion to provide the laminate structure.

The adhesive polymer blend and the fluoropolymer may be extruded sequentially or concurrently. Preferably, the polymers are extruded separately as individual films; the films are subsequently cured in direct contact with each other. When the polymers are extruded sequentially to provide a laminate, either the adhesive polymer blend or the fluoropolymer can be extruded to provide a first layer. After extrusion of the first polymer layer, the second layer can be extruded directly on top of the first layer. Alternatively, a first extruder can extrude the adhesive polymer layer, and a second extruder can extrude the fluoropolymer layer simultaneously with the first extruder and in contact with the first layer. The resulting laminate, either from a concurrent or a sequential extrusion, is then subjected to a curing procedure. The curing procedure preferably is a thermal curing procedure, utilizing either pressure curing techniques or steam curing techniques.

In one form the resulting laminate can be provided as a gasket. This gasket can include one or more layers that are formed of either the fluoropolymer or the adhesive nitrile rubber. In preferred embodiments, the gasket formed to include a fluoroelastomer layer having a thickness of at least 0.03" and typically between about 0.03" to about 1", more preferably, 0.05" to about 0.5"; still more preferably, 0.05" to about 0.1". In other preferred embodiments, the gasket is formed to include a fluoroplastic layer having a thickness between about 0.005" to about 0.05"; more preferably between about 0.015" to about 0.030". Generally, gaskets have a height of less than about 1", more preferably less than about 0.5". In another form the laminate can be provided as a pre-form. Typically the pre-form is formed as a tubular structure that can be cut into thin seals or used in its existing elongated structure. In yet another form, the laminate is provided as a seal. For example, one specific embodiment includes a fuel sender seal having a fluoropolymer barrier (vapor and/or fluid) positioned to inhibit release of volatile organic chemicals. This can include positioning the barrier either as an extreme-most layer on the laminate or embedded within a laminate. In a still yet another form, the extreme-most layer in the laminate comprises an elastomeric layer.

It has been discovered that the bond strength formed in the laminate of seals of the present invention is sufficient to inhibit delamination under the extreme pressure exerted on the seal. Further, the seals of the present invention can be formed to have diameters as large as 8 inches (20.3 cm) or even as large as 10 inches (25.4 cm). The seals can be lathe cut to provide structures having the desired thickness, yet still resist delamination.

This technology can be applied to producing fuel barrier layered composites with two or more layers by injection molding and by a combination of injection and compression molding processes. Extruded pre-forms can be used in these molding techniques.

For the purpose of promoting further understanding and appreciation of the present invention and its advantages, the following Examples are provided. It will be understood, however, that these Examples are illustrative and not limiting in any fashion.

Example 1: Preparation of Adhesive Nitrile Rubber.

An adhesive nitrile rubber was prepared in two stages. First, a masterbatch containing essentially all the desired components except the adhesion promoter, was prepared by combining the components listed in Table 1 in a Banbury mixer. During mixing, the rotors and sides were maintained at about a 100°F (37.8°C), and the door was maintained at about 80°F (26.7°C). Sequence of mixing is illustrated in Table 1.

Table 1

MASTERBATCH				
Event	Time (sec)	Temperature (°F)	Speed (rpm)	Ram (psi)
Nitrile Polymer	0	--	35	40
Antioxidant/Antiozonant	35			
Organic Acid	35			
Acid Acceptor	35			
Filler	35	--	35	30
Adhesion Promoter	35	--	40	30
Filler	55	--	40	60
Sweep	--	250	40	60
Discharge Masterbatch	--	290	40	60

After preparation of the masterbatch, the masterbatch was used to prepare the adhesive nitrile rubber. The mixing was performed essentially as described for the masterbatch. The sequence of mixing is disclosed in Table 2. After thoroughly blending the masterbatch in the curing agent, the resulting adhesive nitrile rubber was discharged.

Table 2

MASTERBATCH				
Event	Time (sec)	Temperature (°F)	Speed (rpm)	Ram (psi)
Masterbatch	0	--	25	60
Curing Agent	0	--	25	60
Discharge	--	220	25	60

The following adhesive nitrile rubber blends were prepared according to the procedure described above.

ADHESIVE NITRILE RUBBER BLEND I		PHR
Nitrile/Butadiene Copolymer	PERBUNAN NT 34.45, Bayer	100.00
Magnesium Oxide	ELASTOMAG 170, C.P. Hall	3.00
Zinc 2-Mercaptotoluimidazole	VANOX ZMTI, Vanderbilt	2.00
Substituted Diphenylamine	NAUGARD 445, Uniroyal	3.00
Carbon Black N-990		48.00
Carbon Black N-650		15.00
DBU	Air Products	1.00
Stearic Acid		2.00
50% 2,5-Dimethyl-2-,5-di(tert-butyl-peroxy) hexane on calcium carbonate	VAROX DBPH-50, Vanderbilt	3.00
	Total:	177.00

ADHESIVE NITRILE RUBBER BLEND II		PHR
Nitrile/Butadiene Copolymer	PERBUNAN NT, Bayer	100.00
Magnesium Oxide	ELASTOMAG 170, C.P. Hall	3.00
Zinc 2-Mercaptotoluimidazole	VANOX ZMTI, Vanderbilt	2.00
Substituted Diphenylamine	NAUGARD 445, Uniroyal	3.00
Carbon Black N-990		48.00
Carbon Black N-650		15.00
Hexamethyleneimine	HMI, DuPont	1.00
Stearic Acid		2.00
50% 2,5-Dimethyl-2-,5-di(tert-butyl-peroxy) hexane on calcium carbonate	VAROX DBPH-50, Vanderbilt	3.00
	Total:	177.00

ADHESIVE NITRILE RUBBER BLEND III		PHR
Nitrile/Butadiene Copolymer	PERBUNAN NT, Bayer	100.00
Magnesium Oxide	ELASTOMAG 170, C.P. Hall	10.00
Zinc 2-Mercaptotoluimidazole	VANOX ZMTI, Vanderbilt	2.00
Substituted Diphenylamine	NAUGARD 445, Uniroyal	3.00
Carbon Black N-990		25.00
Hard Clay		65.00
Trially Isocyanurate TAIC	DIAK #7, DuPont Dow	1.00
Stearic Acid		2.00
Calcium Oxide	90% on DOP, C.P. Hall	11.00
Silane A172	SILANE, Silane Harwick Chem.	1.00
Ricobond 1756	Ricon Resins, Inc.	10.00
50% Dicumyl Peroxide on Calcium Carbonate	VAROX DBPH-50, Vanderbilt	4.00
	Total:	234.00

The resulting adhesive nitrile rubber was discharged onto a two-roll mill to form a thin sheet and cool the material. The adhesive nitrile rubber can be stored until needed to prepare the laminated components. When desired, the adhesive nitrile rubber can be extruded to provide a thin film for subsequent processing.

Example 2: Preparation of Laminate Using a Pressure Curing Process.

An adhesive nitrile rubber film was milled to a 0.05" thick film. Similarly, a fluoroelastomer blend comprising a 50/50 mixture of VTR 7428 and VITON VTR 7395 by DuPont Dow was similarly milled to a 0.05" thick slab. A 3" x 6" piece was cut from each film, and the films were placed one over the other. A 1" wide piece of doubled-up paper or mylar was placed between the two films set in from the 3" side by 1" to locate the interface between the two films after curing. The resulting assembly was placed in a 3" x 6" mold, which was maintained at 320°F (160°C). The hot assembly was then subjected to 220 psi for 20 mins. in a 6" ram press. The resulting cured laminate was removed from the mold. The resultant adhesive nitrile rubber/fluoroelastomer cured laminate showed surprising resistance to delamination.

Similarly, a fluoroplastic (sold under the trade name THV-500 by Dyneon) was provided as a 0.02" thick slab. The adhesive nitrile rubber was milled to a 0.08" thick slab. The same molding procedure described above was followed to provide an adhesive rubber/fluoroplastic laminate.

Example 3: Formation of a Cured Laminate by Co-Extrusion.

The fluoroelastomer blend described in Example 2 was extruded onto a mandrel to form a cylindrical sleeve. One end of the sleeve was secured to the end of the mandrel to prevent it from sliding on the mandrel during the next operation. The extruded sleeve inner diameter (ID) was approximately ¼" smaller than the mandrel. A adhesive nitrile rubber prepared according to Example 1 was extruded on top of the fluoroelastomer sleeve. The sleeve of the adhesive nitrile rubber was made to have an ID approximately ¼" smaller than the outer diameter (OD) of the fluoroelastomer sleeve. The combined uncured laminate was then wrapped via a shrinking media (i.e., wet nylon tape) and then autoclaved or steam cured for 45 to

60 mins. with 80 psi steam (approximately 320 °F (160°C)). The resulting laminate sleeve was used to prepare thin layer gaskets via normal gasket-cutting procedures.

Example 4: Preparation of "O" ring moldings.

A cord of the adhesive nitrile blend (I) prepared according to Example 1 was prepared to have a cross-section of 0.181" in diameter and was cut into 12.75" lengths. Similarly, the fluoroelastomer blend described in Example 2 was cut from 0.60" sheets into two circular films. One circular fluoroelastomer film was placed in the lower cavity of a mold and a adhesive nitrile rubber cord was placed on top in the form of a circle. The second circular film of VITON was placed over the nitrile cord. The resulting assembly was then enclosed in a mold and subjected to pressure curing techniques. The press was closed with three bumps, eventually seeing 7 tons of pressure on the mold. This pressure was maintained for about five minutes at 365°F (185°C). After pressure curing, the resulting laminate was removed from the mold and trimmed to form a O-ring seal weighing 16 g.

The present invention contemplates modifications as would occur to those skilled in the art. It is also contemplated that processes embodied in the present invention can be altered, rearranged, substituted, deleted, duplicated, combined, or added to other processes as would occur to those skilled in the art without departing from the spirit of the present invention. In addition, the various stages, steps, procedures, techniques, phases, and operations within these processes may be altered, rearranged, substituted, deleted, duplicated, or combined as would occur to those skilled in the art. All publications, patents, and patent applications cited in this specification are herein incorporated by reference as if each individual publication, patent, or patent application was specifically and individually indicated to be incorporated by reference and set forth in its entirety herein.

Further, any theory of operation, proof, or finding stated herein is meant to further enhance understanding of the present invention and is not intended to make the scope of the present invention dependent upon such theory, proof, or finding.

While the invention has been illustrated and described in detail in the drawings and foregoing description, the same is considered to be illustrative and not restrictive in character, it is understood that only the preferred embodiments have been shown and described and that all changes and modifications that come within the spirit of the invention are desired to be protected.

What is claimed is:

1. A laminate comprising:

a first layer of a first composition including a nitrile rubber, a curing agent and an adhesion promoter selected from the group consisting of:

a) an azacycloalkyl having between seven and fifteen ring atoms,

b) a cyclic amidine compound, and

c) a polymer blend comprising:

a polymer comprising monomeric units derived from maleic anhydride and butadiene, and

an amount of a co-agent; and

a second layer comprising a fluoropolymer directly bonded to said first layer.

2. The laminate of claim 1 wherein the fluoropolymer includes at least one monomeric residue derived from the group consisting essentially of vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene, pentafluoropropylene, trifluoroethylene, trifluoro chloro ethylene, vinyl fluoride, perfluoromethyl vinyl ether, perfluoroethyl vinyl ether.

3. The laminate of claim 1 comprising a third layer formed of a third polymeric composition.

4. The laminate of claim 3 wherein third polymeric composition includes a nitrile rubber.

5. The laminate of claim 3 wherein the third polymeric composition includes a fluoropolymer.

6. The laminate of claim 1 formed into a gasket.

7. The laminate of claim 1 formed into a hollow tube.

8. A gasket comprising a laminate including a first layer of a first composition including a rubber material, a curing agent and an adhesion promoter selected from the group consisting of:

a) an azacycloalkyl having between seven and fifteen ring atoms,

b) a cyclic amidine compound, and

c) a polymer blend comprising:

a polymer comprising monomeric units derived from maleic anhydride and butadiene, and

an amount of a co-agent; and

a second layer comprising a fluoropolymer directly bonded to said first layer.

9. The laminate of claim 8 wherein the fluoropolymer includes at least one monomeric residue desired from the group consisting essentially of vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene, pentafluoropropylene, trifluoroethylene, trifluoro chloro ethylene, vinyl fluoride, perfluoromethyl vinyl ether, perfluoroethyl vinyl ether.

10. The laminate of claim 8 wherein the rubber material comprises a nitrile rubber.

11. The laminate of claim 8 comprising a third layer formed of a third polymeric composition.

12. The laminate of claim 11 wherein third polymeric composition includes a nitrile rubber.

13. The laminate of claim 11 wherein the third polymeric composition includes a fluoropolymer.

14. A polymeric blend for adhering to a polymeric substrate, said blend comprising:

a nitrile rubber;

a curing system comprising between about 0.5 and about 10 phr of a curing agent and an acid acceptor; and

an adhesion promoter capable of enhancing adhesion to said polymeric substrate said adhesion promoter selected from a group consisting of

a) an azacycloalkyl having between seven and fifteen ring atoms,

b) a cyclic amidine compound, and

c) a polymer blend comprising:

polymer comprising monomeric units derived from maleic anhydride and butadiene, and

an amount of a co-agent.

15. The polymeric blend of claim 14 wherein the co-agent is selected from triallyl cyanurate, triallyl isocyanurate, ethylene dimethacrylate, divinylbenzene, diallyl phthalate, toluene bismaleimide and *m*-phenylene bismaleimide, N,N'-*m*-phenylene bismaleimide, dipropargyl terephthalate, diallyl phthalate, tetraallyl terephthalamide, vinyl-tris(2-methoxyethoxy) silicate and mixtures thereof.

16. The polymeric blend of claim 14 wherein the curing agent is selected from 1,1-bis(tert-butylperoxy)-3,5,5-trimethylcyclohexane, 2,5-dimethyl-2,5-dihydroxyperoxide, di(tertbutyl peroxy)-*p*-diisopropylbenzene, dicumyl peroxide, benzoylperoxide, tert-butylperoxy benzene, 2,5-dimethyl-2-5-di(tert-butylperoxy)hexane, and mixtures thereof.

17. The blend of claim 14 comprising between about 0.5 and about 10 phr of the adhesion promoter.

18. The blend of claim 14 wherein the adhesion promoter is selected from 1,5-diaza-bicyclo(4,2,0)octene-5 ,8-diaza-bicyclo(7,2,0)undecene-8, 1,4-

diaza-bicyclo(3,3,0)octene-4; 3-methyl-1,4-diaza-bicyclo(3,3,0)octene-4; 3,6,7,7-tetramethyl-1,4-diaza-bicyclo(3,3,0)octene-4; 7,8,8-trimethyl-1,5-diaza-bicyclo(4,3,0)nonene-5; 1,8-diaza-bicyclo(7,3,0)tridecene-8; 1,5-diaza-bicyclo(4,4,0)decene-5; 1,5-diaza-bicyclo(4,3,0)nonene-5; 1,8-diaza-bicyclo(7,4,0)tridecene-8; 1,8-diaza-bicyclo(7,3,0)dodecene-8; 1,6-diaza-bicyclo(5,5,0)dodecene-6; 1,7-diaza-bicyclo(6,5,0)tridecene-7; 1,8-diaza-bicyclo(7,5,0)tetradecene-8 and mixtures thereof.

19. The blend of claim 14 wherein the adhesion promoter includes azacycloheptane.

20. The blend of claim 14 wherein the adhesion promoter includes a polymer having monomeric units derived from maleic anhydride and butadiene, and between about 0.5 phr and about 5 phr of a co-agent selected from triallyl cyanurate, triallyl isocyanurate or a mixture thereof.

21. The blend of claim 14 comprising a fatty acid selected from a C_{10} to C_{25} carboxylic acid.

22. The blend of claim 14 comprising about 0.5 to about 10 phr of a metal oxide or metal hydroxide selected from magnesium oxide, calcium hydroxide and calcium hydroxide, and mixtures thereof.

23. The blend of claim 14 comprising at least one antioxidant.

24. A polymeric blend for adhering to a polymeric substrate, said blend comprising:

a nitrile rubber;

a curing system comprising between about 0.5 and about 10 phr of an organic peroxide curing agent and an acid acceptor; and an adhesion promoter capable of enhancing adhesion to said polymeric substrate said adhesion promoter including an azacycloalkyl having between seven and fifteen ring atoms.

25. The blend of claim 24 wherein the adhesion promoter includes azacycloheptane.

26. The blend of claim 24 wherein the organic peroxide curing agent is selected from 2,5 dimethyl-2,5-di(tert-butylperoxy)hexane, dicumyl peroxide or a mixture thereof.

27. The blend of claim 24 and further including between about 20 phr and about 150 phr of a filler.

28. The blend of claim 24 comprising a fatty acid selected from a C_{10} to C_{25} carboxylic acid.

29. A polymeric blend for adhering to a polymeric substrate, said blend comprising:

a nitrile rubber;

a curing system comprising between about 0.5 and about 10 phr of an organic peroxide curing agent and an acid acceptor; and

an adhesion promoter capable of enhancing adhesion to said polymeric substrate said adhesion promoter including a C_7 to C_{11} cyclic amidine.

30. The blend of claim 29 wherein the organic peroxide curing agent is selected from 2,5 dimethyl-2,5-di(tert-butylperoxy)hexane, dicumyl peroxide or mixtures thereof.

31. The blend of claim 29 wherein the cyclic amidine is selected from selected from 1,8-diaza-bicyclo(5,4,0)undecene-7; 1,5-diaza-bicyclo(4,3,0)nonene-5 or mixtures thereof.

32. The blend of claim 29 and further including between about 45 phr and about 100 phr of a filler.

33. The blend of claim 29 comprising a fatty acid selected from a C_{10} to C_{25} carboxylic acid.

34. A polymeric blend for adhering to a polymeric substrate, said blend comprising:

a nitrile rubber;

a curing system comprising between about 0.5 and about 10 phr of an organic peroxide curing agent and an acid acceptor; and

an adhesion promoter capable of enhancing adhesion to said polymeric substrate said adhesion promoter comprising:

a polymer blend having monomeric units derived from maleic anhydride and butadiene, and

a co-agent.

35. The blend of claim 34 wherein the organic peroxide curing agent is selected from 2,5 dimethyl-2,5-di(tert-butylperoxy)hexane, dicumyl peroxide or mixtures thereof.

36. The blend of claim 34 comprising a fatty acid selected from a C_{10} to C_{25} carboxylic acid.

37. The polymeric blend of claim 34 wherein the co-agent is selected from the group consisting of triallyl cyanurate, triallyl isocyanurate, ethylene dimethacrylate, divinylbenzene, diallyl phthalate, toluene bismaleimide and *m*-phenylene bismaleimide, N,N'-*m*-phenylene bismaleimide, dipropargyl terephthalate, diallyl phthalate, tetraallyl terephthalamide, vinyl-tris(2-methoxyethoxy) silicate and mixtures thereof.

38. A process of forming a laminate comprising a first layer of a nitrile rubber blend directed bonded to a second layer of a fluoropolymer, said process comprising:

compounding a nitrile rubber composition with an organic peroxide curing agent and an adhesion promoter capable of enhancing adhesion to said fluoropolymer, said adhesion promoter selected from a group consisting essentially of

a) an azacycloalkyl having between seven and fifteen ring atoms,

b) a cyclic amidine compound, and

c) a polymer blend comprising:

a polymer comprising monomeric units derived from maleic anhydride and butadiene, and

a co-agent;

to provide the nitrile rubber blend;

extruding a first layer comprising the nitrile rubber blend; and

contacting said first layer with a second layer comprising a fluoropolymer to provide a green laminate.

39. The process of claim 38 wherein said compounding includes blending the nitrile rubber composition with an acid acceptor and a fatty acid.

40. The laminate of claim 38 wherein the fluoropolymer includes at least one residue selected from the group consisting essentially of vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene, pentafluoropropylene, trifluoroethylene, trifluoro chloro ethylene, vinyl fluoride, perfluoromethyl vinyl ether, perfluoroethyl vinyl ether.

41. The process of claim 38 comprising steam curing the green laminate to provide a laminate having the first layer directly bonded to the second layer.

42. The process of claim 38 comprising pressure curing the green laminate to provide a laminate having the first layer directly bonded to the second layer.

43. The process of claim 38 wherein said contacting includes injection molding or extrusion.

44. The process of claim 38 and further comprising contacting said first or second layer with a third layer comprising polymeric material.

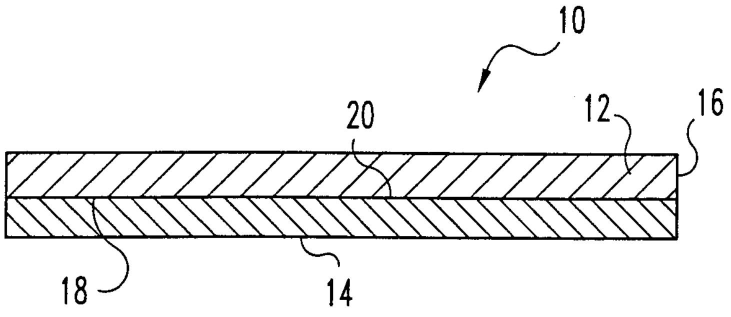


Fig. 1

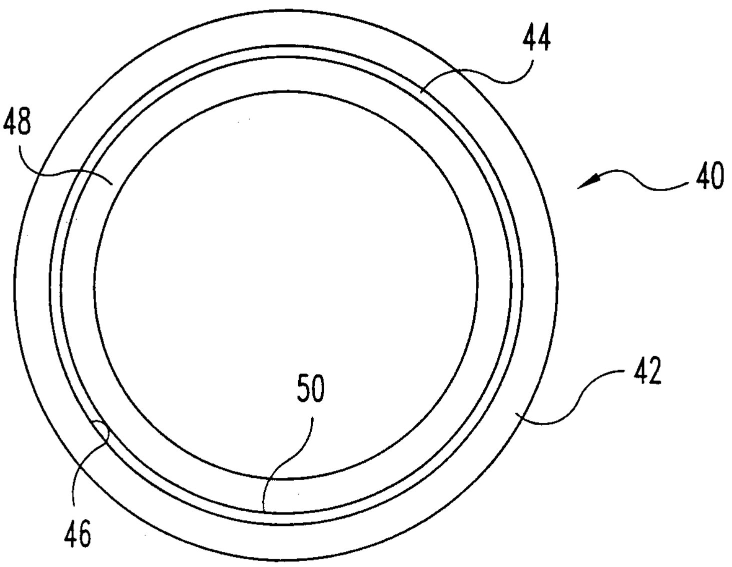


Fig. 2

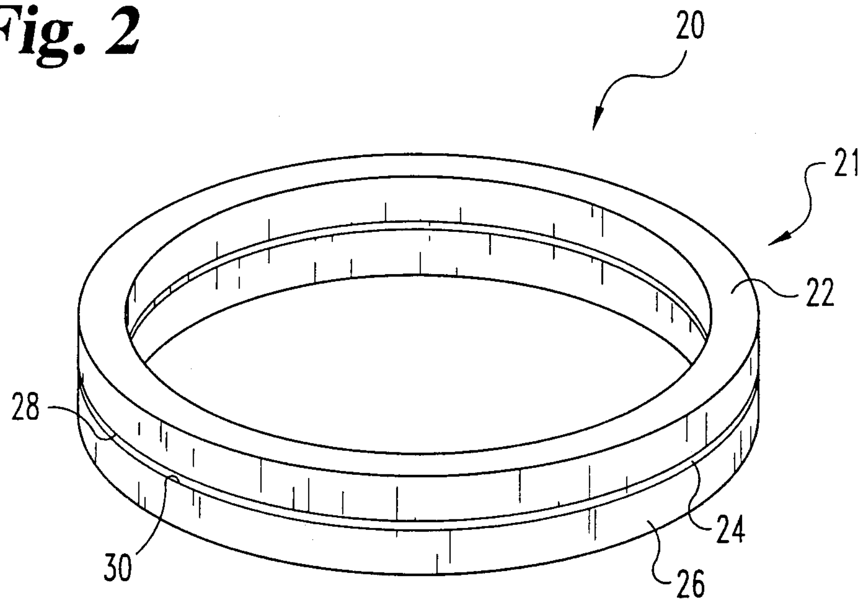


Fig. 3