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ROOFING MEMBRANES

This invention relates to membranes adapted for the waterproofing and sealing of substrate structures, particularly in roofing applications. More particularly, this invention relates to waterproofing membrane laminates adapted to have improved dimensional stability and to exhibit minimal adverse physical change in their laminar structure under the conditions of high temperature normally encountered in a roof top environment.

Flexible sheet-like laminates of support films and self-adhesive bituminous waterproofing layers pre-formed in the factory have been successfully employed in roofing applications as substitutes for the more conventional waterproofing membranes which are constructed at the job site by plying together one or more layers of bitumen-saturated paper or felt and bituminous adhesives. The pre-formed, self-adhesive laminate-membranes offer many advantages including factory controlled preparation, avoidance of heating equipment and handling of hot materials at the job site, as well as many performance advantages.

Flexible pre-formed laminates of the aforementioned type and their use to form waterproofing layers in various kinds of building structures are described for example in U. S. Patent Nos. 3,741,856; 3,853,682; and 3,900,102 to John Hurst. Such patents describe in particular the preparation of flexible laminates containing a support material, for example a layer of a polymeric or metallic film, and a layer of

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self-adhesive or pressure-sensitive adhesive, bitumen-elastomer waterproofing composition. As discussed in particular in U. S. Patent 3,900,102, such laminates may ideally be constructed in the plant in the form of a roll with a protective sheet, for example siliconized paper applied against the self-adhesive bituminous waterproofing layer, transported to the job site, and thereafter applied to a substrate adhesive side down, each successive laminate strip being made to overlap the edge of the previously applied strip of laminate to insure a continuous waterproofing seal.

10        Copending Application 81 18060  
relates to an improved laminate which employs a thin layer of metal film or foil positioned between and adhered to a polymeric film and a layer of a waterproofing pressure-sensitive adhesive or self-adhesive bituminous composition. These laminates may be viewed as comprising a  
15 "composite" support system, consisting of the polymer film-metal film laminate which carries or supports the adhesive layer. Oriented polymer films, such as those of Canadian Patent No. 1,008,738, are the preferred polymer films for use in these laminates. Such oriented films, which can be biaxially oriented or oriented and cross-laminated films,  
20 exhibit reduced wrinkling following adhesion to a substrate and subsequent exposure to heat, for example, exposure to the sun. The thin metal layer provides increased fire protection; prevents oils in the bituminous composition from contacting the polymer film, with a resultant increase in the physical and chemical stability of the film;  
25 and, since it is rigidly bonded to the film and has a substantially lower coefficient of thermal expansion, provides a relatively high level of

dimensional stability to the laminate under high temperature conditions.

In addition, the relative coefficient of thermal expansion of the film and foil are such that, at elevated temperatures, the edges of the laminate tend to curl downward so as to provide a "self-sealing" effect in

5 overlapping (joint) areas of adjacent, overlapping laminates.

Although the laminates of the aforementioned application, and more specifically the composite support system thereof, provide certain advantages, they can be further improved or optimized for roofing applications. For example, when the laminates are subjected to the

10 relatively high surface temperatures of the black roof environment, e.g.

above 72°C (160°F) the oriented polymer film has been found to

undergo cracking leading to membrane degradation. This adversely

affects the appearance of the membrane, largely eliminates the

protection originally afforded the underlying foil and bituminous

15 adhesive by the polymer film, and increases the possibility of leakage,

particularly at overlap joints between adjacent membranes. In addition,

when subjected to the relatively high temperature conditions of 54°C (130°F)

or greater, the laminates display a marked propensity to reverse any

tendency for downward curl and to instead curl upward at their edges,

20 again increasing the possibility of leakage at overlap joints. Thus, it

has been desired to provide improved waterproofing laminates which

have the aforescribed composite support system and incorporate the

advantages thereof but which do not exhibit cracking or peeling of the

polymer film or upward edge curling upon exposure to high

25 temperatures.

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According to the present invention, there is provided a laminate membrane assembly comprising:

(a) a layer of a shrinkable polymer film having a shrinkage onset temperature above 38°C (100°F);

5 (b) another layer of another material having a lower coefficient of thermal expansion than said polymer film below said shrinkage onset temperature and exhibiting a lesser degree of shrinkage than said polymer film above said shrinkage onset temperature, said other material being  
10 selected from the group consisting of metal foils, polymer sheets, woven scrims, and unwoven scrims, and

(c) a layer of a thermoplastic adhesive positioned between and adhering said film and said other layer, said adhesive having sufficient bonding strength  
15 below said onset temperature to substantially inhibit relative movement between said film and said other layer and having sufficient plasticity above said shrinkage onset temperature to permit relative movement between said film and said other layer.

20 The present invention thus provides waterproofing laminates comprising a polymer film in a composite laminate support system, wherein the polymer film can exhibit a decreased tendency to undergo cracking under conditions of high temperature commonly encountered in a rooftop  
25 environment. The laminates of the present invention can display a high level of dimensional stability under the

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conditions of thermal cycling which can be encountered in roofing applications and tend not to undergo the upward edge curling referred to above.

The present invention also relates to  
5 waterproofed roofing assemblies including such membranes. In particular, the invention provides a waterproofed roofing assembly including a roofdeck substrate having thereon a plurality of membranes each including:-

(a) a layer of a shrinkable polymer film having  
10 a shrinkage onset temperature in the range of about 49°C to 66°C (120 to 150°F),

(b) another layer of another material having a lower coefficient of thermal expansion than said polymer film below said shrinkage onset temperature and exhibiting  
15 a lesser degree of shrinkage than said polymer film at and above said shrinkage onset temperature; said other material being selected from the group consisting of metal foils, polymer sheets, woven scrims, and unwoven scrims, and

(c) a layer of a thermoplastic adhesive  
20 positioned between and coextensive with said film and said foil and adhering said film to said other layer;

said thermoplastic adhesive having sufficient bonding strength below said shrinkage onset temperature to substantially inhibit relative movement between said film  
25 and said other layer such that, with increasing temperature below said shrinkage onset temperature, the thermal

expansion of said film is controlled by its adherence to said other layer; and

5       said thermoplastic adhesive having sufficient plasticity at and above said shrinkage onset temperature to permit relative movement between said film and said other layer such that said film undergoes shrinkage at and above said shrinkage onset temperature without substantial inhibition by its adhesion to said other layer.

10       The invention will be more clearly understood from the following description which is given by way of example only with reference to the accompanying drawing, in which:-

15       Figure 1 is a graphical illustration of a characteristic curve of a thermoplastic adhesive of the present invention showing the dependence of the elasticity of the adhesive on temperature,

      Figure 2 is a partial perspective view of a membrane assembly constructed in accordance with one embodiment of the present invention,

20       Figure 3 is a similar view of a membrane assembly of Figure 2 showing shrinkage of the polymer film under conditions of high temperature.

      The polymeric films generally employed as support materials in roofing laminates normally possess a  
25       relatively high coefficient of thermal expansion, e.g. above  $16.7 \times 10^{-6}$  cm/cm/°C ( $30 \times 10^{-6}$  in/in/°F), such that with increasing temperatures in a rooftop environment these films can undergo excessive expansion. This expansion will generally result in wrinkling or buckling of the film which  
30       can destroy the water-tightness of the applied laminate system, particularly in overlap joint areas between

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adjacent laminates. Thus, it has proven beneficial to treat or prepare the polymer film in a manner which results in the film having a shrinkage capability above a certain temperature ("shrinkage onset

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temperature") in order to effectively counteract the otherwise inherent expansion of the film. Imparting this shrinkage behavior to the film is most preferably accomplished by mechanically stretching the film in both its lengthwise and widthwise direction to provide a biaxial orientation thereto or by cross-laminating uniaxially or biaxially oriented (stretched) films. Processes for preparing oriented (biaxially oriented or cross-laminated) polymer films are well known in the art.

Notwithstanding the shrinkage behavior of the oriented polymer films, below the shrinkage onset temperature these films expand as per their relatively high coefficient of thermal expansion and thus, may provide the aforementioned disadvantages of such expansion. This excessive expansion may be controlled by laminating or coextensively bonding the oriented polymer film to a metal foil having a lower coefficient of thermal expansion than the polymer film, e.g., as disclosed in copending Application 81 18060. To this end, the polymer film and metal foil have heretofore been rigidly bonded by adhesives which largely retain their high level of rigidity over the range of temperatures experienced in the roof environment. Thus, these adhesives, when set, are relatively hard, inflexible materials which retain the respectively bonded film and foil in fixed relation under varying thermal conditions, in keeping with the objective of utilizing the metal foil to control thermal expansion of the polymer film.

In accordance with the present invention, it has been determined that the employment of such adhesives is highly undesirable with regard to maintaining the integrity and dimensional stability of the oriented, shrinkable polymer film and the laminate over extended time in rooftop applications. Specifically, it has been determined that such adhesives

or, more specifically, the fixed lamination of the film to the foil by such adhesives, deleteriously inhibit the shrinkage of the polymer film above the shrinkage onset temperature to the effect that the polymer film, in attempting to relieve internal stresses which would normally be relieved by unhindered shrinkage, undergoes substantial cracking and splitting at its interior areas and curling along its edges.

Further in accordance with the present invention, it has now been found that these problems can be effectively overcome by bonding the polymer film to the foil using certain thermoplastic adhesives. The present invention accordingly provides laminate membrane assemblies comprising a shrinkable polymer film having a shrinkage onset temperature above  $38^{\circ}$  ( $100^{\circ}\text{F}$ ); a foil layer having a lower coefficient of thermal expansion than the polymer film below the shrinkage onset temperature of the polymer film and exhibiting a lesser degree of shrinkage than the polymer film above the shrinkage onset temperature; and a thermoplastic adhesive layer positioned between and adhering the film to the foil, the adhesive having sufficient bonding strength and rigidity below the shrinkage onset temperature to substantially inhibit relative movement between the polymer film and the foil and having sufficient plasticity at and above the shrinkage onset temperature to permit relative movement of the film and the foil.

The maintenance of a relatively rigid bond between the film and the foil below the shrinkage onset temperature provides that the expansion of the laminate below that temperature is controlled primarily as a function of the coefficient of thermal expansion of the foil, i.e., the thermal expansion of the film is controlled by its adherence to the foil and the coefficient of thermal expansion of the laminate assembly is close to that of the foil per se. However, although the thermal

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expansion and movement of the film is substantially inhibited below the shrinkage onset temperature, it need not be, and preferably is not, totally inhibited. The film may expand and move relative to the foil to a minor degree in order to relieve stresses generated by the inherent  
5 tendency of the film to expand. If not relieved, such stresses may result in wrinkling or buckling of the film. This minor relative movement may prove specially desirable at temperatures approaching the shrinkage onset temperature, at or before which the cumulative film expansion is at its greatest level. Accordingly, the thermoplastic  
10 adhesive preferably exhibits a minor level of plasticity even at temperatures below the shrinkage onset temperature. The dimensional stability of the inventive laminates below the shrinkage onset temperature is thus significantly enhanced by coupling the substantial inhibition of the thermal expansion of the polymer film with the  
15 preferred condition of allowance of a minor degree of expansion and movement of the film, particularly at temperatures approaching the shrinkage onset temperature.

At and above shrinkage onset temperature, the thermoplastic adhesive of the present invention softens to permit relative movement  
20 between the film and foil. As used herein, the term "thermoplastic" is to be taken in its usual and ordinary sense, i.e., to refer to the condition or property of softening or fusing when heated and of hardening again when cooled. The thermoplastic adhesives used in the present invention become sufficiently plastic at or slightly below the  
25 shrinkage onset temperature, e.g., about 0.5 to 6°C (1-10°F) below the shrinkage onset temperature to permit relative movement between the film and the foil, i.e. to permit shrinkage onset of the film and to satisfactorily

accommodate the shrinkage of the film at that point.

- Thereafter, as a function of increasing temperature, the adhesives become increasingly plastic, as necessary to satisfactorily accomodate additional shrinkage of the film. Satisfactory accomodation of the
- 5 shrinkage of the polymer film is that which allows the film to shrink at least to a degree sufficient to relieve internal stresses therewithin and, thereby, substantially decrease or eliminate the cracking and splitting of the film and edge curling of the laminate which would otherwise occur. Thus, the relative movement of the film and foil is sufficiently
- 10 uninhibited to permit the film to shrink to the degree necessary to achieve relief of internal stress. Notwithstanding the thermal dependence of the plasticity of the adhesive, however, it should provide sufficient adhesion at all temperatures to which the laminate is exposed to retain the film and foil in adherent, laminated relationship.
- 15 As noted above, at temperatures slightly below the shrinkage onset temperature the thermoplastic adhesive may acquire sufficient plasticity to permit relative movement of the polymer film. In such instances, the polymer film, which still tends to expand at such temperatures, may undergo such expansion without substantial inhibition by the adhesive.
- 20 Although this may be beneficial in permitting the aforementioned desired level of minor expansion and movement of the film below the shrinkage onset temperature, it is nonetheless preferred that the adhesive acquire the necessary plasticity to permit relative movement of the film at a temperature closely approaching or at the shrinkage onset temperature.
- 25 Where the adhesive acquires the necessary plasticity within about  $-12^{\circ}\text{C}$  ( $10^{\circ}\text{F}$ ) of the shrinkage onset temperature, the level of uninhibited expansion of the polymer film is relatively minimal and does not generally adversely affect the dimensional stability of the laminate.

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Any flexible polymer film or sheet which can be treated or coated to provide a shrinkage capability to the film or sheet when heated can be used in the present invention. Biaxially oriented or oriented and cross  
5 -laminated films of such polymers and materials as polyolefins, polyvinylidene chloride polystyrene, polyvinyl chloride, polyethylene terephthalate, polyethylene vinyl acetate copolymer, butadiene-acrylonitrile copolymer, and ethylene-propylene-diene monomer terpolymer may be  
10 employed. Preferred films are biaxially oriented and oriented and cross-laminated polyolefins, especially polyethylene. Oriented and cross-laminated high density polyethylene is an especially preferred film material.

The shrinkage onset temperature of the polymer  
15 film may fall for example within the range of 38°C to 93°C (100 - 200°F). The preferred biaxially oriented and oriented and cross-laminated polyethylenes generally have a shrinkage onset temperature within the range of about 49°C to 66°C (120-150°F). It is preferred to employ polymer  
20 films which shrink about 1% to 3%, i.e. which shrink in a widthwise and lengthwise direction an amount equal to about 1% to 3% of the initial surface area of the polymer film. This level of shrinkage has been found to satisfactorily counteract or compensate for the thermal expansion of most  
25 polymer films while ultimately exhibiting, after shrinkage, satisfactory physical and dimensional stability and a satisfactory

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coverage or surface area of polymer film on the laminate.

The polymer film preferably has a thickness in the range of about  $7.62 \times 10^{-3}$  cm to  $25.4 \times 10^{-3}$  cm (3 to 10 mils). Generally, the laminates of the invention are

5 constructed with the polymer film initially being coextensive with the foil layer and bonded to the foil by the thermoplastic adhesive across its entire length.

The polymer films may contain or be coated with materials designed to prevent degradation, e.g., ultraviolet absorbers.

The adhesive used to bond the polymer film to the foil layer may be any hot melt, organic solvent-based, or water-based adhesive  
 5 exhibiting the desired thermoplastic behavior. Consistent with the aforementioned shrinkage onset temperatures of polymer films used herein, the adhesives most suited for use herein are those which become sufficiently plastic to permit relative movement between the film and foil at temperatures within the range of about 32°C to 93°C (90-200°F).  
 10 a given polymer film, an adhesive may exhibit relatively minor levels of plasticity or "give" below the shrinkage onset temperature and gradually increase in plasticity with increasing temperature. As the shrinkage onset temperature is approached or reached, the increase in plasticity should accelerate to a level permitting relative movement of  
 15 the film and foil.

Thermoplastic adhesives and methods of formulating and preparing some are well known in the art. Thermoplastic adhesives known in the art which can be used herein include those based on ethylene  
 copolymers, propylene copolymers, polyvinylesters, polyamides, EPDM,  
 20 polyvinylacetates, acrylic resins, and mixtures thereof. Preferred adhesives are those based on ethylene copolymers, particularly ethylene-vinyl acetate (EVA) copolymers.

The desired adhesiveness and thermoplastic and viscometric properties may be achieved in the adhesive by various methods known  
 25 in the art. Appropriate mixtures of polymers may be used, as well as modulation of comonomer content and molecular weight in a given base polymer. In addition, known additives such as plasticizers, modifier resins, waxes, processing oils, fillers and thickening agents, may

be used to modulate the thermoplastic and viscometric properties of the adhesive. Anti-oxidants and preservatives may also be included. The utilization of modifiers and additives to adjust the properties of thermoplastic adhesives is well known and, in general, procedures  
5 known in the art may be employed for achieving desired properties.

As one quantitative measure which may be used in determining the suitability of a given adhesive for use in the present invention, one may measure the elastic component of Young's modulus,  $E'$ , as a function of temperature, utilizing procedures known in the art. Such  
10 measurements may be graphically presented as in FIG. 1 wherein the vertical axis represents measurement of  $E'$  in dynes/cm<sup>2</sup> on a logarithmic scale, the horizontal axis shows increasing temperature, and  $T^1$  is the shrinkage onset temperature of the polymer film. In adhesives suitable for use herein,  $E'$  should be relatively constant at  
15 temperatures below  $T^1$ , as depicted by the "plateau" region of the curve of FIG. 1 (although  $E'$  may decrease slightly below  $T^1$ , evidencing the preferred minor degree of increasing plasticity below  $T^1$ ) and, at temperatures at or slightly below  $T^1$ ,  $E'$  should decrease rapidly and thereafter continue to decrease, as depicted by the "break"  
20 in the curve of FIG. 1 at  $T^1$  and the continued downward slope thereafter.

The change in  $E'$  as a function of temperature will generally serve as an indication of changes in the plasticity of the adhesive, with decreasing  $E'$  evidencing increasing plasticity. Suitable values for  $E'$   
25 can vary over a wide range depending on the type of polymeric film or foil which is used.

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Particularly preferred adhesives for use in this invention comprise EVA in a weight percentage range of about 60% to 80% modified with a rosin ester and a picco resin to increase adhesiveness and achieve substantial softening (plasticity) in the range of 49°C to 60°C (120 - 140°F). The ring and ball softening point (ASTM E-28-67) of the particularly preferred adhesives is in the range of 93°C to 121°C (200-250°F), most preferably 104°C to 121°C (220 to 250°C).

10 A relatively thin layer of the thermoplastic adhesive can be used in the inventive laminates. Generally, an adhesive layer of  $1.78 \times 10^{-3}$  cm to  $3.3 \times 10^{-3}$  cm in thickness provides satisfactory adhesion and thermal performance.

15 The material in the other layer, which herein is frequently referred to as a "foil" layer, is selected from the group consisting of metal foils e.g. of aluminium, copper, zinc, etc, polymer sheets, such as polyester sheets; and woven or unwoven scrim materials, which could be, such as  
20 nonwoven and woven polyester scrims, nonwoven and woven glass scrims, and woven polyamide scrims. The thickness of the other layer is normally in the range of about  $0.25 \times 10^{-3}$  cm to  $25.4 \times 10^{-3}$  cm (0.1 to 10 mils).

As indicated previously, the coefficient of  
25 thermal expansion of the other material is lower than that of the polymer film. In addition it is preferred that the

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coefficient of thermal expansion is less than  $13.9 \times 10^{-6}$  cm/cm/ $^{\circ}$ C ( $25 \times 10^{-6}$  in/in/ $^{\circ}$ F). Aluminium foil, with an approximate coefficient of thermal expansion of  $6.67 \times 10^{-6}$  cm/cm/ $^{\circ}$ C ( $12 \times 10^{-6}$  in/in/ $^{\circ}$ F) is the preferred foil

5 material of the invention.

Above the shrinkage onset temperature, the other material should have a lower degree of shrinkage than the polymer film. Depending on the

type of foil layer used, it may simply shrink less than the polymer film, retain an essentially constant dimension or, in most instances, continue to undergo a minor level of expansion, consistent with its relatively low coefficient of thermal expansion.

5 In a preferred embodiment, the laminates of this invention also comprise an adhesive layer adhered to and coextensive with the surface of the foil layer opposite the thermoplastic adhesive layer. Self adhesive or pressure sensitive bituminous waterproofing adhesives are preferred, particularly comprising a mixture of a bituminous material  
10 and a natural or synthetic polymer, preferably a rubber or other elastomeric polymer. The amount of polymer employed in such compositions is typically from about 1 to 100, preferably about 20 to 50, percent by weight of the bituminous material. The term "bituminous adhesive" as used herein includes adhesive compositions  
15 containing asphalt, tar such as coal tar, or pitch. The bituminous adhesive layer may be reinforced with fibers and/or particulate fillers. The adhesive composition may also contain a conventional extender component such as mineral oil. Suitable polymers include thermoplastic polymers such as polyethylene and the like. As aforementioned, the  
20 preferred polymer component is rubber which may be a virgin rubber or reclaimed rubber which is blended into the bitumen at elevated temperature to form a smooth mix. Generally, suitable bituminous adhesive compositions have softening points (measured by the Ring and Ball method) of 70° to 120°C., preferably 75° to 100°C., and  
25 penetration values of 50 to 400, preferably 50 to 100 dmm. at 25C. (150 g/5-ASTM D217).

In order to give optimum sealing and waterproofing performance the adhesive layer should be at least 0.025 cm (0.010 in) thick and preferably in the range of about 0.064 to about 0.508 cm

(0.025 to about 0.200 in) thick. The adhesive layer can be comprised of one or more layers of the aforementioned bituminous adhesive, not necessarily of the same composition, to give an adhesive layer within the overall aforementioned thickness range.

- 5 Further, the adhesive layer can have a reinforcement such as an open weave fabric, gauze, scrim or the like located therein to strengthen it. The bituminous adhesive layer, at least at its surface remote from the foil layer, is preferably pressure-sensitive and tacky at normal ambient temperature in order that it be self-adhesive to a substrate. The
- 10 bituminous adhesive layer serves to form a continuous waterproofing layer which is self-sealing against punctures at high and low temperature. Normally, the adhesiveness of the bituminous adhesive composition is sufficient to provide a satisfactory bond with the foil layer.

- 15 Referring further to the drawings, FIG. 2 is a partial perspective view of a preferred laminate of the present invention. The laminate 10 comprises an uppermost, shrinkable polymer film 11 bonded over its entire surface to a foil layer 13 by thermoplastic adhesive layer 12. A relatively thick layer of a bituminous adhesive composition 14 is bonded
- 20 to foil 13 to provide an adhesive capability to the laminate for facile application to a substrate. To facilitate handling of the laminate prior to application, a release layer (not shown), e.g., siliconized paper, can be mated to the exposed, adhesive surface of layer 14. The release layer is readily removed to expose the adhesive surface of layer 14 just
- 25 prior to application. The use of release layers in this fashion is described, for example, in U. S. Patent No. 3,900,102.

FIG. 3 illustrates the laminate 10 after exposure to temperatures above the shrinkage onset temperature of polymer film 11. Thus, polymer film 11 has smaller widthwise and lengthwise dimensions than in FIG. 2 and adhesive layer 12 has become sufficiently plastic to permit shrinkage to the smaller dimension.

The laminate 10 retains an essentially flat profile through repeated temperature cycling due to its ability to suppress and accomodate expansion of the polymer film and to permit necessary shrinkage of the polymer film.

- 5 In waterproofing applications of the inventive laminates, a plurality of the laminates may be applied to a substrate in side-by-side, abutting fashion or in an overlapping arrangement and sealed at the abutting or overlapping joint, e.g. with a suitable liquid adhesive or adhesive tape. The laminates may be affixed to the substrate by, for example, spot  
10 application of adhesive at the job site or by nailing. A ballasting layer such as gravel may also be used to anchor the laminate on the substrate.

- The preferred laminates of this invention comprising a bituminous adhesive layer adhered to the outer foil surface, e.g., bituminous  
15 adhesive layer 14, are preferably applied to the substrate in overlapping fashion with the adhesive layer down and a marginal portion of the adhesive layer bonded to the facing layer of the underlying (overlapped) laminate to provide a watertight seal. The remainder of the adhesive layer serves to adhere the laminate to the substrate.  
20 While this is the preferred method of application, the laminate may also be applied with the adhesive layer uppermost, e.g., as described in the copending Application 82 11497.

- As an additional component, the laminates may comprise a coating or laminated layer on the surface of the polymer film remote from the  
25 thermoplastic adhesive layer. In particular, white coatings or layers which reflect incident radiation may be used to decrease temperature build up in the laminate and otherwise afford protection thereto. These coatings or layers may be applied at the job site or factory applied.

The laminates of this invention may be fabricated by coating the thermoplastic adhesive in a fluid state, e.g., as a melt or solution, on the polymer film and laminating the foil layer to the coated polymer film while the adhesive is still sufficiently fluid to satisfactorily adhere to the foil. A bituminous adhesive layer may thereafter be applied to the foil by methods well known in the art, followed by application of release paper to the exposed surface of the bituminous adhesive. The laminates are generally stored and shipped in rolls and unrolled and applied at a job site with removal of the release paper, e.g. as illustrated in U. S. Patent No. 3,900,102.

The present invention is further illustrated by the following Example which is intended as illustrative and not limitative.

#### EXAMPLE

A 0.2 mm (8 mil) polyethylene sheet consisting of four cross-laminated biaxially oriented polyethylene plies was coated with an EVA based hot melt thermoplastic adhesive comprising about 70% polyethylene-co-vinyl acetate with a vinyl acetate content of 25%, about 20% of a rosin ester, about 8% of a picco resin, and about 3% wax. The sheet was coated by first melting the adhesive composition and applying the fused composition to the sheet with a roller applicator. Immediately after application of the adhesive, i.e. prior to substantial cooling of the adhesive, the coated sheet was transported into contact with a  $8.89 \times 10^{-4}$  cm (0.35 mil)

aluminium foil sheet having the same width as the polyethylene sheet, and the resultant laminate subjected to sufficient pressure between opposed rolls to provide an adhesive layer thickness of about  $2.54 \times 10^{-3}$  cm (1 mil).

- 5 One of the opposed pressurizing rolls was chilled to provide a rapid set of the adhesive after compression.

The adhesive utilized in this Example had a ring and ball softening point of about  $104^{\circ}\text{C}$  ( $220^{\circ}\text{F}$  (ASTM-E 28-67)), a density of about 0.975 gm/cc (ASTM-1475), a  
10 tensile strength of about  $4.3 \times 10^6$  Dyne/cm<sup>2</sup> ( $62.9 \text{ lb/in}^2$ ) (ASTM D-638-68) and elongation of about 995% (ASTM-D0638-68).

The polymer film was measured to have coefficient of thermal expansion of about  $37.8 \times 10^{-6}$  cm/cm/ $^{\circ}\text{C}$  ( $68 \times 10^{-6}$  in/in/ $^{\circ}\text{F}$ ) while that of the aluminium foil was  
15 measured as about  $7.8 \times 10^{-6}$  cm/cm/ $^{\circ}\text{C}$  ( $14 \times 10^{-6}$  in/in/ $^{\circ}\text{F}$ ). The shrinkage onset temperature of the polymer film was about  $57^{\circ}\text{C}$  ( $135^{\circ}\text{F}$ ).

A waterproofing bituminous adhesive consisting of

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asphalt, styrene-butadiene rubber, and oil was then applied to the exposed surface of the aluminium foil to complete the assembly. The bituminous adhesive layer was about 0.1 cm (42 mils) in thickness.

5               For purposes of comparison, a "control" laminate similar to the above was prepared utilizing in place of the thermoplastic adhesive an ethylene-acrylic acid copolymer based laminating adhesive sold by the Dow Chemical Co as "Dow 435". This adhesive had a melting point above 260°C  
10 (500°F) and did not exhibit significant plasticity below 121°C (250°F).

The respective laminates were adhered to a substrate and subjected to repeated thermal cycling over a temperature range of -32°C (-25°F) to 104°C (220°F). The  
15 inventive laminate maintained a flat profile on the substrate without buckling or edge curling. The polymer film of the inventive laminate retained a smooth, flat appearance and, by visual examination, did not crack or peel. Over the same period of time (about 6 days; 12  
20 thermal cycles) the control laminate curled and buckled and the polyethylene film underwent substantial cracking.

In a separate test, the respective adhered laminates were subjected to respective temperatures of 82°C (180°F), 72°C (160°F) and 49°C (120°F) for extended periods  
25 of time. After 21 days at 82°C (180°F) the polyethylene film of the control laminate was cracked and wrinkled.

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Similar results were observed after 50 days at 72°C (160°F). After one week at 49°C (120°F), the control laminate was curled and buckled. In contrast, after similar periods of time at the respective temperatures, the  
5 inventive laminate retained its smooth, flat profile on the substrate and no cracking of the polyethylene film was observed.

C L A I M S

1. A laminate membrane assembly comprising:

(a) a layer of a shrinkable polymer film having a shrinkage onset temperature above 38°C (100°F);

(b) another layer of another material having a lower coefficient of thermal expansion than said polymer film below said shrinkage onset temperature and exhibiting a lesser degree of shrinkage than said polymer film above said shrinkage onset temperature, said other material being selected from the group consisting of metal foils, polymer sheets, woven scrims, and unwoven scrims, and

(c) a layer of a thermoplastic adhesive positioned between and adhering said film and said other layer, said adhesive having sufficient bonding strength below said onset temperature to substantially inhibit relative movement between said film and said other layer and having sufficient plasticity above said shrinkage onset temperature to permit relative movement between said film and said other layer.

2. A membrane according to claim 1 further comprising an adhesive layer adhered to the surface of said other layer opposite said layer of a thermoplastic adhesive.

3. A membrane according to claim 2 wherein said adhesive layer comprises a bituminous adhesive composition.

4. A membrane according to claim 1, 2 or 3



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wherein said polymer film is biaxially oriented or oriented and cross-laminated.

5. A membrane according to claim 4 wherein said polymer film is a polyethylene film.

5 6. A membrane according to claim 5 wherein said polyethylene film is a high density polyethylene film.

7. A membrane according to any preceding claim wherein said thermoplastic adhesive is an ethylene-vinyl acetate copolymer based adhesive.

10 8. A membrane according to any preceding claim wherein said thermoplastic adhesive acquires said plasticity at a temperature within the range of about 32°C to 93°C (90 to 200°F).

15 9. A membrane according to claim 8 wherein said thermoplastic adhesive contains one or more modifying resins.

20 10. A membrane according to any preceding claim wherein said other layer has a coefficient of thermal expansion of less than  $13.9 \times 10^{-6}$  cm/cm/°C ( $25 \times 10^{-6}$  in/in/°F).

11. A membrane according to any preceding claim wherein said polymer film is capable of undergoing about 1% to about 3% shrinkage.

25 12. A membrane of claim 11 wherein said other layer is aluminium foil.

13. A membrane according to any preceding claim



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wherein the polymer film has a shrinkage onset temperature in the range of 49°C to 66°C (120 to 150°F).

14. A membrane according to claim 1 and substantially as hereinbefore described with or without  
5 reference to the accompanying drawings.

15. A membrane according to claim 1 substantially as described in the Example herein.

16. A waterproofed roofing assembly including a roofdeck substrate having thereon a plurality of membranes  
10 according to any preceding claim.

17. A waterproofed roofing assembly including a roofdeck substrate having thereon a plurality of membranes each including:-

(a) a layer of a shrinkable polymer film having  
15 a shrinkage onset temperature in the range of about 49°C to 66°C (120 to 150°F),

(b) another layer of another material having a lower coefficient of thermal expansion than said polymer film below said shrinkage onset temperature and exhibiting  
20 a lesser degree of shrinkage than said polymer film at and above said shrinkage onset temperature; said other material being selected from the group consisting of metal foils, polymer sheets, woven scrims, and unwoven scrims, and

(c) a layer of a thermoplastic adhesive  
25 positioned between and coextensive with said film and said foil and adhering said film to said other layer;



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said thermoplastic adhesive having sufficient bonding strength below said shrinkage onset temperature to substantially inhibit relative movement between said film and said other layer such that, with increasing temperature  
5 below said shrinkage onset temperature, the thermal expansion of said film is controlled by its adherence to said other layer; and

said thermoplastic adhesive having sufficient plasticity at and above said shrinkage onset temperature to  
10 permit relative movement between said film and said other layer such that said film undergoes shrinkage at and above said shrinkage onset temperature without substantial inhibition by its adhesion to said other layer.

18. An assembly according to claim 16 or 17  
15 wherein said membranes are disposed in overlapping fashion.

19. An assembly according to claim 18 wherein said membranes further comprise a bituminous adhesive layer adhered to that surface of said other layer remote from said layer of a thermoplastic adhesive, a marginal portion  
20 of respective bituminous adhesive layers being bonded to the facing layers of respective adjacent membranes to form waterproof overlap joints.

20. An assembly according to claim 19 wherein said membranes are disposed with the respective bituminous  
25 adhesive layers facing said substrate and adhering said membranes to said substrate.



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21. An waterproofed assembly according to claim  
16 or 17 and substantially as hereinbefore described.

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