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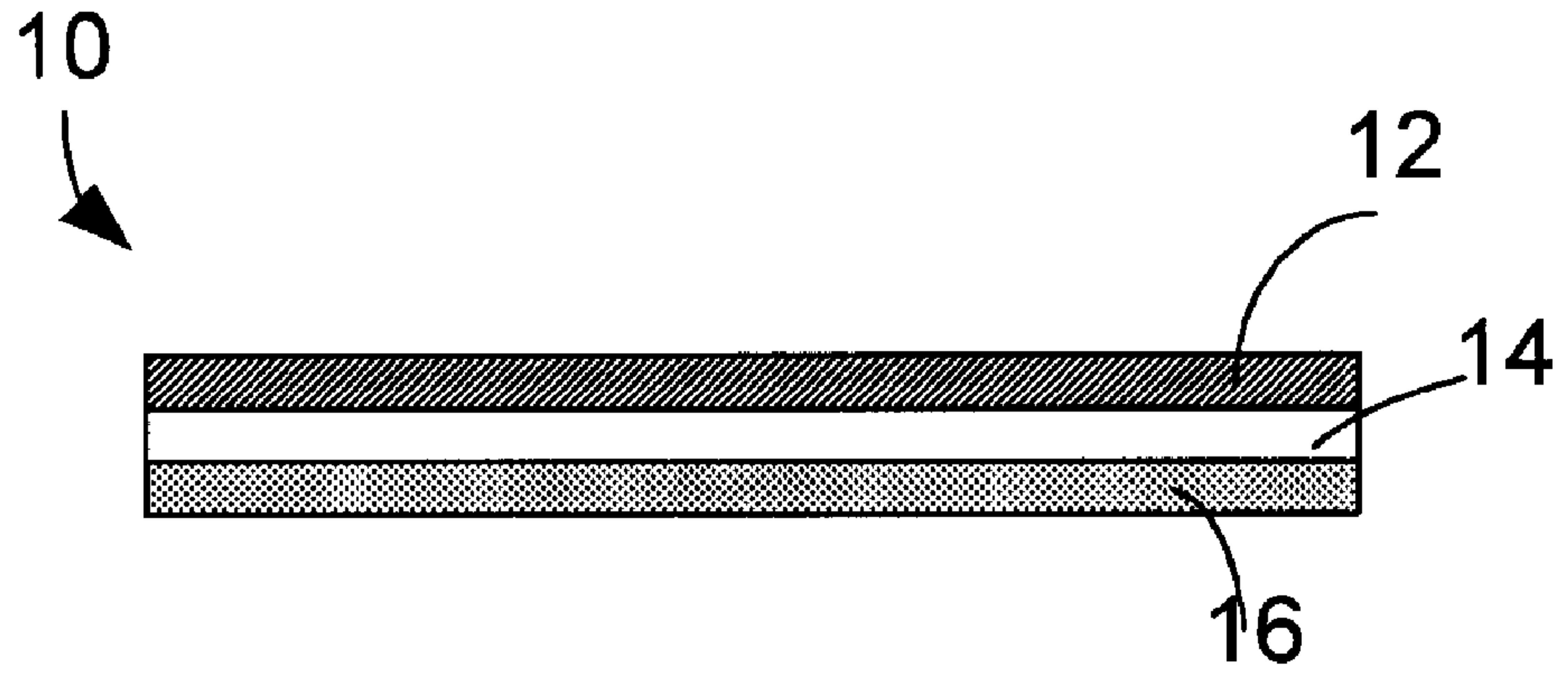
(54) **Titre : REVETEMENT STRATIFIE THERMORETRACTABLE**
(54) **Title: HEAT SHRINKABLE LAMINATED COVERING**



(57) **Abrégé/Abstract:**
The present invention provides a laminated heat shrinkable covering comprising: a) at least one heat shrinkable layer comprising a crosslinked polymeric material; b) a functional layer having at least one property superior to said heat shrinkable layer, said at least one property selected from a group consisting of: high temperature penetration resistance, softening point, impact resistance, long-term thermal stability, tensile strength, toughness, stiffness, thermal insulation, electrical conductivity or static dissipation, and impermeability to gases and moisture; and c) an adhesive layer.

Abstract

The present invention provides a laminated heat shrinkable covering comprising: a) at least one heat shrinkable layer comprising a crosslinked polymeric material; b) a functional layer having at least one property superior to said heat shrinkable layer, said at least one property selected from a group consisting of: high temperature penetration resistance, softening point, impact resistance, long-term thermal stability, tensile strength, toughness, stiffness, thermal insulation, electrical conductivity or static dissipation, and impermeability to gases and moisture; and c) an adhesive layer.

Title: HEAT SHRINKABLE LAMINATED COVERING

Field of Invention

[0001] The present invention relates to heat shrinkable coverings, and in particular to heat shrinkable coverings used for the mechanical and corrosion protection of oil, gas and water transmission pipelines and having improved high service temperature, and high temperature mechanical and chemical properties such as penetration resistance, impact resistance, tensile strength, stiffness, thermal insulation, and permeability resistance.

Background

[0002] Heat shrinkable protective coverings are used in variety of applications, including the sealing and protection of pipe weld joints, electrical cable splices, and the like, from adverse mechanical and environmental conditions, such as impact, penetration, moisture, and corrosion.

[0003] There is increasing demand in the oil and gas industry for higher performance heat-shrinkable coverings to protect and insulate steel transmission pipelines operating at temperatures of 120°C, or higher, in order to withstand higher oil and gas temperatures resulting from deeper drilling, or to facilitate pumping efficiency. This imposes severe mechanical and chemical demands on traditional thermoplastic polymer materials, such as polyolefins, used for pipe coating and field joint systems.

[0004] Current pipeline joint protection systems manufactured from thermoplastic polyolefins, such as polyethylene and polypropylene, are typically deficient in mechanical performance, such as penetration and impact resistance, at temperatures above their softening point or crystalline melting point. This can be addressed to some degree by imparting some thermoset characteristic to the polymer by crosslinking the thermoplastic. This renders the polymer resistant to melting and flowing when it is heated to a temperature close to or above the crystalline melting point but it does not totally prevent the polymer from softening. Hence the polymer will still remain susceptible to damage by impact or penetration, for example, at elevated temperatures close to or above the softening point of the polymer, namely those temperatures which are experienced by high temperature pipelines. In addition, higher temperatures render the polymer more susceptible to thermal degradation, chemical attack, and permeation by moisture and gases.

Summary of Invention

[0005] This invention describes a method of overcoming the above mentioned deficiencies through the use of a polymer-based laminated covering wherein one or more of the polymer layers comprising the laminate provides resistance to, or protection from, one or more of the adverse conditions noted above, such as softening at the pipeline operating temperature, or overcomes a mechanical or chemical deficiency, and wherein one or more of the polymer layers provides the heat-shrinkable properties necessary to impart controlled recovery of the laminated covering over the pipe or pipe joint on application of heat. The heat-shrinkable layer(s) is typically crosslinked to render the material thermoset and resistant to melting on application of the heat required to effect recovery of the laminated covering over the pipe or pipe joint. Crosslinking of the heat-shrinkable layer may be accomplished by a moisture cure or radiation cure process.

[0006] The layers comprising the laminated covering are prepared using suitable polymeric materials, including polyolefins such as polyethylene and polypropylene, crosslinked polyolefins, polyolefins modified with the addition of reinforcing fillers and nanofillers, thermoplastics chosen for their low permeability, such as ethylene vinyl alcohol and polyvinylidene fluoride, and so-called engineering thermoplastics having high softening points and superior mechanical performance, such as nylons, polyesters, and polyurethanes.

[0007] The present invention provides a laminated heat shrinkable covering comprising: a) at least one heat shrinkable layer comprising a crosslinked polymeric material; b) a functional layer having at least one property superior to said heat shrinkable layer, said at least one property selected from a group consisting of: high temperature penetration resistance, softening point, impact resistance, long-term thermal stability, tensile strength, toughness, stiffness, thermal insulation, electrical conductivity or static dissipation, and impermeability to gases and moisture; and c) an adhesive layer.

[0008] In an embodiment of the invention, the heat shrinkable layer comprises a crosslinked polyolefin material.

[0009] In a further embodiment of the invention, the functional layer comprises a polymeric material.

[00010] In a still further embodiment of the invention, the functional layer comprises a non-crosslinked polymeric material.

[00011] In another embodiment of the invention, the crosslinked polyolefin material and/or the non-crosslinked polymeric material comprises propylene homopolymer or copolymer of propylene with an olefin other than propylene, such as ethylene. The propylene homopolymer or copolymer may further be modified with a functional group selected from a group consisting of: silanes, acrylic acids, alkyl acrylic acids, glycidyl acrylates, alkyl acrylates, anhydrides and combinations thereof.

[00012] In a still another embodiment of the invention, the crosslinked polyolefin material and/or the non-crosslinked polymeric material comprises propylene-ethylene copolymers.

[00013] In a further embodiment of the invention, the crosslinked polyolefin material and/or the non-crosslinked polymeric material comprises ethylene copolymers. The copolymers may be selected from a group consisting of: vinyl acetate, vinyl alcohol, alkyl acrylates, and higher olefins, such as butane, hexane, and octane.

[00014] In a still further embodiment of the invention, the crosslinked polyolefin material and/or the non-crosslinked polymeric material comprises a polyethylene homopolymer selected from a group consisting of: high density polyethylene, medium density polyethylene, linear medium density polyethylene, low density polyethylene, linear low density polyethylene, and combinations thereof.

[00015] In another embodiment of the invention, the crosslinked polyolefin material and/or the non-crosslinked polymeric material comprises an elastomer selected from a group consisting of: ethylene-propylene diene elastomers; crystalline propylene-ethylene elastomers, and thermoplastic polyolefin elastomers.

[00016] In a further embodiment of the invention, the crosslinked polyolefin material and/or the non-crosslinked polymeric material comprises polymers prepared using metallocene catalysts, also known as single-site, stereo-specific, or constrained geometry catalysts, and may also comprise a bimodal molecular weight distribution.

[00017] In a further embodiment of the invention, the crosslinked polyolefin material and/or the non-crosslinked polymeric material comprises a blend of two or more of the polyolefin polymers described above.

[00018] In a still further embodiment of the invention, the crosslinked polyolefin material and/or the non-crosslinked polymeric material comprises a compound selected from a group consisting of: a filled polyolefin, a polyolefin nanocomposite, an engineering thermoplastic, a barrier polymer, a thermally insulating polymer and an electrically conductive polymer.

[00019] In an embodiment of the invention, the filler in the filled polyolefin is selected from the group consisting of: clay, mica, talc, silica, wollastonite, wood, glass fibres, and metal oxides.

[00020] In an embodiment of the invention, the polyolefin nanocomposite comprises a polyolefin and an exfoliated clay additive.

[00021] In an embodiment of the invention, the engineering thermoplastic is selected from the group consisting of: nylons, polyesters, and polyurethanes.

[00022] In an embodiment of the invention, the barrier polymer is selected from the group consisting of: ethylene vinyl alcohol, polyvinyl alcohol and polyvinylidene fluoride.

[00023] In an embodiment of the invention, the thermally insulating polymer comprises a polyolefin and a low conductivity insulating filler selected from the group consisting of: hollow glass, ceramic and polymer microspheres.

[00024] In an embodiment of the invention, the electrically conductive polymer comprises a polyolefin and an electrically conductive filler comprising carbon black or a metal powder.

[00025] In an embodiment of the invention, the at least one heat shrinkable layer further comprises at least one additive selected from a group consisting of: cross-linking promoters, compatibilisers, modifiers, pigments, antioxidant stabilizers, heat stabilizers, ultraviolet (UV) stabilizers, fillers, flame retardants, and process aids.

[00026] The said antioxidant stabilizer may be selected from a group consisting of: hindered phenols, hindered amines, phosphites, bisphenols, benzimidazoles, phenylenediamines, and dihydroquinolines.

[00027] The said compatibiliser may be selected from one or more of ethylene-propylene copolymers; ethylene-propylene diene elastomers; crystalline propylene-ethylene elastomers; thermoplastic polyolefin elastomers; metallocene polyolefins; copolymers of ethylene with vinyl acetate, vinyl alcohol, and/or alkyl acrylates; polybutenes; hydrogenated and non-hydrogenated polybutadienes; butyl rubber; polyolefins modified with reactive functional groups selected from the group comprising silanes, alcohols, amines, acrylic acids, methacrylic acids, acrylates, methacrylates, glycidyl methacrylates, and anhydrides; polyolefin ionomers; polyolefin nanocomposites; block copolymers selected from the group comprising styrene-butadiene, styrene-butadiene-styrene, styrene-ethylene/propylene and styrene-ethylene/butylene-styrene; thermoplastic elastomers comprising polypropylene blended with an elastomer such as ethylene propylene.

[00028] In an embodiment of the invention, the adhesive layer is bonded to the heat shrinkable layer.

[00029] In another embodiment of the invention, the adhesive layer is bonded to the functional layer.

[00030] In a further embodiment of the invention, the articles comprise a first heat shrinkable layer and a second heat shrinkable layer.

[00031] In a further embodiment of the invention, the second heat-shrinkable layer is crosslinked to a lesser degree than the first heat-shrinkable layer.

[00032] In a still further embodiment of the invention, the second heat shrinkable layer is positioned between the first heat shrinkable layer and the functional layer and wherein the second heat shrinkable layer is bonded to the first heat shrinkable layer and the functional layer, and the functional layer is bonded to the adhesive layer.

[00033] In yet a further embodiment of the invention, the second heat shrinkable layer is positioned between the functional layer and the adhesive layer and wherein the second heat shrinkable layer is bonded to the functional layer and the adhesive layer, and the functional layer is bonded to the first heat-shrinkable layer.

Brief Description of the Figures

[00034] Preferred embodiments of the invention will now be described, by way of example to the accompanying drawings, in which:

[00035] Figure 1 is a cross-section illustration of a heat shrinkable covering comprising a heat shrinkable, crosslinked polymeric, first layer; a polymeric, second layer; and an adhesive/primer third layer;

[00036] Figure 2 is a cross-section illustration of a heat shrinkable covering comprising a polymeric, first layer; a heat shrinkable, crosslinked polymeric, second layer; and an adhesive/primer third layer;

[00037] Figure 3 is a cross-section illustration of a heat shrinkable covering comprising a heat shrinkable, crosslinked polymeric, first layer; a heat shrinkable, crosslinked polymeric, second layer; a polymeric third layer; and an adhesive/primer fourth layer; and

[00038] Figure 4 is a cross-section illustration of a heat shrinkable covering comprising a heat shrinkable, crosslinked polymeric, first layer; a polymeric second layer; a heat shrinkable, crosslinked polymeric, third layer; and an adhesive/primer fourth layer.

Detailed Description

[00039] The present invention provides a laminated heat shrinkable covering comprising: (a) at least one heat shrinkable layer comprising a crosslinked polymeric material; (b) a functional layer having at least one property superior to said heat shrinkable layer, said at least one property selected from a group consisting of: high temperature penetration resistance, softening point, impact resistance, long-term thermal stability, tensile strength, toughness, stiffness, thermal insulation, electrical conductivity or static dissipation, and impermeability to and gases and moisture; and (c) an adhesive layer.

[00040] The laminated material possesses the advantage of heat shrinkability while retaining the desired physical and other properties.

[00041] In a preferred embodiment, the heat shrinkable layer comprises a crosslinked polyolefin material and the functional layer comprises a polymeric material and more preferably a non-crosslinked polymeric material.

[00042] In a further preferred embodiment, the at least one heat shrinkable layer is bonded to the functional layer. Depending on the intended application, either the heat shrinkable layer or the functional layer may constitute an outer lamina of the laminated heat shrinkable covering.

[00043] The laminated heat shrinkable coverings according to the invention can be manufactured in forms such as extruded tubing and sheets which may be suitable for protective or insulative coverings for pipe weld joints, electrical cable splices, and the like.

[00044] The use of both crosslinked and non-crosslinked layers for the manufacture of laminated heat shrinkable articles such as protective coverings, provides numerous advantages over conventional heat shrinkable coverings. In particular, the use of separate crosslinked and non-crosslinked layers of different composition and functionality allows the heat shrinkable covering to be tailored more specifically to the intended application.

[00045] The multilayer construction of the heat shrinkable covering allows for the use of non-crosslinkable materials which could not be used on their own.

The present invention allows for the utilization of non-crosslinkable materials having beneficial properties, for example polymers which have high softening points for superior high temperature penetration resistance, by combining them with a crosslinkable material. Multilayer construction allows the use of functional fillers such as reinforcing fillers, nanocomposites, and flame retardants while maintaining required levels of crosslinking and installation performance. Multilayer construction also allows for custom tailoring the crosslinking levels of individual layers for optimization of installation performance, inter-layer adhesion, and split resistance. Additionally, multilayer construction enables the provision of anisotropic shrinkage characteristics to the article through the ability to impart different stretch ratios to the individual layers.

[00046] As compared to prior art heat shrinkable protective coverings, the present invention provides a cost effective solution for providing superior performance under a diverse range of operating conditions. By combining layers of different composition and functionality, optimum performance can be achieved at reduced cost. The present invention allows for the use of inner layers comprising reduced cost materials for a cheaper overall system cost. For example, the multilayer construction allows for the use of a thinner crosslinked outer layer and a subsequent reduction in material thickness of the generally highest cost component.

[00047] Figure 1 shows a cross-section of one embodiment of the laminated heat shrinkable covering 10 wherein the heat shrinkable layer 12 forms the outer lamina, the functional layer 14 the intermediate lamina and the adhesive layer 16, the inner lamina. The heat shrinkable layer 12 and the functional layer 14 are bonded to one another by laminating the two layers together (for methods of preparation, see further discussion set out below). Articles according to the invention having the heat shrinkable layer on the outside and the functional layer on the inside are particularly suitable for applications requiring improved high temperature penetration resistance, resistance to permeation by gases and moisture, and thermal insulation, for example.

[00048] Figure 2 shows a cross-section of another embodiment of the laminated heat shrinkable covering 20 wherein the functional layer 24 forms the outer lamina, the heat shrinkable layer 22 the intermediate lamina, and adhesive layer 26, the inner lamina. Articles according to the invention having the heat shrinkable layer on the inside and the functional layer on the outside are particular suitable for applications requiring improved impact resistance, surface toughness, and chemical resistance, for example.

[00049] In a further embodiment of the invention, the laminated heat shrinkable covering may comprise one or more heat shrinkable layers. As shown in Figure 3, the laminated heat shrinkable covering 30 may comprises a first and second heat shrinkable layer 32, 34 bonded directly to one another. The functional layer 36 is layered between the second heat shrinkable layer 34 and the adhesive layer 38. Alternatively, as show in Figure 4, the laminated heat shrinkable covering 40 may comprise a first and second heat shrinkable layer 42, 44 wherein the first and second heat shrinkable layers are separated by the functional layer 46, and wherein the covering 40 further comprises an adhesive/primer layer 48. In either of the embodiments illustrated in Figures 3 and 4, a heat shrinkable layer constitutes the outer lamina and the adhesive layer constitutes the inner lamina.

[00050] ***Heat Shrinkable Layer(s)***

[00051] The heat shrinkable layer comprises a polymeric material which has been crosslinked and more preferably a crosslinked polyolefin material. Crosslinking is the formation of permanent covalent bonds between individual polymer chains which act to bind the polymer chains together and prevent them from irreversibly separating during subsequent heating. It is this crosslinked structure which, while retaining the elastomeric nature of the material, renders the material thermoset and resistant to melting which, in turn, is a desirable property for producing heat-shrinkable articles. Crosslinking also provides the article with heat resistance, allowing it to maintain mechanical toughness and integrity at high service temperatures.

[00052] In some embodiments of the invention, the laminated heat shrinkable covering may comprise more than one heat shrinkable layer. In embodiments comprising a first and second heat shrinkable layer, each of the heat shrinkable layers can be prepared using the same crosslinked polyolefin material to provide layers having similar chemical and physical properties. Alternatively, the first and second heat shrinkable layer can be prepared with different polyolefin materials. Depending on the intended applications of the heat shrinkable covering, the first and second heat shrinkable layers may be prepared using polymeric materials having differing softening points and performance properties such as mechanical strength and chemical resistance.

[00053] For example, the first heat shrinkable layer can be prepared with a polyolefin material characterized by a high softening point and/or higher performance properties, the second heat shrinkable layer can be prepared with a polyolefin material having a lower softening point and/or performance properties. In such instances, the second heat shrinkable layer can often be prepared using a lower cost version of the materials used to prepare the first heat shrinkable layer thereby improving the cost effectiveness of the heat shrinkable covering while maintaining the desired level of performance and durability. The degree of crosslinking may also be varied between the first and second heat shrinkable layer depending on the intended application. For example, it may be required that the second heat shrinkable layer have a lower degree of crosslinking than the first heat shrinkable layer in order that the second heat shrinkable layer preferentially softens when heated, thereby providing improved adhesion to the functional or adhesive layer beneath and ensuring an integrally bonded composite structure. An additional benefit is the improvement in split resistance of the heat shrinkable covering during heat recovery through the mitigation of the high recovery stresses of the highly crosslinked first heat shrinkable layer by the relatively more fluid second heat shrinkable layer.

[00054] The heat shrinkable layer can be prepared using any polyolefin material which can be crosslinked. In one preferred embodiment, the heat shrinkable layer is prepared using polyolefin material comprising propylene polymer, such as polypropylene homopolymer or copolymer of propylene with an olefin other than propylene, such as ethylene. The propylene homopolymer or copolymer may further be modified with a functional group selected from a group consisting of: silanes, acrylic acids, alkyl acrylic acids, glycidyl acrylates, alkyl acrylates, anhydrides and combinations thereof. Where the polypropylene is a copolymer, it preferably contains at least about 80 percent by weight propylene.

[00055] The polypropylene homopolymer or coplymer is preferably isotactic in nature, having a density of about 0.85 to 0.91 g/cm^3 and a melt flow index of about 0.1 to 10 dg/min. The crystalline melting point of the polypropylene homopolymer or copolymer is usually in the range of about 160-170°C, with about 165°C being typical.

[00056] In another embodiment of the invention, the heat shrinkable layer may be prepared using a polyolefin material comprising ethylene homopolymers or copolymers modified with reactive functional group such as, but not limited to: vinyl acetate; vinyl alcohol; and alkyl acrylates; or combinations thereof.

[00057] The heat shrinkable layer may be prepared using a polyethylene such as high density polyethylene (HDPE), medium density polyethylene (MDPE), linear medium density polyethylene (LMDPE), low density polyethylene (LDPE) or linear low density polyethylene (LLDPE), or blends thereof. The terms HDPE, MDPE and LDPE as used herein are defined in accordance with the American Society for Testing and Materials (ASTM) D1248 standard definitions. LDPE is defined to have a density from 0.910 to 0.925 g/cm^3. MDPE have densities ranging from 0.926 to 0.940 g/cm^3 and HDPE has a density of at least 0.941 g/cm^3. The polyethylene includes both ethylene homopolymers, and copolymers of ethylene with higher alpha olefins such as butene, hexene and octene, and may be of a predominantly linear molecular structure. The polyethylene may preferably be manufactured using metallocene catalysts, also known as single-site, stereo-specific or constrained geometry catalysts, and may also comprise a bimodal molecular weight distribution.

[00058] In yet a further embodiment of the invention, the heat shrinkable layer may be prepared using a polyolefin material comprising an elastomer such as but not limited to: ethylene-propylene diene elastomers; crystalline propylene-ethylene elastomers, or thermoplastic polyolefin elastomers.

[00059] The heat shrinkable layer may also be prepared using polyolefins prepared with metallocene catalysts, also known as single-site, stereo-specific, or constrained geometry catalysts, and may also comprise a bimodal molecular weight distribution.

[00060] The heat shrinkable layer may further be prepared using a blend of any of the polymers and/or elastomers described above.

[00061] In a preferred embodiment, the heat shrinkable layer is prepared using a blend of polypropylene and polyethylene. Preferably, the polypropylene has a melt viscosity, as measured by melt flow index, which is similar to that of the polyethylene component at the same temperature and under the same shear conditions required for processing the blend, to ensure optimum blend compatibility.

[00062] The polyolefin material may further comprise one or more optional additives and fillers known in the art in addition to the polymeric base. Additives useful for preparing the heat shrinkable layer include but are not limited to: cross-linking promoters (also known as radiation sensitizers), compatibilisers, modifiers, pigments, antioxidant stabilizers, heat stabilizers, ultraviolet (UV) stabilizers, fillers, flame retardants, or process aids.

[00063] The polyolefin material may be prepared using polyolefin polymers which have been modified with reactive functional group such as, but not limited to: silanes, acrylic acids; alkyl acrylic acids, such as methyl acrylic acid;

acrylates; alkyl acrylates, such as methyl acrylates; anhydrides; or combinations thereof.

[00064] In a preferred embodiment, silane modified olefin polymers may be employed to provide a polyolefin material which is moisture crosslinkable. In one embodiment, the polyolefin polymers are modified with an alkoxysilane such as vinyltrimethoxy silane and vinyltriethoxy silane.

[00065] In another preferred embodiment, the polyolefin material may further comprise a radiation sensitizer to promote crosslinking of the polyolefin material when it is subjected to electron beam or gamma radiation. The radiation sensitizer is preferably selected from the family of multifunctional monomers typically used as crosslink promoters for polyolefin-based polymers. Preferred monomers include trimethylol propane triacrylate, trimethylol propane trimethacrylate, tetramethylol tetraacrylate, ethylene glycol dimethacrylate, triallyl cyanurate and triallyl isocyanurate.

[00066] The polyolefin material may also further comprise an antioxidant stabilizer. The antioxidant stabilizer may be chosen from any suitable antioxidant or blend of antioxidants designed to prevent degradation of the composition during melt processing and subsequent heat aging of the final product. Examples of suitable antioxidants and heat stabilizers include those classes of chemicals known as hindered phenols, hindered amines, phosphites, bisphenols, benzimidazoles, phenylenediamines, and dihydroquinolines. These are preferably added in an amount of about 0.1 to 5% by weight of the blend, depending upon the aging properties required and the type and quantity of optional destabilizing ingredients in the composition, for example halogenated flame retardants or mineral fillers. It should also be noted that these antioxidants and stabilizers, if added in excessive amounts, may become "radiation scavengers", acting to reduce the effectiveness of the radiation to induce the desired crosslinking reaction and the resultant degree of crosslinking obtainable for a given radiation dosage.

[00067] In embodiments wherein the polyolefin material comprises a blend of two or more polymers, it may be desirable to include one or more compatiblisers or modifiers. The addition of a particular compatibliser or modifier will depend on the particular polyolefin material used. The function of the compatibiliser or modifier is to promote the miscibility of different copolymers when they are blended together. The compatibiliser is preferably added in the amount from about 1 to 50% and most preferably from about 5 to 10% by weight of the blend. Examples of possible compatibilisers and modifiers include, but are not limited to: ethylene-propylene copolymers; ethylene-propylene diene elastomers; crystalline propylene-ethylene elastomers; thermoplastic polyolefin elastomers; metallocene polyolefins; copolymers of ethylene with vinyl acetate, vinyl alcohol, and/or alkyl acrylates; polybutenes; hydrogenated and non-hydrogenated polybutadienes; butyl rubber; polyolefins modified with reactive functional groups selected from the group comprising silanes, alcohols, amines, acrylic acids, methacrylic acids, acrylates, methacrylates, glycidyl methacrylates, and anhydrides; polyolefin ionomers; polyolefin nanocomposites; block copolymers selected from the group comprising styrene-butadiene, styrene-butadiene-styrene, styrene-ethylene/propylene and styrene-ethylene/butylene-styrene; thermoplastic elastomers comprising polypropylene blended with an elastomer such as ethylene propylene.

[00068] The constituents of the blend comprising the polyolefin material may be melt blended either in-situ with forming of the final product during melt processing, or prior to forming by melt mixing using a machine designed specifically for that purpose, such as a continuous twin-screw compounder, kneader, or internal batch mixer.

[00069] ***Functional Layer***

[00070] The choice of material for preparing the functional layer will depend on the desired performance properties of the finished laminated article and the choice of the materials used to prepare the heat shrinkable layer(s). The functional layer is prepared with a material having at least one performance property superior to the heat shrinkable layer(s). The performance property may be one or more of: high temperature penetration resistance, softening point, impact resistance, long-term thermal stability, tensile strength, toughness, stiffness, thermal insulation, electrical conductivity or static dissipation, impermeability to gases and moisture, and reduced cost. Preferably, the functional layer comprises a polymeric material and even more preferably, a non-crosslinked polymeric material.

[00071] In the present specification, "high temperature" denotes operating temperatures typically 120°C, or higher. Materials which are suitable for use at "high temperatures" are those with an expected thermal stability and service life of at least 20 years at said operating temperature, typically defined in terms of time to reach 50% retained elongation.

[00072] In the present specification, a functional layer having the property of "high temperature penetration" refers to a functional layer which is characterized as having a penetration of less than 0.4mm at 130°C as determined by DIN 30678.

[00073] In the present specification, a functional layer having the property of "softening point" refers to a functional layer which is characterized as having a Vicat softening point of at least 130°C as determined by ASTM D1525, or a heat deflection temperature under load (DTUL) of at least 80°C at 0.45MPa as determined by ASTM D648.

[00074] In the present specification, a functional layer having the property of "impact resistance" refers to a functional layer which is characterized as withstanding an impact energy of at least 5 J per mm. of coating thickness as determined by DIN 30678.

[00075] In the present specification, a functional layer having the property of "long term thermal stability" refers to a functional layer which is characterized as having a service life at the operating temperature of at least 20 years as determined by Arrhenius extrapolation of thermal aging data as described in ASTM D3045, or similar.

[00076] In the present specification, a functional layer having the property of "tensile strength" refers to a functional layer which is characterized as having a tensile strength of 20 MPa or greater as determined by ASTM D638.

[00077] In the present specification, a functional layer having the property of "stiffness" refers to a functional layer which is characterized as having a flexural modulus of 1,000 MPa or greater as determined by ASTM D790.

[00078] In the present specification, a functional layer having the property of "thermal insulation" refers to a functional layer which is characterized as having a thermal conductivity less than about 0.20 W/mK.

[00079] In the present specification, a functional layer having the property of "electrical conductivity or static dissipation" refers to a functional layer which is characterized as having a volume resistivity of less than about 10^{12} ohm.cm as determined by ASTM D257.

[00080] The polymeric material used to prepare the functional layer may comprise any of the polyolefin polymers and elastomers described above with respect to the heat shrinkable layer. As compared to the heat shrinkable layer, the functional layer is preferably not crosslinked prior to lamination.

[00081] The functional layer may be filled with one or more conventional fillers such as, but not limited to: clay, mica, talc, silica, wollastonite, wood, glass fibres, and metal oxides. The propylene, ethylene, and other polyolefin polymers described above can be combined with any of these inorganic fillers to reduce costs or improve performance.

[00082] The functional layer may also comprise nanocomposites of any of the polymers described above wherein the polymer contains an exfoliated clay additive.

[00083] The functional layer may also comprise a lower cost polymer or recycled polymer in order to reduce the overall cost of the finished laminated article.

[00084] The polymeric material used to prepare the functional layer may be an engineering thermoplastic, which as used herein, refers to any thermoplastic that exhibits higher temperature resistance, higher softening point and/or superior mechanical properties, such as penetration resistance, impact resistance, stiffness and toughness, as compared with the heat-shrinkable layer(s). Examples of engineering thermoplastics useful for preparing the invention include materials such as nylons, polyesters, and polyurethanes.

[00085] The polymeric material used to prepare the functional layer may be a barrier resin having low moisture and/or gas permeability. Examples of barrier resins which can be used to practice the invention include, but are not limited to: ethylene vinyl alcohol, polyvinyl alcohol or polvinylidene fluoride. Choice of a suitable barrier resin will depend on the extent of allowable moisture and/or gas transmission of the intended application.

[00086] The polymeric material used to prepare the functional layer may be a polymer or polymer composite having thermal insulation properties, namely those having a lower thermal conductivity relative to the heat shrinkable layer(s). Such materials include polymers incorporating insulating fillers such as wood and hollow glass, ceramic or polymer microspheres.

[00087] The polymeric material used to prepare the functional layer may be a polymer or polymer composite having electrical conductive properties, namely those having a lower volume resistivity relative to the heat shrinkable layer(s).

Such materials include polymers incorporating conductive fillers such as carbon black or metal powders, or intrinsically conductive polymers such as polyaniline.

[00088] ***Adhesive Layer***

[00089] The adhesive layer can be prepared using any suitable adhesive. The choice of adhesive will depend on the intended application of the laminated heat shrinkable covering and specifically the operating temperature of the application. It is also dependant upon the composition of the heat shrinkable layer, the functional layer, and the substrate to which it needs to bond. For example, the adhesive layer may be prepared using a mastic-based sealant for lower temperature applications or that requiring superior corrosion protection. For higher temperature applications, hot melt or curable adhesives such as those based on modified polyolefins, or polyamides, may be used.

[00090] The adhesive layer may further comprise a primer layer, for example a curable epoxy resin, in instances where the heat shrinkable covering is required to bond to a metal substrate, such as a steel pipe.

[00091] ***Preparation***

[00092] The laminated heat shrinkable covering according to the invention may be prepared by extruding the heat shrinkable layer using conventional methods well known in the art. In embodiments comprising more than one heat shrinkable layers, the heat shrinkable layers can be combined, through extrusion lamination or direct co-extrusion of the multiple heat shrinkable layers, to form a laminate structure having discrete but intimately bonded layers. Each of the heat shrinkable layers may be prepared having identical or different functional properties or cost.

[00093] Once extruded, the heat shrinkable layer or layers may be crosslinked by irradiation, preferably with electron beam, gamma or UV radiation depending on its composition. Preferably, the heat shrinkable layer or layers are irradiated by electron beam radiation at a dosage from about 1 to 20 megarads in an electron beam accelerator, for example a "Dynamitron" manufactured by Radiation Dynamics Inc. The desired dosage is dependent upon the desired properties of the article. Too low a dosage will result in the article having a low degree of crosslinking, poor mechanical toughness and a tendency to prematurely soften or melt at elevated temperatures. Too high a dosage may result in degradation, especially with polypropylene, with a resultant unacceptable deterioration in mechanical properties. Preferably the radiation dosage is between about 5 and 10 megarads for the manufacture of laminated heat-shrinkable articles according to the invention. The dosage of radiation should be sufficient to provide the article with a level of crosslinking, as measured by the gel fraction, of about 20 to 90 percent. Preferably, the gel fraction of the crosslinked layer is from about 30 to 70 percent and more preferably from about 40 to 70 percent.

[00094] Alternatively, if the heat shrinkable layer comprises a silane-modified polymer, crosslinking is effected by subjecting the heat shrinkable layer to moisture, preferably at an elevated temperature, which will induce crosslinking of the silane groups via a combined hydrolysis and condensation reaction. Atmospheric moisture is usually sufficient to permit the crosslinking to occur, but the rate of crosslinking may be increased by the use of an artificially moistened atmosphere, or by immersion in liquid water. Also, subjecting the composition to combined heat and moisture will accelerate the crosslinking reaction. Most preferably, crosslinking is affected at a temperature above 50°C and most preferably by exposing the composition to a temperature of 85°C and a relative humidity of 90% for approximately 100 hours.

[00095] Articles produced according to the invention can be rendered heat-shrinkable since they exhibit the property of not melting when heated to a temperature close to or above the crystalline melting point of the highest melting point polymer component. This is important because the crosslinked structure allows the article to be stretched with minimal force and without melting, and to retain its mechanical integrity when heated to this temperature. The article is fixed in this stretched state by rapidly cooling it below the crystalline melting point while holding the article in its stretched position, the reformed rigid crystalline regions of the polymeric components of the material preventing the article from spontaneously recovering to its original dimensions.

[00096] Following crosslinking, the heat shrinkable layer is bonded to the polymeric functional layer by laminating the layers together. In embodiments comprising a first and second heat shrinkable layer, the heat shrinkable layers may be directly laminated to one another. Alternatively, the laminate may be formed with the functional layer sandwiched between the first and second heat shrinkable layers. The heat shrinkable and functional layers are laminated together by heating the layers to a temperature at which the individual layers will fuse intimately together and then applying pressure, using casting rollers for example, to ensure adequate bonding of the layers.

[00097] The laminated article thus formed is then stretched using mechanical, pneumatic or hydraulic methods. Cooling the article in its stretched state may be accomplished by air, water or other heat-transfer medium. Subsequent re-heating of the stretched article above the melting point of the highest melting point component will cause the crystalline regions to re-melt and the structure to elastomerically recover to its original unstretched dimensions. The crosslinked structure provides the initial recovery force and ensures that the article does not melt and that it maintains its mechanical integrity.

[00098] The resulting laminated structure comprising at least one heat shrinkable layer and functional layer is then further laminated with an adhesive layer by passing the stretched sheet beneath a hot adhesive coating applicator or doctor blade.

[00099] The following examples illustrate suitable combinations of polymeric materials for use in the invention and the production of the heat shrinkable coverings therewith.

[000100] **Example One**

[000101] A composition comprising a silane-grafted polypropylene-polyethylene blend, a silanol condensation catalyst, an antioxidant masterbatch and black pigment was heated above the melt temperature of the resin components in an extruder and formed into sheet of 0.045in. thickness. The sheet was then crosslinked by conditioning it at a temperature of 95°C and a relative humidity of 90% for approximately 100 hours.

[000102] The crosslinked sheet was then extrusion laminated to an uncrosslinked polypropylene functional layer by melt extruding said polypropylene onto the pre-heated crosslinked sheet and passing the layers between heated casting rollers.

[000103] The laminated sheet was then re-heated to a temperature of approximately 150°C, and stretched by approximately 30% using a machine-direction (MDO) mechanical stretcher. Whilst in the stretched state, the sheet was rapidly cooled by feeding it between water-cooled steel rollers to below the crystalline melting point of the composition to fix the sheet at the stretched dimensions. The laminated sheet was subsequently extrusion laminated with a layer of hot melt adhesive.

[000104] The laminated sheet was then tested to determine the degree of crosslinking and for the mechanical properties as indicated below:

[000105]

Property	Test Method	Performance
UltimateTensile Strength (MPa)	ASTM D638	35
Ultimate Elongation (%)	ASTM D638	420
Flexural Modulus/ Stiffness (MPa)	ASTM D790	1080

Hardness (Shore D)	Shore D Hardness	72
Hot Tensile Strength @ 200°C (psi)*	Internal Specification	5
Water Absorption (%)	ASTM D570	0.5
100°C Penetration (mm)	DIN 30678	<0.1
110°C Penetration (mm)	DIN 30678	0.2
130°C Penetration (mm)	DIN 30678	0.3
Adhesive Peel Strength @ 23°C (N/cm)	DIN 30672	243
Adhesive Peel Strength @ 110°C (N/cm)	DIN 30672	77

* Hot Tensile Strength determines the degree of crosslinking by measuring the strength of the composition above the melting point and hence the strength of the crosslinked network only.

[000106] Example Two

[000107] A composition comprising a polyethylene, a radiation sensitizer, an antioxidant masterbatch and black pigment was heated above the melt temperature of the resin components in an extruder and formed into sheet of 0.045in. thickness. The extruded sheet was then crosslinked at a dosage of approximately 10 megarads using a Radiation Dynamics "Dynamitron" electron beam accelerator.

[000108] The crosslinked sheet was then extrusion laminated to an uncrosslinked polypropylene functional layer by melt extruding said polypropylene onto the pre-heated crosslinked sheet and passing the layers between heated casting rollers.

[000109] The laminated sheet was then re-heated to a temperature of approximately 150°C, and stretched by approximately 30% using a machine-direction (MDO) mechanical stretcher. Whilst in the stretched state, the sheet was rapidly cooled by feeding it between water-cooled steel rollers to below the crystalline melting point of the composition to fix the sheet at the stretched dimensions. The laminated sheet was subsequently extrusion laminated with a layer of hot melt adhesive.

[000110] The laminated sheet was then tested to determine the degree of crosslinking and mechanical properties, as described above.

Although the invention has been described with reference to illustrative embodiments, it is to be understood that the invention is not limited to these precise embodiments.

What is claimed is:

1. A laminated heat shrinkable pipe joint covering comprising:

    a) at least one heat shrinkable layer comprising a crosslinked polymeric material;

    b) a functional layer having at least one of the following properties:

    (i) high temperature penetration resistance defined as a penetration of less than 0.4mm at 130°C;

    (ii) softening point defined as a Vicat softening point of at least 130°C;

    (iii) impact resistance defined as an ability to withstand an impact energy of at least 5 J per mm. of coating thickness;

    (iv) long-term thermal stability defined as a service life of at least 20 years at an operating temperature of at least 120°C;

    (v) tensile strength of at least of 20 MPa;

    (vi) stiffness defined as a flexural modulus of at least 1,000 MPa;

    (vii) thermal insulation defined as a thermal conductivity less than about 0.20 W/mK;

    (viii) electrical conductivity or static dissipation defined as a volume resistivity of less than about 10^{12} ohm.cm; or

    (ix) impermeability to gases and moisture; and

c) an adhesive layer which forms an inner lamina of the covering;

wherein the functional layer comprises a non-crosslinked polymeric material, and wherein the functional layer and the at least one heat shrinkable layer are laminated together by application of heat and pressure.

2. The laminated heat shrinkable covering according to claim 1, wherein the crosslinked polymeric material is a crosslinked polyolefin material.

3. The laminated heat shrinkable covering according to claim 1, wherein the heat shrinkable layer comprises a crosslinked polyolefin material comprising a propylene homopolymer or a copolymer of propylene with an olefin other than propylene.

4. The laminated heat shrinkable covering according to any one of claims 1 to 3, wherein the non-crosslinked polymeric material of the functional layer comprises a propylene homopolymer or a copolymer of propylene with an olefin other than propylene.

5. The laminated heat shrinkable covering according to claim 3 or 4, wherein the copolymer of propylene is a copolymer of propylene with ethylene.

6. The laminated heat shrinkable covering according to claim 3 or 4, wherein the propylene homopolymer or copolymer of propylene is modified with a functional group selected from a group consisting of: silanes, acrylic acids, alkyl acrylic acids, glycidyl acrylates, alkyl acrylates, anhydrides and combinations thereof.

7. The laminated heat shrinkable covering according to claim 1, wherein the heat shrinkable layer comprises a crosslinked polyolefin material comprising ethylene homopolymers or ethylene copolymers.

8. The laminated heat shrinkable covering according to claim 1, wherein the non-crosslinked polyolefin material of the functional layer comprises ethylene homopolymers or ethylene copolymers.

9. The laminated heat shrinkable covering according to claim 7 or 8, wherein the ethylene copolymer is modified with one or more reactive functional groups selected from a group consisting of: vinyl acetate, vinyl alcohol, alkyl acrylates, and a higher olefin.

10. The laminated heat shrinkable covering according to claim 9, wherein the higher olefin is selected from a group consisting of butene, hexene, and octene.

11. The laminated heat shrinkable covering according to claim 7 or 8, wherein the ethylene homopolymer is selected from a group consisting of: high density polyethylene, medium density polyethylene, linear medium density polyethylene, low density polyethylene, linear low density polyethylene, and combinations thereof.

12. The laminated heat shrinkable covering according to claim 1, wherein the heat shrinkable layer comprises a crosslinked polyolefin material comprising an elastomer selected from a group consisting of: ethylene-propylene diene elastomers; crystalline propylene-ethylene elastomers, and thermoplastic polyolefin elastomers.

13. The laminated heat shrinkable covering according to claim 1, wherein the non-crosslinked polymeric material of the functional layer comprises an elastomer selected from a group consisting of: ethylene-propylene diene elastomers; crystalline propylene-ethylene elastomers, and thermoplastic polyolefin elastomers.

14. The laminated heat shrinkable covering according to claim 1, wherein the heat shrinkable layer comprises a combination of two or more of the polymers recited in any one of claims 3 to 13.

15. The laminated heat shrinkable covering according to claim 1, wherein the non-crosslinked polymeric material functional layer comprises a compound selected from a group consisting of: a filled polyolefin, a polyolefin nanocomposite, an engineering thermoplastic, a barrier polymer, a thermally insulating polymer, and an electrically conductive polymer.

16. The laminated heat shrinkable covering according to claim 15, wherein a filler in the filled polyolefin is selected from the group consisting of: clay, mica, talc, silica, wollastonite, wood, glass fibres, and metal oxides.

17. The laminated heat shrinkable covering according to claim 15, wherein the polyolefin nanocomposite comprises a polyolefin and an exfoliated clay additive.

18. The laminated heat shrinkable covering according to claim 15, wherein the engineering thermoplastic is selected from the group consisting of: nylons, polyesters, and polyurethanes.

19. The laminated heat shrinkable covering according to claim 15, wherein the thermally insulating polymer comprises a polyolefin and a low conductivity insulating filler selected from the group consisting of: hollow glass, ceramic and polymer microspheres.

20. The laminated heat shrinkable covering according to claim 15, wherein the electrically conductive polymer comprises an intrinsically conductive polymer, or an electrically conductive filler comprising carbon black or a metal powder.

21. The laminated heat shrinkable covering according to claim 20, wherein the intrinsically conductive polymer is a polyaniline.

22. The laminated heat shrinkable covering according to any one of claims 1 to 21, wherein the at least one heat shrinkable layer further comprises at least one additive selected from a group consisting of: cross-linking promoters,

compatibilisers, modifiers, pigments, antioxidant stabilizers, heat stabilizers, ultraviolet (UV) stabilizers, fillers, flame retardants, and process aids.

23. The laminated heat shrinkable covering according to claim 22, wherein the compatibiliser is selected from a group consisting of: ethylene-propylene copolymers; ethylene-propylene diene elastomers; crystalline propylene-ethylene elastomers; thermoplastic polyolefin elastomers; metallocene polyolefins; copolymers of ethylene with vinyl acetate, vinyl alcohol, and/or alkyl acrylates; polybutenes; hydrogenated and non-hydrogenated polybutadienes; butyl rubber; polyolefins modified with reactive functional groups selected from the group comprising silanes, alcohols, amines, acrylic acids, methacrylic acids, acrylates, methacrylates, glycidyl methacrylates, and anhydrides; polyolefin ionomers; polyolefin nanocomposites; block copolymers selected from the group comprising styrene-butadiene, styrene-butadiene-styrene, styrene-ethylene/propylene and styrene-ethylene/butylene-styrene; and thermoplastic elastomers comprising polypropylene blended with an elastomer.

24. The laminated heat shrinkable covering according to claim 23, wherein the thermoplastic elastomer comprises polypropylene blended with ethylene propylene.

25. The laminated heat shrinkable covering according to any one of claims 1 to 24, wherein the at least one heat shrinkable layer is bonded to the functional layer.

26. The laminated heat shrinkable covering according to any one of claims 1 to 25, wherein the adhesive layer is bonded to the heat shrinkable layer, wherein the heat shrinkable layer forms an intermediate lamina of the covering, and wherein the functional layer forms an outer lamina of the covering.

27. The laminated heat shrinkable covering according to any one of claims 1 to 25, wherein the adhesive layer is bonded to the functional layer, wherein the functional layer forms an intermediate lamina of the covering, and wherein the heat shrinkable layer forms an outer lamina of the covering.

28. The laminated heat shrinkable covering according to claim 1, wherein the covering comprises at least two of said heat shrinkable layers, including a first heat shrinkable layer and a second heat shrinkable layer.

29. The laminated heat shrinkable covering according to claim 28, wherein the second heat shrinkable layer is positioned between the first heat shrinkable layer and the functional layer and wherein the second heat shrinkable layer is bonded to the first heat shrinkable layer and the functional layer, and the functional layer is bonded to the adhesive layer, and wherein the first heat shrinkable layer forms an outer lamina of the covering.

30. The laminated heat shrinkable covering according to claim 28, wherein the second heat shrinkable layer is positioned between the functional layer and the adhesive layer and wherein the second heat shrinkable layer is bonded to the functional layer and the adhesive layer, and the functional layer is bonded to the first heat-shrinkable layer, and wherein the first heat shrinkable layer forms an outer lamina of the covering.

31. The laminated heat shrinkable covering according to claim 29 or 30, wherein the second heat-shrinkable layer is crosslinked to a lesser degree than the first heat-shrinkable layer.

32. A laminated heat shrinkable pipe joint covering comprising:

a) at least two heat shrinkable layers, including a first heat shrinkable layer and a second heat shrinkable layer, each of the heat shrinkable layers comprising a crosslinked polymeric material;

b) a functional layer having at least one of the following properties:

(i) high temperature penetration resistance defined as a penetration of less than 0.4mm at 130°C;

(ii) softening point defined as a Vicat softening point of at least 130°C;

(iii) impact resistance defined as an ability to withstand an impact energy of at least 5 J per mm. of coating thickness;

(iv) long-term thermal stability defined as a service life of at least 20 years at an operating temperature of at least 120°C;

(v) tensile strength of at least of 20 MPa;

(vi) stiffness defined as a flexural modulus of at least 1,000 MPa;

(vii) thermal insulation defined as a thermal conductivity less than about 0.20 W/mK;

(viii) electrical conductivity or static dissipation defined as a volume resistivity of less than about 10^{12} ohm.cm; or

(ix) impermeability to gases and moisture; and

c) an adhesive layer which forms an inner lamina of the covering;

wherein the second heat shrinkable layer is positioned between the first heat shrinkable layer and the functional layer and wherein the second heat shrinkable layer is bonded to the first heat shrinkable layer and the functional layer, and the functional layer is bonded to the adhesive layer, and wherein the first heat shrinkable layer forms an outer lamina of the covering.

33. The laminated heat shrinkable covering according to claim 32, wherein the second heat-shrinkable layer is crosslinked to a lesser degree than the first heat-shrinkable layer.

34. A method for manufacturing a laminated heat shrinkable covering, comprising:

(a) extruding a first heat shrinkable layer comprising a crosslinked polymeric material;

(b) crosslinking the first heat shrinkable layer;

(c) bonding the first heat shrinkable layer to a functional layer, said layers being laminated together by application of heat and pressure, thereby forming a laminated article, wherein the functional layer comprises a non-crosslinked polymeric material;

(d) stretching the laminated article and cooling the article in its stretched state, thereby forming a laminated structure; and

(e) applying an adhesive layer to the laminated structure;

wherein the functional layer has at least one of the following properties:

(i) high temperature penetration resistance defined as a penetration of less than 0.4mm at 130°C;

(ii) softening point defined as a Vicat softening point of at least 130°C;

(iii) impact resistance defined as an ability to withstand an impact energy of at least 5 J per mm. of coating thickness;

(iv) long-term thermal stability defined as a service life of at least 20 years at an operating temperature of at least 120°C;

(v) tensile strength of at least of 20 MPa;

(vi) stiffness defined as a flexural modulus of at least 1,000 MPa;

(vii) thermal insulation defined as a thermal conductivity less than about 0.20 W/mK;

(viii) electrical conductivity or static dissipation defined as a volume resistivity of less than about 10^{12} ohm.cm; or

(ix) impermeability to gases and moisture.

Figure 1

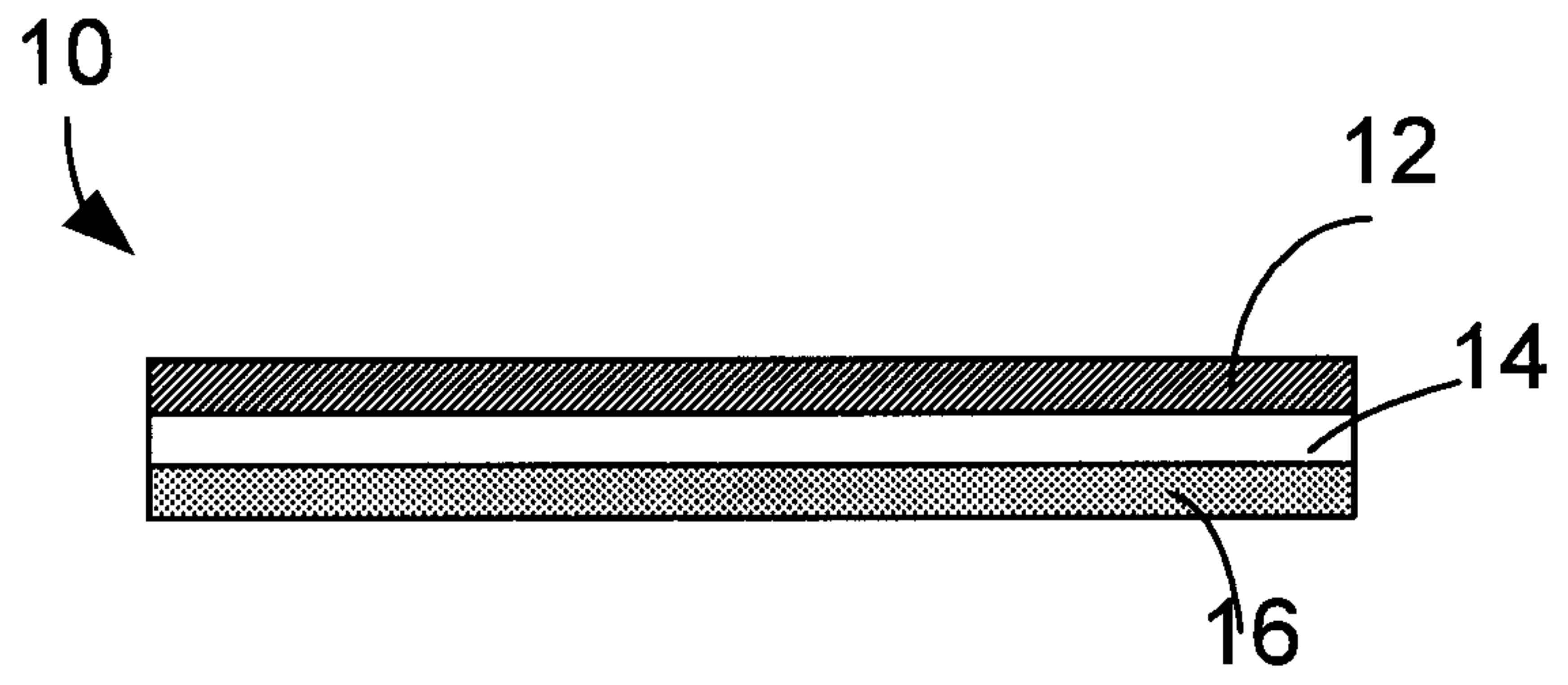


Figure 2

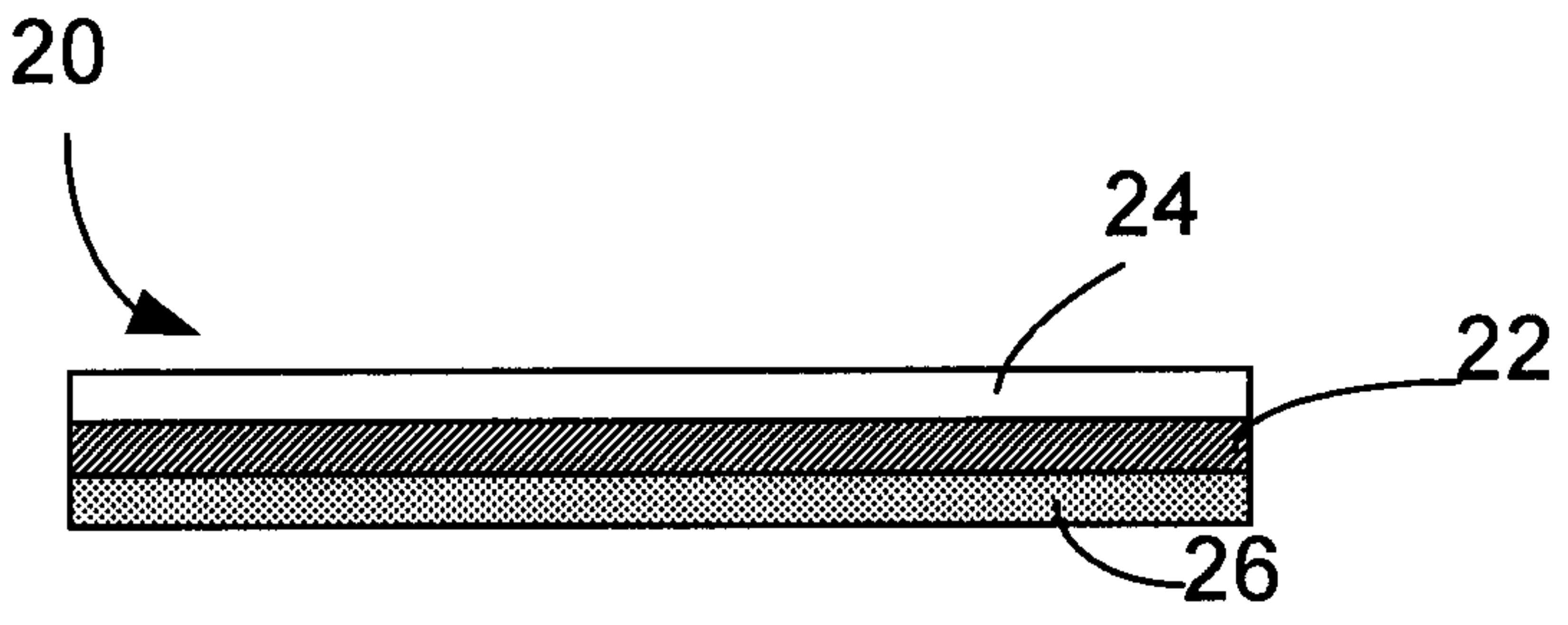


Figure 3

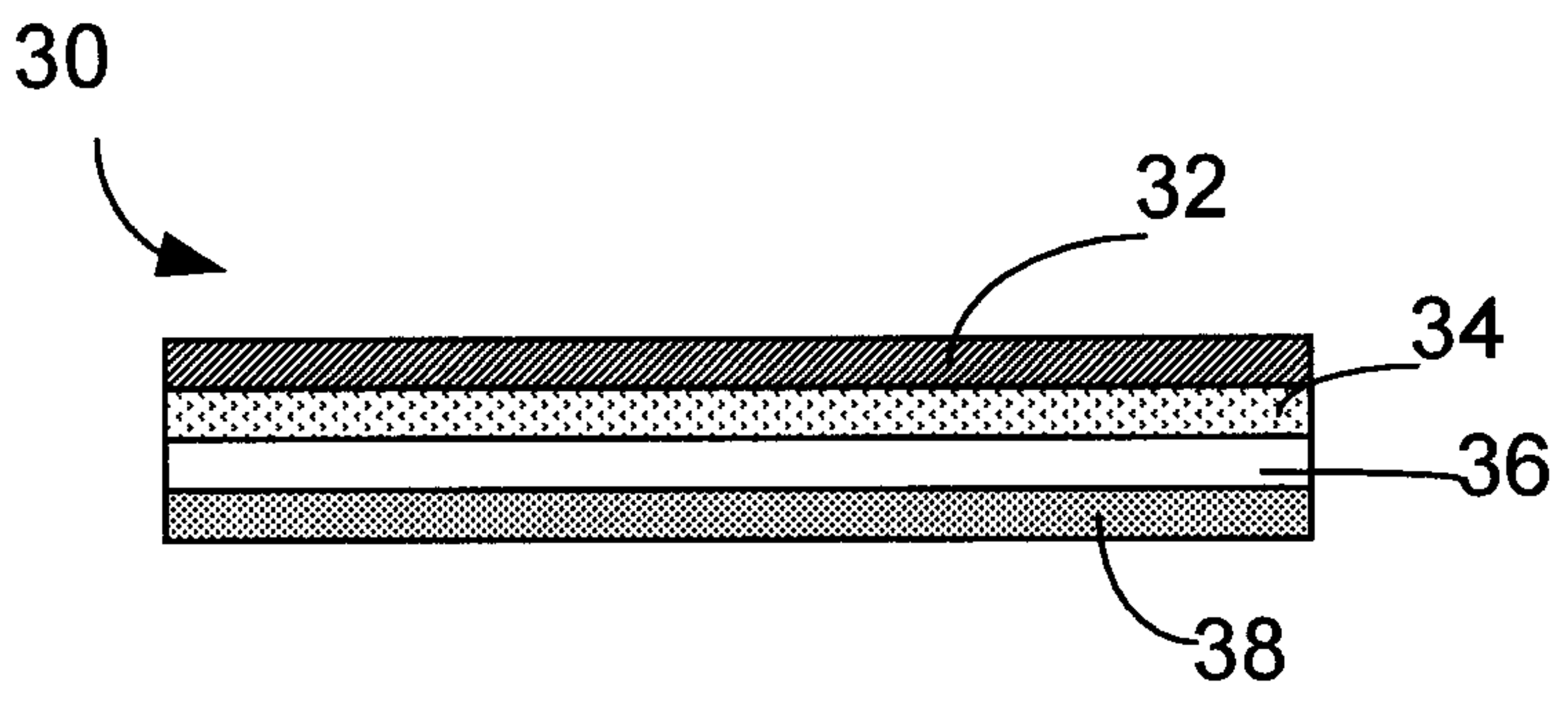
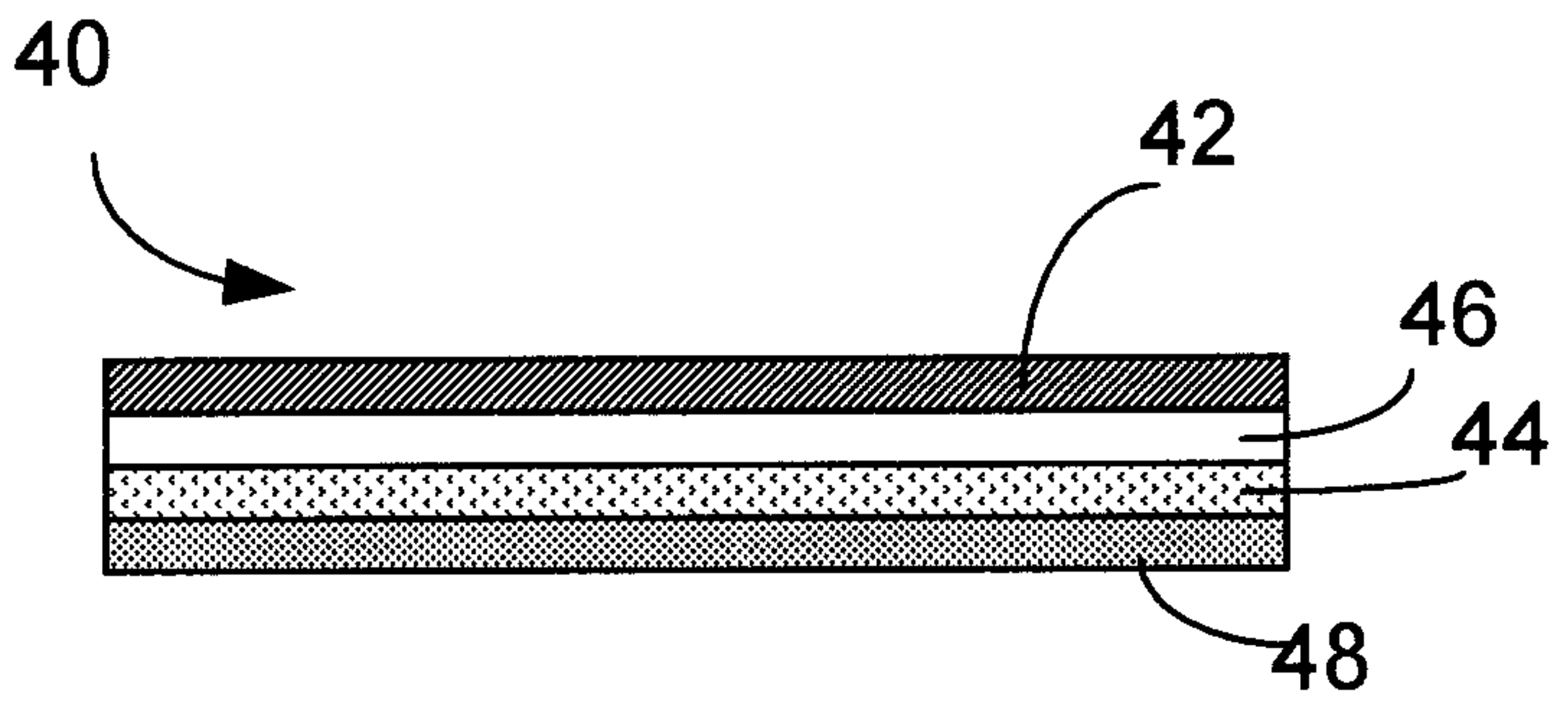
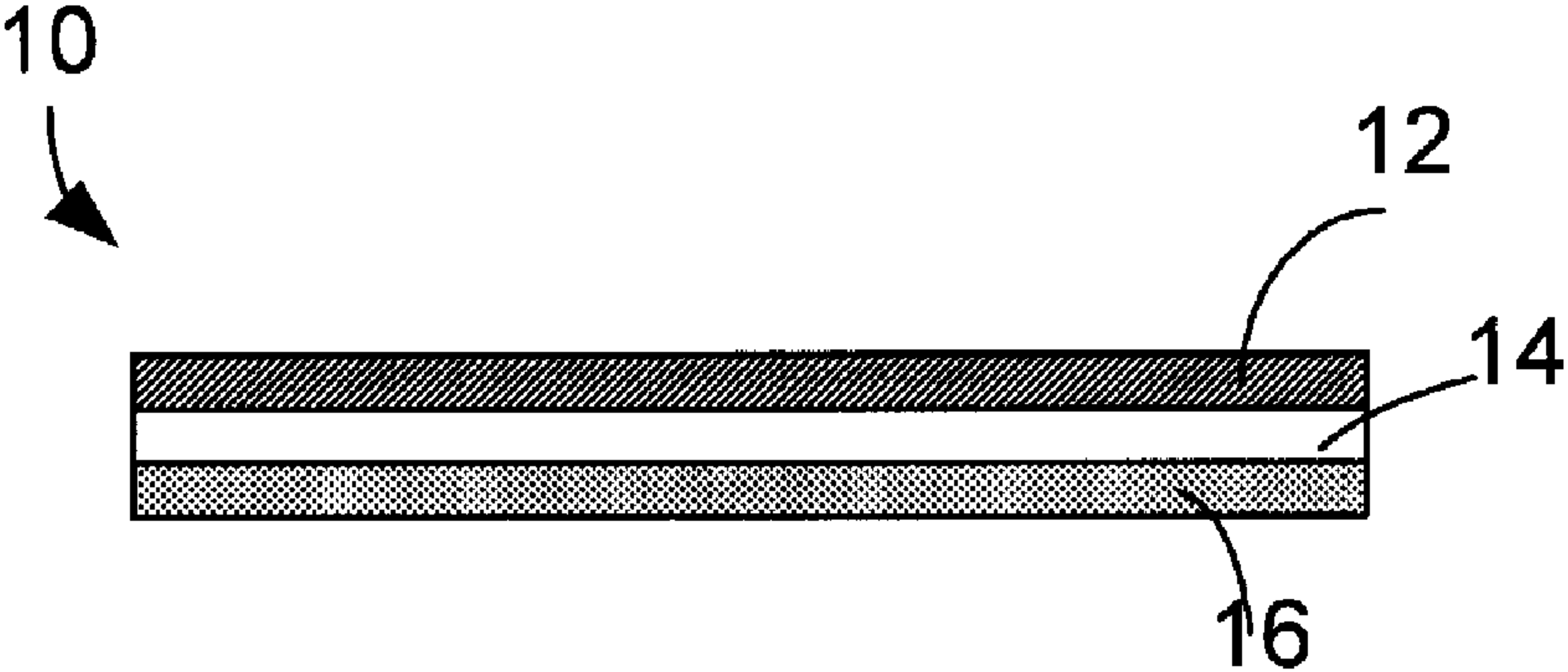


Figure 4

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