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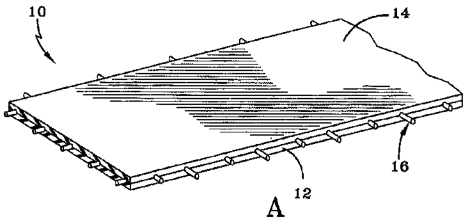
(54) **Titre** : MEMBRANES THERMOPLASTIQUES COMPRENANT UN POLYMERE AVEC UNE FONCTIONNALITE REACTIVE AVEC LES ISOCYANATES

(54) **Title**: THERMOPLASTIC MEMBRANES INCLUDING POLYMER WITH ISOCYANATE-REACTIVE FUNCTIONALITY



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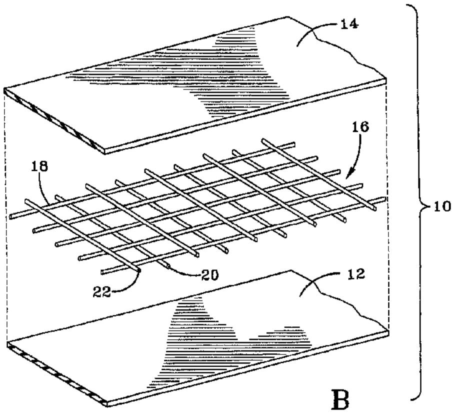

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(57) **Abrégé/Abstract**:
A thermoplastic membrane comprising at least one layer, wherein the at least one layer includes a first thermoplastic polymer and a second polymer having at least one isocyanate-reactive substituent dispersed within said first thermoplastic polymer.

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(54) Title: THERMOPLASTIC MEMBRANES INCLUDING POLYMER WITH ISOCYANATE-REACTIVE FUNCTIONALITY

(57) Abstract: A thermoplastic membrane comprising at least one layer, wherein the at least one layer includes a first thermoplastic polymer and a second polymer having at least one isocyanate-reactive substituent dispersed within said first thermoplastic polymer.

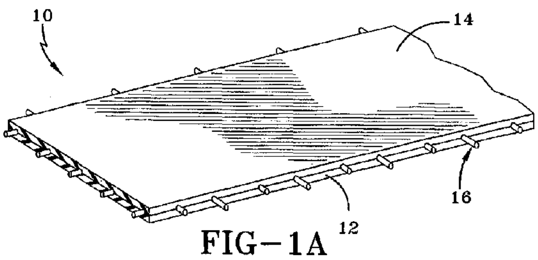

FIG-1A

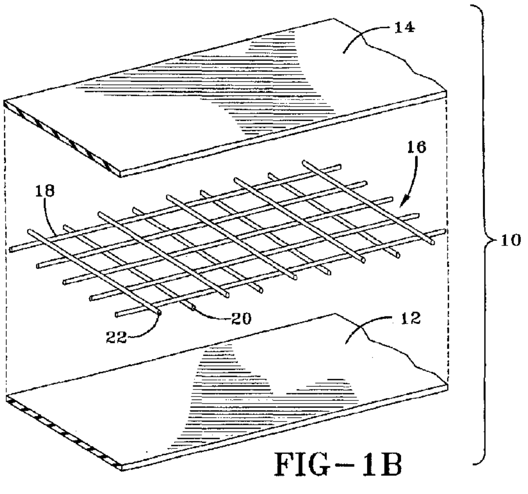

FIG-1B

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THERMOPLASTIC MEMBRANES INCLUDING POLYMER WITH ISOCYANATE-REACTIVE FUNCTIONALITY

FIELD OF THE INVENTION

[0002] Embodiments of the present invention are directed toward thermoplastic membranes containing polymer with isocyanate-reactive functionality and the use of these membranes in roofing systems that employ polyurethane adhesives.

BACKGROUND OF THE INVENTION

[0003] Flat or low-sloped roofs are often covered with polymeric membranes. Common among the membranes that have the mechanical properties needed to be technologically useful are thermoset membranes prepared with EPDM rubber, or thermoplastic membranes prepared with ethylene-propylene reactor copolymers or blends of polyethylene and polypropylene. These membranes typically contain carbon black and/or mineral fillers, which provide advantageous mechanical properties to the membranes.

[0004] U.S. Pat. No. 4,996,812 discloses a composite roof structure including a layer of adhesive material, such as a foamed, cellular polyurethane adhesive, along with a flexible rubber or thermoplastic membrane including a fleece-like matting layer secured to the underside thereof. The adhesive is typically sprayed onto the roof substrate wherein, prior to solidification of the adhesive, the fleece-lined membrane is pressed into the adhesive so that the matting becomes embedded therein.

[0005] To simplify installation and to minimize costs associated with the polymeric membranes, a need exists for a non-fleece membrane sheet that can be directly adhered to the roof substrate. Since the industry is accustomed to using polyurethane-type foam adhesives, it would be highly desirable to use polyurethane adhesives in this regard.

[0005a] In accordance with one aspect there is provided an adhered roofing system comprising:

(i) a roof substrate;

(ii) a thermoplastic membrane comprising:

an upper layer laminated to a lower layer where the lower layer includes from about 3 to about 25 wt.% of a block copolymer including at least one hard segment and at least one soft segment having at least one isocyanate-reactive substituent dispersed within a thermoplastic polyolefin, and where the upper layer is substantially devoid of a polymer having an isocyanate-reactive substituent; and

(iii) a polyurethane adhesive securing the membrane to the roof substrate such that the lower layer of the membrane is in direct contact with said polyurethane adhesive.

[0005b] In accordance with another aspect there is provided a method of adhering a thermoplastic membrane to a roof substrate, the method comprising:

(i) applying a polyurethane adhesive to the roof substrate; and

(ii) applying a thermoplastic membrane to the polyurethane adhesive, where the thermoplastic membrane includes a first layer, which forms a top surface of the membrane, laminated to a second layer, which forms the bottom surface of the membrane, where the second layer includes from about 3 to about 25 wt.% of a block copolymer including at least one hard segment and at least one soft segment having at least one isocyanate-reactive substituent dispersed within a thermoplastic polyolefin, where the first layer is substantially devoid of a polymer having an isocyanate-reactive substituent, and wherein the second layer of the thermoplastic membrane is in direct contact with said adhesive layer.

SUMMARY OF THE INVENTION

[0006] Embodiments of the present invention provide a thermoplastic membrane comprising at least one layer, wherein the at least one layer includes a first thermoplastic polymer and a second polymer having at least one isocyanate-reactive substituent dispersed within said first thermoplastic polymer.

[0007] Other embodiments of the present invention provide a method of adhering a thermoplastic membrane to a roof substrate, the method comprising applying a polyurethane adhesive to the roof substrate and applying a thermoplastic membrane to the polyurethane adhesive, where the thermoplastic membrane includes at least one layer, wherein the at least one layer includes a first thermoplastic polymer and a second polymer having at least one isocyanate-reactive substituent dispersed within said first thermoplastic polymer, and where the membrane is devoid of a fleece backing.

[0008]

BRIED DESCRIPTION OF THE DRAWINGS

[0009] Fig. 1a is a perspective view of a multi-layered membrane including two laminated layers according to embodiments of the present invention.

[0010] Fig. 1b is a perspective view of a multi-layered membrane shown in exploded view including two laminated layers according to embodiments of the present invention.

[0011] Fig. 2 is a perspective view of a multi-layered membrane including co-extruded laminated layers according to embodiments of the present invention.

[0012] Fig. 3 is a perspective, cross-sectional view of a roof assembly according to embodiments of the present invention.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0013] Embodiments of the present invention are based, at least in part, on the discovery of a thermoplastic roofing membrane including at least one layer having a an appreciable impact on the layer or membrane. Due to the presence of the isocyanate-reactive polymer within lower layer 12, the membrane can be secured to a roof substrate by use of a polyurethane adhesive, which is believed to react or interact with the isocyanate-reactive polymer.

[0015] In one or more embodiments, the membranes of the present invention are multi-layered membranes that include one or more coextruded layers. In this respect, U.S. Publ. Nos. 2009/0137168, 2009/0181216, 2009/0269565, 2007/0193167, and 2007/0194482. In one or more embodiments, at least one of the coextruded layers includes a isocyanate-reactive polymer according to one or more aspects of the present invention. For example, and with reference to Fig. 2, lower or bottom layer 12 includes coextruded layers 24 and 26, and upper layer 14 optionally includes coextruded layers 28 and 30. Lower layer 12 and upper layer 14 may be laminated to each other with optional scrim 16 disposed therebetween. Coextruded layer 26, which may be referred to as the bottom coextruded layer 26, includes the isocyanate-reactive polymer according the present invention. Due to the presence of the isocyanate-reactive polymer within bottom coextruded layer 26, the membrane can be secured to a roof substrate by use of a polyurethane adhesive, which is believed to react or interact with the isocyanate-reactive polymer. In one or more embodiments, upper layer 14 may include isocyanate-reactive polymer; e.g., top layer 30 may include isocyanate-reactive polymer. As a result of this configuration, adjacent membranes can be lap-sealed using a polyurethane adhesive.

[0016] In one or more embodiments, the thickness of coextruded layers 24 and 26 may be the same or substantially similar. In other embodiments, the thickness of coextruded bottom layer 26 may be thinner than coextruded upper layer 24, which will provide economic benefit by minimizing the amount of the isocyanate-reactive polymer within the overall membrane while still providing the isocyanate-reactive polymer in a location that will allow it to provide adequate bonding to the adhesive.

[0017] In one or more embodiments, the remaining layers of the multi-layered membrane may include the isocyanate-reactive polymer. In other embodiments, the remaining layers of the multi-layered membrane may be devoid of isocyanate-reactive substituents are dispersed. As noted above, at least one layer of the membrane includes a isocyanate-reactive polymer, which is likewise dispersed within the thermoplastic component or matrix. Inasmuch as the isocyanate-reactive polymer may also be a thermoplastic polymer, reference may be made to first and second thermoplastic polymers. For example, the thermoplastic polymer forming the matrix, which accounts for the major volume fraction of any given layer, may be referred to as a first thermoplastic polymer, and where the isocyanate-reactive polymer is also a thermoplastic polymer, it may be referred to as a second thermoplastic polymer bearing an isocyanate-reactive functionality or group.

[0022] In one or more embodiments, the thermoplastic component includes a thermoplastic olefinic polymer, which includes one or more *mer* units deriving from olefinic monomer. Blends of polymers may also be used. These blends include physical blends as well as reactor blends. In one or more embodiments, the thermoplastic olefinic polymer may derive from recycled thermoplastic polyolefin membranes as described in copending application serial number US 2008/0227914 A1.

[0023] In one or more embodiments, the thermoplastic olefinic polymer may include an olefinic reactor copolymer, which may also be referred to as in-reactor copolymer. Reactor copolymers are generally known in the art and may include blends of olefinic polymers that result from the polymerization of ethylene and α-olefins (*e.g.*, propylene) with sundry catalyst systems. In one or more embodiments, these blends are made by in-reactor sequential polymerization. Reactor copolymers useful in one or more embodiments include those disclosed in U.S. Patent No. 6,451,897, which is incorporated therein by reference. Reactor copolymers, which are also referred to as TPO resins, are commercially available under the tradename HIFAX^{TM} (Lyondellbassel); these materials are believed to include in-reactor blends of ethylene-propylene rubber and polypropylene or polypropylene copolymers. In one or more embodiments, the in-reactor copolymers may be physically blended with other polyolefins. For example, in reactor copolymers may be blended with linear low density polyethene.

may be from about 2.5 to about 4, in other embodiments from about 2.7 to about 3.5, and in other embodiments from about 2.8 to about 3.2.

[0027] In one or more embodiments, propylene-based polymers may be characterized by a melt temperature (T_m) that is from about 165°C to about 130°C, in other embodiments from about 160 to about 140°C, and in other embodiments from about 155°C to about 140°C. In one or more embodiments, particularly where the propylene-based polymer is a copolymer of propylene and a comonomer, the melt temperature may be below 160°C, in other embodiments below 155°C, in other embodiments below 150°C, and in other embodiments below 145°C. In one or more embodiments, they may have a crystallization temperature (T_c) of about at least 90°C, in other embodiments at least about 95°C, and in other embodiments at least 100°C, with one embodiment ranging from 105° to 115°C.

[0028] Also, these propylene-based polymers may be characterized by having a heat of fusion of at least 25 J/g, in other embodiments in excess of 50 J/g, in other embodiments in excess of 100 J/g, and in other embodiments in excess of 140 J/g.

[0029] In one or more embodiments, the propylene-based polymers may be characterized by a flexural modulus, which may also be referred to as a 1% secant modulus, in excess of 120,000 psi, in other embodiments in excess of 125,000, in other embodiments in excess of 130,000 psi, in other embodiments in excess of 133,000 psi, in other embodiments in excess of 135,000 psi, and in other embodiments in excess of 137,000 psi, as measured according to ASTM D-790.

[0030] Useful propylene-based polymers include those that are commercially available. For example, propylene-based polymers can be obtained under the tradename PP7620Z™ (Fina), PP33BF01™ (Equistar), or under the tradename TR3020™ (Sunoco).

[0031] In one or more embodiments, the thermoplastic polymer may include a blend of olefinic polymers. Useful blends include those described in International Application No. PCT/US06/033522. For example, a particular blend may include (i) a plastomer, (ii) a low density polyethylene, and (iii) a propylene-based polymer.

[0032] In one or more embodiments, the plastomer includes an ethylene-α-olefin copolymer. The plastomer employed in one or more embodiments of this invention includes those described in U.S. Patent Nos. 6,207,754, 6,506,842, 5,226,392, and 5,747,592. This copolymer may include from about 1.0 to about 15 mole percent, in other embodiments from about 2 to about 12, in other embodiments from about 3 to about 9 mole percent, and in other embodiments from about 3.5 to about 8 mole percent *mer* units deriving from α-olefins, with the balance including *mer* units deriving from ethylene. The α-olefin employed in preparing the plastomer of one or more embodiments of this invention may include butene-1, pentene-1, hexene-1, octene-1, or 4-methyl-pentene-1.

[0033] The plastomer of one or more embodiments of this invention can be characterized by a density of from about 0.865 g/cc to about 0.900 g/cc, in other embodiments from about 0.870 to about 0.890 g/cc, and in other embodiments from about 0.875 to about 0.880 g/cc per ASTM D-792. In these or other embodiments, the density of the plastomers may be less than 0.900 g/cc, in other embodiments less than 0.890 g/cc, in other embodiments less than 0.880 g/cc, and in other embodiments less than 0.875 g/cc.

[0034] In one or more embodiments, the plastomer may be characterized by a weight average molecular weight of from about 7×10^4 to 13×10^4 g/mole, in other embodiments from about 8×10^4 to about 12×10^4 g/mole, and in other embodiments from about 9×10^4 to about 11×10^4 g/mole as measured by using GPC with polystyrene standards. In these or other embodiments, the plastomer may be characterized by a weight average molecular weight in excess of 5×10^4 g/mole, in other embodiments in excess of 6×10^4 g/mole, in other embodiments in excess of 7×10^4 g/mole, and in other embodiments in excess of 9×10^4 g/mole. In these or other embodiments, the plastomer may be characterized by a molecular weight distribution (M_w/M_n) that is from about 1.5 to 2.8, in other embodiments 1.7 to 2.4, and in other embodiments 2 to 2.3.

apparatus such as an internal mixer and then subsequently fabricated into membrane sheets or laminates.

[0068] In one or more embodiments, the membranes of the present invention may be prepared by extruding a polymeric composition into a sheet. Multiple sheets may be extruded and joined to form a laminate. A membrane including a reinforcing layer may be prepared by extruding at least one sheet on and/or below a reinforcement (*e.g.*, a scrim). In other embodiments, the polymeric layer may be prepared as separate sheets, and the sheets may then be calandered with the scrim sandwiched therebetween to form a laminate. In one or more embodiments, the membranes of the present invention are prepared by employing co-extrusion technology. Useful techniques include those described in co-pending US 2007/0193167 and US 2007/0194482.

[0069] Following extrusion, and after optionally joining one or more polymeric layers, or optionally joining one or more polymeric layer together with a reinforcement, the membrane may be fabricated to a desired thickness. This may be accomplished by passing the membrane through a set of squeeze rolls positioned at a desired thickness. The membrane may then be allowed to cool and/or rolled for shipment and/or storage.

[0070] The polymeric composition that may be extruded to form the polymeric sheet may include the ingredients or constituents described herein. For example, the polymeric composition may include thermoplastic polyolefin, and isocyanate-reactive polymers defined herein. The ingredients may be mixed together by employing conventional polymer mixing equipment and techniques. In one or more embodiments, an extruder may be employed to mix the ingredients. For example, single-screw or twin-screw extruders may be employed.

Industrial Applicability

[0071] The membranes of one or more embodiments of the present invention are useful in a number of applications. In one embodiment, the membranes may be useful for roofing membranes that are useful for covering flat or low-sloped roofs. In other embodiments, the membranes may be useful as geomembranes. Geomembranes include those membranes employed as pond liners, water dams, animal waste treatment liners, and pond covers.

[0072] As described above, the membranes of one or more embodiments of the present invention may be employed as roofing membranes. These membranes include thermoplastic roofing membranes including those that meet the specifications of ASTM D-6878-03. These membranes maybe employed to cover flat or low/sloped roofs. These roofs are generally known in the art as disclosed in US 2006/0179749, and International Application No. PCT/US2005/024232. As shown in Fig. 3, a flat or low-sloped roof assembly 40 may include a roof deck 82, and optional insulation layer 84, and membrane 10 according to the present invention.

[0073] Advantageously, the membranes of the present invention can be used to prepare adhered roofing systems, including fully-adhered systems and partially-adhered systems. In one or more embodiments, the membranes are used in conjunction with polyurethane type adhesives. Generally, the polyurethane adhesive can be applied to a roof substrate to form a layer of adhesive, and then the membranes of the present invention, which are devoid of any fleece backing, can subsequently be contacted to the layer of adhesive disposed on the substrate. Advantageously, the process can be used to construct a roofing system meeting the standards of UL and Factory Mutual for wind uplift in the absence of a fleece or other backing material applied to the membrane.

[0074] The substrate to which the polyurethane adhesive composition is applied may include a roof deck, which may include steel, concrete, and/or wood. In other embodiments, the polyurethane adhesive composition may be applied to insulation materials, such as insulation boards and cover boards. As those skilled in the art appreciate, insulation boards and cover boards may carry a variety of facer materials including, but not limited to, paper facers, fiberglass-reinforced paper facers, fiberglass facers, coated fiberglass facers, metal facers such as aluminum facers, and solid facers such as wood. In yet other embodiments, the polyurethane-based adhesive composition may be applied to existing membranes. These existing membranes may include cured rubber systems such as EPDM membranes, thermoplastic polymers systems such as TPO membranes, or asphalt-based systems such as modified asphalt membranes and/or built roof systems. Advantageously, practice of the present invention provides adhesion to asphalt-based substrates by offering sufficient oil resistance, which is required to maintain sufficient adhesion to asphalt systems.

[0075] In one or more embodiments, the polyurethane adhesive that is applied to the roof deck, as the methods and techniques for applying the adhesive to the substrate, includes those polyurethane adhesives that are commonly used in the art. In this respect, U.S. Pat. No. 4,996,812. As is known in the art, one type of polyurethane adhesive system employs an isocyanate component and a polyol component, with the two components typically being mixed in a mix apparatus, such as a spray nozzle. These systems are typically referred to as two-part polyurethane adhesives. In other embodiments, an isocyanate prepolymer is employed and curing of the prepolymer relies upon moisture within the atmosphere, rather than on the use of a polyol. These systems are typically referred to as one-part polyurethane adhesive systems.

[0076] In one or more embodiments, suitable isocyanates include, but are not limited to, aromatic polyisocyanates such as diphenyl methane, diisocyanate in the form of its 2,4'-, 2,2'-, and 4,4'-isomers and mixtures thereof, the mixtures of diphenyl methane diisocyanates (MDI) and oligomers thereof known in the art as "crude" or polymeric MDI having an isocyanate functionality of greater than 2, toluene diisocyanate in the form of its 2,4' and 2,6'-isomers and mixtures thereof, 1,5-naphthalene diisocyanate, and 1,4' diisocyanatobenzene. Exemplary isocyanate components include polymeric Rubinate 1850 (Huntsmen Polyurethanes), polymeric Lupranate M70R (BASF), and polymeric Mondur 489N (Bayer).

[0077] In one or more embodiments, suitable polyols include diols, polyols, and glycols, which may contain water as generally known in the art. Primary and secondary amines are suitable, as are polyether polyols and polyester polyols. Useful polyester polyols include phthalic anhydride based PS-2352 (Stepen), phthalic emulsifiers/solubilizers to maintain emulsification/solubilization and a minimal amount of the surfactant to obtain good cell nucleation and cell stabilization. Examples of surfactants include Pelron surfactant 9920, Goldschmidt surfactant B8522, and GE 6912. U.S. Patent Nos. 5,686,499 and 5,837,742.

[0081] Suitable emulsifiers/solubilizers include DABCO Kitane 20AS (Air Products), and Tergitol NP-9 (nonylphenol + 9 moles ethylene oxide).

[0082] In one or more embodiments, the equivalent ratio of isocyanate groups to isocyanate-reactive groups (i.e. polyol functionality) introduced to prepare the developing foam is at least 2.7:1, in other embodiments at least 2.85:1, in other embodiments at least 3.0:1, in other embodiments at least 3.15:1, and in other embodiments at least 3.25:1. In these or other embodiments, the equivalent ratio of isocyanate groups to isocyanate-reactive groups is less than 3.6:1, in other embodiments less than 3.5:1, and in other embodiments less than 3.4:1. As those skilled in the art appreciate, the equivalent ratio refers to ratio of the number of moles of isocyanate groups in a given weight of isocyanate reactant to the number of moles of isocyanate-reactive groups in a given weight of isocyanate-reactive reactant.

[0083] In one or more embodiments, time is permitted between the application of the adhesive composition and application of the membrane panel. This time allows the foam reactants to react and begin to develop sufficient "cream," then rise. Generally, the membrane is applied during the cream time or the rise time, but before the tack-free time, which is the period of time when the adhesive loses sufficient green strength. In one or more embodiments, this time provided is less than 1 hour, in other embodiments less than 30 minutes, in other embodiments less than 10 minutes, and in other embodiments less than 3 minutes.

[0084] In one or more embodiments, the application of the adhesive composition to the substrate can be performed by completely covering the substrate with the adhesive. In other embodiments, the substrate may be partially covered. In one or more embodiments, the adhesive is applied to the roof substrate in the form of a bead that may be about ¼ to about 1 inch in diameter or thickness. The adhesive is then allowed to cream and then rise, which can expand the size of the bead up to 2-3 inches in thickness or diameter. The membrane can then be rolled out or otherwise applied to the substrate, which thereby further spreads the foam adhesive. In one or more embodiments, these beads may be applied in strips at a distance of from about 1 foot to about 3 feed (or even up to 5 feet) in distance from one another. Spacing of strips can be adjusted to achieve various wind uplift ratings.

[0085] In one or more embodiments, the membrane panel may be applied to the adhesive layer using several known techniques. For example, the membrane panel may be unrolled on to the adhesive layer.

[0086] Practice of this invention is not limited by the selection of any particular roof deck. Accordingly, the roofing systems herein can include a variety of roof decks. Exemplary roof decks include concrete pads, steel decks, wood beams, and foamed concrete decks.

[0087] Practice of this invention is likewise not limited by the selection of any particular insulation board. Moreover, the insulation boards are optional. Several insulation materials can be employed including polyurethane or polyisocyanurate cellular materials. These boards are known as described in U.S. Patent Nos. 6,117,375, 6,044,604, 5,891,563, 5,573,092, U.S. Publication Nos. 2004/01099832003/0082365, 2003/0153656, 2003/0032351, and 2002/0013379, as well as U.S. Serial Nos. 10/640,895, 10/925,654, and 10/632,343.

[0088] In other embodiments, these membranes may be employed to cover flat or low-slope roofs following a re-roofing event. In one or more embodiments, the membranes may be employed for re-roofing as described in U.S. Publication No. 2006/0179749, which are incorporated herein by reference.

[0089] In order to demonstrate the practice of the present invention, the following examples have been prepared and tested. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

[0091] As can be seen from the results in the table, the polyurethane adhesive adequately adhered to the membrane prepared exclusively with isocyanate-reactive polymer as shown in Sample 5. The mode of failure was cohesive, which refers to the fact that the adhesive itself was the mode of failure, not the adhesion between the membrane and the adhesive. Similar results were obtained at loadings down to 8 weight percent isocyanate-reactive polymer, as shown in Sample 3. At 5 weight percent isocyanate-reactive polymer, some level of adhesion was observed with cohesive failure within the adhesive, but some surfaces of the membrane showed no adhesion. Where the membrane sample did not include isocyanate-reactive polymer, no adhesion to the membrane was observed. It is believed that the results obtained in these tests demonstrate the usefulness of the invention, but it is also believed that lower loadings could be technologically useful where other conventional ingredients are employed within the membranes, such as fillers.

[0092] Various modifications and alterations that do not depart from the scope of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.

CLAIMS

1. An adhered roofing system comprising:

   (i) a roof substrate;

   (ii) a thermoplastic membrane comprising:

   an upper layer laminated to a lower layer where the lower layer includes from about 3 to about 25 wt.% of a block copolymer including at least one hard segment and at least one soft segment having at least one isocyanate-reactive substituent dispersed within a thermoplastic polyolefin, and where the upper layer is substantially devoid of a polymer having an isocyanate-reactive substituent; and

   (iii) a polyurethane adhesive securing the membrane to the roof substrate such that the lower layer of the membrane is in direct contact with said polyurethane adhesive.

2. The roofing system of claim 1, where the isocyanate-reactive substituent is a hydroxyl group.

3. The roofing system of claim 1, where the lower layer is a coextruded layer that includes at least two sublayers with one sublayer being the lowermost sublayer of the thermoplastic membrane thereby forming the bottom surface of the thermoplastic membrane, and wherein the lowermost sublayer includes the block copolymer having the at least one isocyanate-reactive substituent.

4. The roofing system of any one of claims 1 to 3, where the length of the block copolymer having at least one isocyanate-reactive substituent is at least one times the entanglement length of the block copolymer.

5. The roofing system of any one of claims 1 to 4, where a scrim reinforcement is disposed between the upper and lower layers.

6. A method of adhering a thermoplastic membrane to a roof substrate, the method comprising:

(i) applying a polyurethane adhesive to the roof substrate; and

(ii) applying a thermoplastic membrane to the polyurethane adhesive, where the thermoplastic membrane includes a first layer, which forms a top surface of the membrane, laminated to a second layer, which forms the bottom surface of the membrane, where the second layer includes from about 3 to about 25 wt.% of a block copolymer including at least one hard segment and at least one soft segment having at least one isocyanate-reactive substituent dispersed within a thermoplastic polyolefin, where the first layer is substantially devoid of a polymer having an isocyanate-reactive substituent, and wherein the second layer of the thermoplastic membrane is in direct contact with said adhesive layer.

7. The method of claim 6, where the second layer is laminated to at least the first layer, or where the second layer is coextruded with the at least first layer.

8. The method of claim 6 or 7, where the isocyanate-reactive substituent is a hydroxyl group.

9. The method of any one of claims 6 to 8, where the membrane further includes a scrim reinforcement disposed between the first and second layers.

10. The method of claim 9, where the lower layer is a coextruded layer that includes at least two sublayers with one sublayer being the lowermost sublayer of the thermoplastic membrane thereby forming the bottom surface of the thermoplastic membrane, and wherein the lowermost sublayer includes the block copolymer having the at least one isocyanate-reactive substituent.

11. The method of any one of claims 6 to 10, where the length of the block copolymer having the at least one isocyanate-reactive substituent is at least one times the entanglement length of the block copolymer.

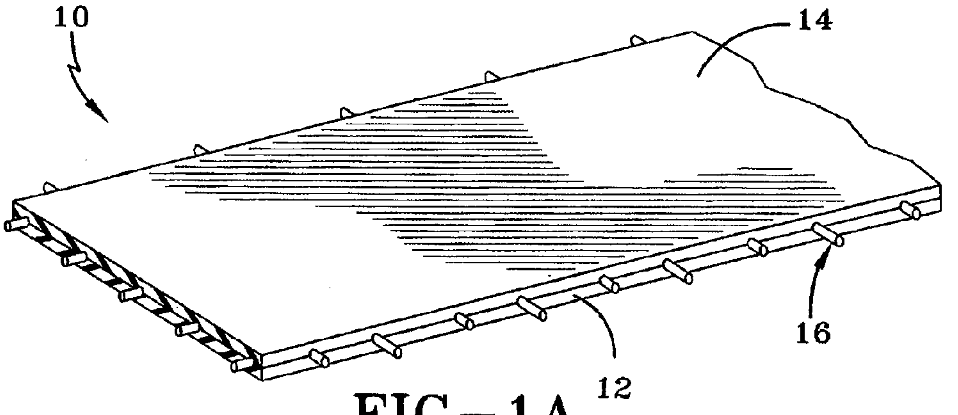


FIG-1A

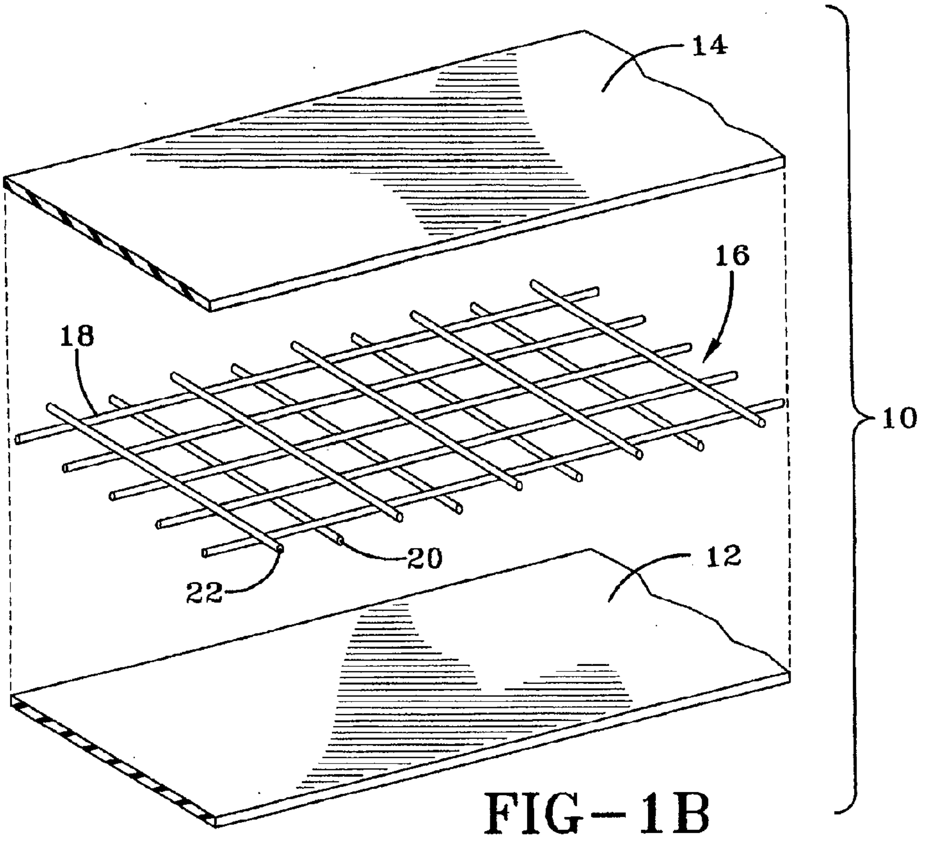


FIG-1B

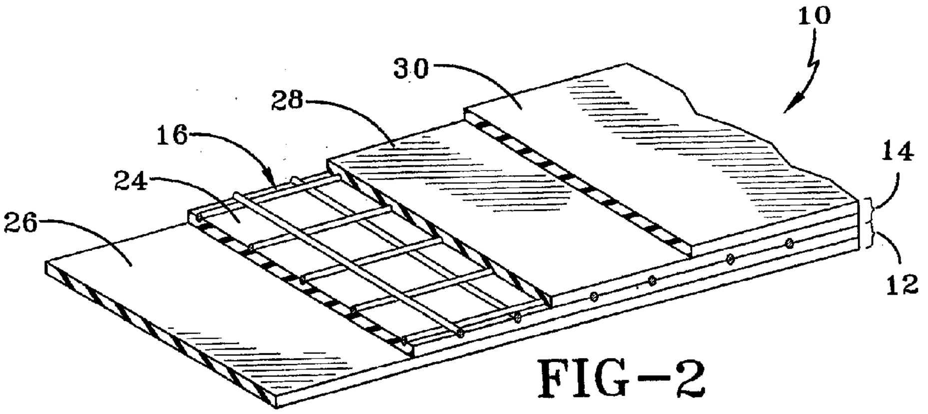


FIG-2

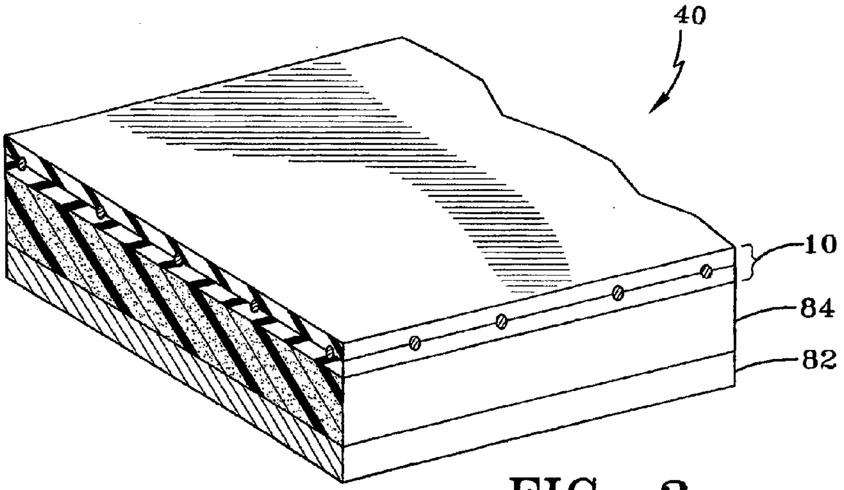
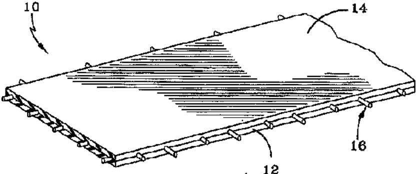


FIG-3



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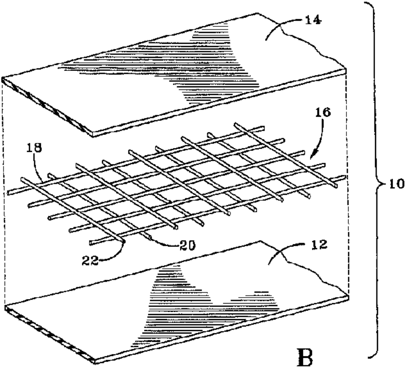

B