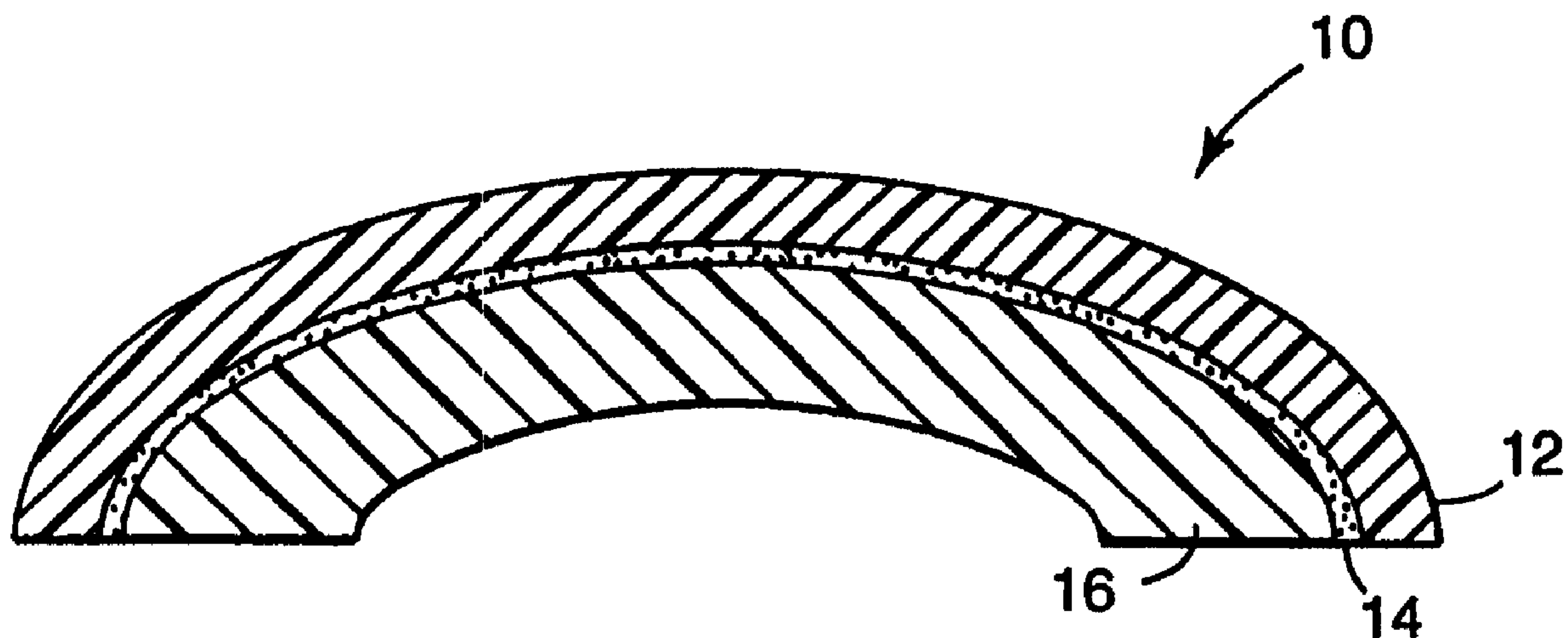




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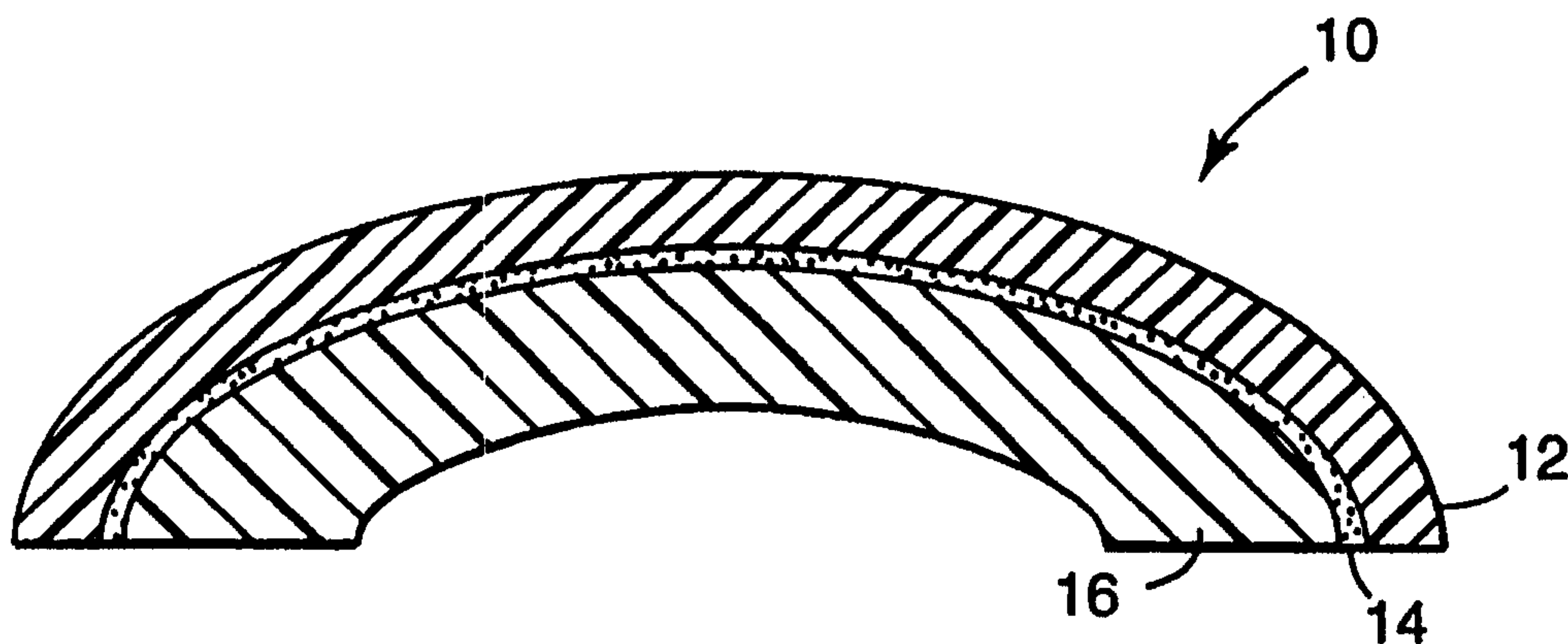
An article comprising (a) a curved substrate having a surface energy below 45 dynes/cm²; (b) flexible retroreflective sheeting; and (c) a crosslinked tackified pressure-sensitive adhesive adhering the sheeting to the curved substrate. The adhesive comprises: (i) from about 65 to about 99 parts by weight of at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, and mixtures thereof, the alkyl group of which comprises from about 4 to about 12 carbon atoms, which as a homopolymer has a glass transition temperature less than -25 °C; (ii) from about 1 to about 10 part(s) by weight of a polar monomer copolymerizable with the monomer(s) of component (i); (iii) optionally from 0 to about 25 parts by weight of a non-polar ethylenically unsaturated monomer copolymerizable with components (i) and (ii) selected from the group consisting of alkyl acrylates, N-alkyl acrylamides, and combinations thereof, whose homopolymer has a solubility parameter of no greater than 10.50 and a T_g greater than 15 °C; (iv) from about 1 to about 65 parts by weight of a tackifier based upon the total weight of components (i), (ii), and (iii); and (v) optionally from 0 to about 1 part by weight of a crosslinking agent based upon the total weight of components (i), (ii), and (iii). Another embodiment of the present invention is a method of making the articles of the present invention using bulk UV polymerization.



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(54) Title: ARTICLE COMPRISING A FLEXIBLE RETROREFLECTIVE SHEETING**(57) Abstract**

An article comprising (a) a curved substrate having a surface energy below 45 dynes/cm²; (b) flexible retroreflective sheeting; and (c) a crosslinked tackified pressure-sensitive adhesive adhering the sheeting to the curved substrate. The adhesive comprises: (i) from about 65 to about 99 parts by weight of at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, and mixtures thereof, the alkyl group of which comprises from about 4 to about 12 carbon atoms, which as a homopolymer has a glass transition temperature less than -25 °C; (ii) from about 1 to about 10 part(s) by weight of a polar monomer copolymerizable with the monomer(s) of component (i); (iii) optionally from 0 to about 25 parts by weight of a non-polar ethylenically unsaturated monomer copolymerizable with components (i) and (ii) selected from the group consisting of alkyl acrylates, N-alkyl acrylamides, and combinations thereof, whose homopolymer has a solubility parameter of no greater than 10.50 and a T_g greater than 15 °C; (iv) from about 1 to about 65 parts by weight of a tackifier based upon the total weight of components (i), (ii), and (iii); and (v) optionally from 0 to about 1 part by weight of a crosslinking agent based upon the total weight of components (i), (ii), and (iii). Another embodiment of the present invention is a method of making the articles of the present invention using bulk UV polymerization.

ARTICLE COMPRISING A FLEXIBLE RETROREFLECTIVE SHEETING

Field of Invention

5 This invention relates to retroreflective articles comprising a curved low surface energy substrate, flexible retroreflective sheeting, and a layer of pressure-sensitive adhesive. More particularly, this invention relates to crosslinked tackified acrylic adhesives having good low temperature properties particularly suitable for adhesion to curved substrates having low surface energy.

10

Background

 Retroreflective materials have the property of redirecting incident light back towards its originating source. This advantageous property has led to the wide-spread use of retroreflective sheeting on a variety of articles. Very often
15 retroreflective sheeting is used on flat inflexible articles, for example, road signs and barricades. However, situations frequently arise which require sheeting to be used on irregular or curved surfaces. For example, retroreflective sheeting may be adhered to irregular surfaces of traffic control devices, such as traffic cones, poles, barrels (drums), tubes, or nose cones or to vehicle bumpers or mud flaps, which
20 requires the sheeting to adhere to a curved surface of varying circumference. In situations where the underlying surface is irregular or curved, the retroreflective sheeting desirably possesses good conformability and flexibility without sacrificing retroreflective performance.

 There may also be situations where the underlying substrate expands and
25 contracts at a different rate than the retroreflective sheeting. For example, for a temperature drop of 40°C (104°F), a traffic control device such as a low density polyethylene barrel would contract by about 0.80%, based on a coefficient of linear thermal expansion of 200×10^{-6} (m/mK) at 20°C. For the same temperature change, a retroreflective sheeting with a polycarbonate layer would contract by
30 only about 0.23%, based on a coefficient of linear thermal expansion of 57×10^{-6} (m/mK) at 20°C. Thus, the barrel contracts almost 3.5 times more than the retroreflective sheeting. Because the retroreflective sheeting is wrapped outside

of the barrel, conventional sheetings may wrinkle and lift off the barrel in response to the temperature change. In these situations, the retroreflective sheeting preferably accommodates the differences in thermal expansion and contraction without compromising retroreflectivity and without lifting off the substrate.

5 Further, the adhesive between the sheeting and the barrel preferably accommodates these differences in thermal expansion and contraction.

Traffic control devices and vehicle parts often have low energy irregular or curved surfaces. In addition, these substrates are subject to weathering, temperature fluctuations, and impact from vehicles. Preferably, both the
10 retroreflective sheeting and the adhesive used to secure the sheeting to these substrates perform well despite these constraints.

The two common types of retroreflective sheeting are microsphere-based sheeting and cube-corner sheeting.

Microsphere-based sheeting, sometimes referred to as "beaded" sheeting,
15 is well known in the art and employs a multitude of microspheres, typically at least partially embedded in a binder layer and having associated specular or diffuse reflecting materials (e.g., pigment particles, metal flakes or vapor coats, etc.) to retroreflect incident light. The microspheres are separate from each other and therefore do not severely hinder the sheeting's ability to be flexed. Illustrative
20 examples of such retroreflectors are disclosed in U.S. Patent Nos. 3,190,178 (McKenzie), 4,025,159 (McGrath), and 5,066,098 (Kult).

Cube-corner sheeting typically uses a multitude of rigid interconnected cube-corner elements to retroreflect incident light. Many types of flexible cube-corner sheeting are known in the art. See for example U.S. Patent No. 3,992,080
25 (Rowland), U.S. Patent No. 4,576,850 (Martens), or U.S. Patent No. 5,450,235 (Smith et al.).

A substantial number of pressure-sensitive adhesives (PSAs) are known in the art which have good adhesion to low energy substrates and include, but are not limited to, rubber-based adhesives, tackified KRATONS™, non-polar
30 acrylates, tackified acrylics, and polyalphaolefins.

However, not all of these adhesives perform satisfactorily on curved substrates (particularly those substrates which experience expansion and contraction), at low temperatures, after exposure to chemicals and other roadway contaminants, and have adequate weathering resistance.

5 Delamination, buckling, and even pop-off of the flexible sheeting often occur because of adhesive failure. Thus, an article having an adhesive which performs suitably despite these constraints would be advantageous.

Summary of the Invention

10 The present invention provides retroreflective articles comprising a curved substrate having a low energy surface, flexible cube-corner sheeting, and a layer of pressure-sensitive adhesive, and a method for making such articles.

 The article of the present invention comprises (a) a curved substrate having a surface energy below 45 dynes/cm²; (b) flexible retroreflective sheeting;
15 and (c) a crosslinked tackified pressure-sensitive adhesive adhering the sheeting to the curved substrate. The adhesive comprises: (i) from about 65 to about 99 parts by weight of at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, and mixtures thereof, the alkyl group of which comprises from about 4 to about
20 12 carbon atoms, which as a homopolymer has a glass transition temperature less than -25°C; (ii) from about 1 to about 10 part(s) by weight of a polar monomer copolymerizable with the monomer(s) of component (i); (iii) optionally from 0 to about 25 parts by weight of a non-polar ethylenically unsaturated monomer copolymerizable with components (i) and (ii) selected from the group consisting of
25 alkyl acrylates, N-alkyl acrylamides, and combinations thereof, whose homopolymer has a solubility parameter of no greater than 10.50 and a T_g greater than 15°C; (iv) from about 1 to about 65 parts by weight of a tackifier based upon the total weight of components (i), (ii), and (iii); and (v) optionally from 0 to
30 about 1 part by weight of a crosslinking agent based upon the total weight of components (i), (ii), and (iii).

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Curved substrates include, but are not limited to, a traffic post (having a radius of curvature of about 0.025 meters (1 inch)), a barrel (having a radius of curvature of about 0.23 meters (9 inches)), a nose cone
5 (having a radius of curvature of about 0.91 meter (3 feet)) and a railroad car (having a radius of curvature of about 1.5 meters (5 feet)). Curvature is the magnitude of the rate of change of the direction of the curve with respect to arc length. The radius of curvature at a point is the
10 reciprocal of the curvature at that point. (See Calculus and Analytical Geometry, Thomas, 4th ed., Addison Wesley). The curved substrates of the present invention may have more than one radius of curvature. For example, the radius of curvature of a traffic cone varies with direction.
15 Preferably, the curved substrates of the present invention have a radius of curvature ranging from about 2.5 cm (1 inch) to about 1.5 meters (5 feet).

The flexible sheeting may be either microsphere-based or cube-corner type and is preferably sufficiently
20 flexible and conformable to be conformed to the surface of the substrate.

Another embodiment of the present invention is a method of making the articles of the present invention using bulk UV polymerization.

25 According to one aspect of the present invention, there is provided an article comprising: (a) a curved substrate having a surface energy below 45 dynes/cm²; (b) flexible retroreflective sheeting; and (c) a crosslinked tackified pressure-sensitive adhesive adhering said sheeting
30 to said substrate, said adhesive comprising the reaction

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product of: (i) from about 65 to about 99 parts by weight of at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, and mixtures thereof, the alkyl group of which comprises from 4 to 12 carbon atoms, which as a homopolymer has a glass transition temperature less than -25°C ; (ii) from about 1 to about 10 part(s) by weight of a polar monomer copolymerizable with the monomer(s) of component (i); (iii) optionally from 0 to about 25 parts by weight of a non-polar ethylenically unsaturated monomer copolymerizable with components (i) and (ii) selected from the group consisting of alkyl acrylates, N-alkyl acrylamides, and combinations thereof, whose homopolymer has a solubility parameter of no greater than 10.50 and a T_g greater than 15°C ; (iv) from about 1 to about 65 parts by weight of a tackifier based upon the total weight of components (i), (ii), and (iii); and (v) optionally from 0 to about 1 part by weight of a crosslinking agent based upon the total weight of components (i), (ii) and (iii).

According to another aspect of the present invention, there is provided a method of bonding a crosslinked tackified acrylic adhesive to a curved substrate having low surface energy, the method comprising the steps of: (a) filling a vessel with a precursor comprising 100 parts by weight of components (i), (ii), (iii), (vi), and optionally (v), wherein the precursor comprises: (i) from about 65 to about 99 parts by weight of at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, and mixtures thereof, the alkyl group of which comprises from 4 to 12 carbon atoms, which as a homopolymer has a glass transition temperature less

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than -25°C ; (ii) from about 1 to about 10 part(s) by weight of a polar monomer that is solution copolymerizable with the monomer(s) of component (i); (iii) optionally from 0 to about 25 parts by weight of a non-polar ethylenically unsaturated monomer copolymerizable with components (i) and (ii) selected from the group consisting of alkyl acrylates, N-alkyl acrylamides, and combinations thereof, whose homopolymer has a solubility parameter of no greater than 10.50 and a T_g greater than 15°C ; (iv) optionally from 0 to about 1 part by weight of a crosslinking agent based upon the total weight of components (i), (ii), and (iii); and (v) from about 0.01 to about 1 parts by weight of a photoinitiator based upon the total weight of components (i), (ii), and (iii); (b) exposing said vessel filled with said precursor to low intensity ultraviolet radiation yielding a hot melt coatable adhesive; (c) adding from about 1 to about 65 parts by weight of a tackifier based upon the total weight of components (i), (ii), and (iii) and melt mixing said tackifier with said hot melt coatable adhesive in an extruder wherein the vessel is physically dispersed yielding a compounded tackified hot melt coatable adhesive; (d) extruding said compounded tackified hot melt coatable adhesive onto a liner; (e) exposing said compounded tackified hot melt coatable adhesive to radiation yielding a crosslinked adhesive; (f) applying said crosslinked adhesive to either a curved low energy surface or a retroreflective sheeting; and (g) joining the retroreflective sheeting to the curved low energy surface, said crosslinked adhesive disposed between the retroreflective sheeting and the curved low energy surface.

Brief Description of the Drawings

Fig. 1 is a cross-sectional view (enlarged) of an illustrative article of the present invention, comprising

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retroreflective sheeting (12) adhered to a curved low surface energy substrate (16) with a pressure-sensitive adhesive layer (14).

5 This figure is not to scale and is intended to be merely illustrative and non-limiting.

Detailed Description of Illustrative Embodiments

The present invention provides an article comprising flexible retroreflective sheeting, a curved polymeric low energy substrate, and an adhesive for adhering
10 this flexible sheeting to the substrate.

The adhesive of the present invention provides good adhesion between the sheeting and the substrate even though the flexible sheeting may have a "stiff" backing and the substrate has a curved and a low energy surface.
15 Further, the

article of the present invention comprises an adhesive which preferably accommodates thermal expansion and contraction, resists severe weathering, resists impact from vehicles, and has good low temperature applicability and performance. Not all adhesives which have good performance on low energy
5 surfaces under some laboratory conditions (e.g., rubber-based adhesives, tackified KRATONS™, polyalphaolefin-based adhesives, non-polar acrylate-based adhesives, tackified acrylic adhesives, etc.) can meet these criteria.

The curved nature of the substrate requires an adhesive having high shear strength. High shear strength may be obtained from polar monomer interaction,
10 crosslinking, or a combination thereof. Stiffer sheeting also may affect the shear requirement on a curved substrate. The flexible sheeting of the present invention may have a relatively stiff backing. For example, the seal or backing layer may comprise polycarbonate, polymethylmethacrylate, or poly(ethylene terephthalate).

The articles of the present invention may have either concave or convex
15 substrates.

The sheeting may be overlapped, be spliced so that the edges meet, or be placed so that the edges do not contact one another. More than one piece of sheeting may be adhered to the substrate. Regardless of the sheeting placement, the differential in the coefficient of thermal expansion between the sheeting and
20 the substrate remains an important factor.

The substrate has a low energy surface and therefore a low bonding modulus is desirable. A low energy surface is defined herein as a surface which exhibits low polarity and low critical surface tension (less than about 45 dynes /cm², preferably less than 40 dynes / cm²).

25 Tackifiers and plasticizers are commonly added to adhesives to improve wetting at the surface. For example, a compatible and stable tackifier such as a rosin ester, a terpene phenolic resin, or a hydrocarbon resin may be incorporated into the adhesive. Although the use of a tackifier dramatically improves the tack at room temperature as well as the bond strength as measured by peel force at low
30 speeds (i.e., 0.3 meters/minute (12 inches per minute)), inclusion of these tackifiers raises the glass transition temperature (T_g) of the PSA reducing low

temperature performance and low temperature applicability. Plasticizers tend to improve bonding, but decrease peel strength.

Additionally, loss of adhesive shear strength and of cohesive strength is also observed if large amounts of tackifier or plasticizer are incorporated into the PSA. Moreover, some tackifiers can adversely affect the weathering properties of an adhesive.

Good low temperature applicability and performance are desirable for the adhesives useful in the present invention. The PSAs preferably may be applied to curved substrates at temperatures ranging down to about -1 to 4°C (30 to 40°F). Higher levels of polar monomer adversely affect low temperature performance (e.g., impact and tack). Preferably, the adhesives of the present invention have good cold impact down to at least about -7 to -1°C (20 to 30°F), more preferably down to at least about -17°C (0°F). Cold impact performance was evaluated by impacting the articles of the present invention with a vehicle traveling at 88.5 km/hr (55 mph) at the desired temperature.

The glass transition temperature (T_g) of the adhesives useful in the present invention is typically within the range of about 0°C to about -40°C, preferably within about -15°C to about -30°C as measured by DMA (dynamic mechanical analysis). T_g values in these preferred ranges allow the adhesive to possess good peel strength and have good low temperature properties.

The articles of the present invention are subject to harsh weather conditions such as temperature extremes, atmospheric pollutants, road salt, and infrared, visible, and ultraviolet light. Acrylic PSAs exhibit excellent outdoor durability, whereas rubber-based PSAs show poor ultraviolet and oxidative stability due to chemical unsaturation of the hydrocarbon elastomer.

The crosslinked tackified acrylic adhesives of the present invention surprisingly meet all of these criteria, whereas the other adhesives which typically perform well on low energy surfaces are deficient in one or more areas.

Pressure-Sensitive Adhesives

An adhesive is used to adhere the flexible sheeting to the curved substrate having low surface energy. Adhesives useful in this invention are pressure-sensitive. Typically, for cube-corner sheeting, an adhesive is laminated to one side of the sealing member. For microsphere-based sheeting, the adhesive is laminated to one side of the backing.

The adhesives of the present invention preferably have good adhesion to the curved polymeric low surface energy substrate, weatherability, and low temperature performance and applicability.

The adhesives of the present invention are crosslinked tackified acrylic pressure-sensitive adhesives.

Acrylic Acid and Meth(acrylic) Acid Esters

The acrylic copolymers useful in the adhesive of the invention preferably are present at ranges of from about 65 to about 99 parts by weight, preferably about 78 to about 98 parts by weight, and more preferably about 95 to about 98 parts by weight. Useful acrylic copolymers include at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, the alkyl group of which comprises from 4 to about 12 carbon atoms, and mixtures thereof. Such acrylates or methacrylate esters generally have, as homopolymers, glass transition temperatures below about -25°C. Higher amounts of this monomer relative to the other comonomers affords the PSA higher tack at low temperatures.

Preferred acrylate or methacrylate ester monomers include, but are not limited to, those selected from the group consisting of n-butyl acrylate (BA), n-butyl methacrylate, isobutyl acrylate, 2-methyl butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, isooctyl acrylate (IOA), isooctyl methacrylate, isononyl acrylate, isodecyl acrylate, and mixtures thereof.

Particularly preferred acrylates include those selected from the group consisting of isooctyl acrylate, n-butyl acrylate, 2-methyl butyl acrylate, 2-ethylhexyl acrylate, and mixtures thereof.

Polar Monomers

Low levels of (typically about 1 to about 10 parts by weight, preferably from about 2 to about 7 parts by weight, and more preferably about 2 to about 5 parts by weight) of a polar monomer such as a carboxylic acid can be used to increase the cohesive strength of the pressure-sensitive adhesive. At higher levels, these polar monomers tend to diminish the tack and decrease low temperature performance.

Useful copolymerizable acidic monomers include, but are not limited to, those selected from the group consisting of ethylenically unsaturated carboxylic acids, ethylenically unsaturated sulfonic acids, and ethylenically unsaturated phosphoric acids. Examples of such compounds include those selected from the group consisting of acrylic acid (AA), methacrylic acid, itaconic acid, fumaric acid, crotonic acid, citraconic acid, maleic acid, β -carboxyethyl acrylate, sulfoethyl methacrylate, and the like, and mixtures thereof.

Other useful copolymerizable monomers include, but are not limited to, acrylamides, N,N-dialkyl substituted acrylamides, N-vinyl lactams, and N,N-dialkylaminoalkyl acrylates. Illustrative examples include, but are not limited to, those selected from the group consisting of N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, N,N-diethyl acrylamide, N,N-diethyl methacrylamide, N,N-dimethylaminoethyl methacrylate, N,N-dimethylaminopropyl methacrylate, N,N-dimethylaminoethyl acrylate, N,N-dimethylaminopropyl acrylate, N-vinyl pyrrolidone, N-vinyl caprolactam, and the like, and mixtures thereof.

Non-polar Ethylenically Unsaturated Monomers

The non-polar ethylenically unsaturated monomer is a monomer whose homopolymer has a solubility parameter as measured by the Fedors method (see Polymer Handbook, Bandrup and Immergut) of not greater than 10.50 and a Tg greater than 15°C. The non-polar nature of this monomer tends to improve the low energy surface adhesion of the adhesive. These non-polar ethylenically unsaturated monomers are selected from the group consisting of alkyl acrylates,

N-alkyl acrylamides, and combinations thereof. Illustrative examples include, but are not limited to, 3,3,5-trimethylcyclohexyl acrylate, cyclohexyl acrylate, isobornyl acrylate, N-octyl acrylamide, or combinations thereof.

Optionally, from 0 to 25 parts by weight of a non-polar ethylenically unsaturated monomer may be added.

Tackifiers

To obtain high bonding characteristics to low energy surfaces, the most commonly used tackifiers in acrylic pressure-sensitive adhesives include terpene phenolics, rosins, rosin esters, esters of hydrogenated rosins, synthetic hydrocarbon resins and combinations thereof.

Hydrogenated rosin esters and hydrogenated C₉ aromatic resins are the preferred tackifiers because of performance advantages which include: high levels of "tack", outdoor durability, oxidation resistance, and limited interference in post crosslinking of acrylic PSAs.

Tackifiers may be added at a level of about 1 to about 65 parts per 100 parts of the monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, the polar monomer, and the nonpolar ethylenically unsaturated monomer to achieve desired "tack". However, tackifiers typically are added at a level of about 1 to about 50 parts per 100 parts of the monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, the polar monomer, and the nonpolar ethylenically unsaturated monomer. Preferably, about 15 to about 50 parts of tackifier are added based on 100 parts of the monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, the polar monomer, and the nonpolar ethylenically unsaturated monomer. However, the addition of tackifiers can reduce shear or cohesive strength and raise the T_g of the acrylic PSA which is undesirable for cold temperature performance.

Crosslinkers

In order to increase the shear or cohesive strength of acrylic pressure-sensitive adhesives, a crosslinking additive is usually incorporated into the PSA.

Two main types of crosslinking additives are commonly used. The first crosslinking additive is a thermal crosslinking additive such as a multifunctional aziridine. One example is 1,1'-(1,3-phenylene dicarbonyl)-bis-(2-methylaziridine) (CAS No. 7652-64-4), referred to herein as "Bisamide". Such chemical

5 crosslinkers can be added into solvent-based PSAs after polymerization and activated by heat during oven drying of the coated adhesive.

In another embodiment, chemical crosslinkers which rely upon free radicals to carry out the crosslinking reaction may be employed. Reagents such as, for example, peroxides serve as a source of free radicals. When heated sufficiently,

10 these precursors will generate free radicals which bring about a crosslinking reaction of the polymer. A common free radical generating reagent is benzoyl peroxide. Free radical generators are required only in small quantities, but generally require higher temperatures to complete the crosslinking reaction than those required for the bisamide reagent.

15 The second type of chemical crosslinker is a photosensitive crosslinker which is activated by high intensity ultraviolet (UV) light. Two common photosensitive crosslinkers used for hot melt acrylic PSAs are benzophenone and 4-acryloxybenzophenone which is copolymerized into the PSA polymer. Another photocrosslinker, which can be post-added to the solution polymer and activated

20 by UV light is a triazine; for example 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine. These crosslinkers are activated by UV light generated from artificial sources such as medium pressure mercury lamps or a UV blacklight.

Hydrolyzable, free-radically copolymerizable crosslinkers, such as monoethylenically unsaturated mono-, di- and trialkoxy silane compounds

25 including, but not limited to, methacryloxypropyltrimethoxysilane (sold under the tradename "Silane A-174" by Union Carbide Chemicals and Plastics Co.), vinyl dimethylethoxysilane, vinylmethyldiethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane, vinyltriphenoxysilane, and the like are also useful crosslinking agents.

Crosslinker is typically present from 0 to about 1 part by weight based on 100 parts by weight of acrylic acid or meth(acrylic) acid esters, polar monomers, and non-polar ethylenically unsaturated monomers.

5 Aside from thermal, moisture, or photosensitive crosslinkers, crosslinking may also be achieved using high energy electromagnetic radiation such as gamma or e-beam radiation. In this case, no crosslinker may be required (i.e., component (v)).

Other additives

10 Because acrylic pressure-sensitive adhesives have excellent oxidative stability, additives such as antioxidant and UV light absorbers are generally not needed.

Small amounts of heat stabilizer can be utilized in hot melt acrylic PSAs to increase thermal stability during processing.

15

Plasticizers

Optionally, low levels of plasticizer (i.e., less than 10 parts by weight) may be combined with tackifier to adjust the T_g in order to optimize the peel and the low temperature performance of the adhesive. Plasticizers which may be added to
20 the adhesive of the invention may be selected from a wide variety of commercially available materials. In each case, the added plasticizer must be compatible with the tackified acrylic PSA being used in the formulation. Representative plasticizers include polyoxyethylene aryl ether, dialkyl adipate, 2-ethylhexyl diphenyl phosphate, t-butylphenyl diphenyl phosphate, di(2-ethylhexyl) adipate,
25 toluenesulfonamide, dipropylene glycol dibenzoate, polyethylene glycol dibenzoate, polyoxypropylene aryl ether, dibutoxyethoxyethyl formal, and dibutoxyethoxyethyl adipate.

Polymerization Methods

30 Adhesives useful in this invention can be polymerized by conventional free-radical polymerization methods.

For example, components (i), (ii), (iii), and optionally (iv) and (v), may be charged into a four-neck reaction vessel which is equipped with a stirrer, a thermometer, a condenser, addition funnel and a thermowatch. Then, a concentrated thermal free-radical initiator solution is added to the addition funnel.

- 5 The whole reaction vessel and addition funnel and their contents are then purged with nitrogen to create an inert atmosphere. Once purged, the solution within the vessel is heated to the activation temperature of the initiator, the initiator is added from the funnel, and the mixture is stirred during the course of the reaction.

- Another polymerization method is a two step ultraviolet (UV) radiation
10 initiated polymerization of a 100% solids monomer mixture. First, the low viscosity monomers are mixed at the appropriate ratios and a photoinitiator is added to the mixture. The mixture is purged with nitrogen to remove dissolved oxygen. Short exposure to UV light results in a partially polymerized syrup with moderate viscosity that can be easily coated. Further photoinitiator and
15 crosslinker are added to the syrup. The syrup is then coated (while excluding O₂) at a desired thickness, usually about 0.01 to about 0.25 millimeters (0.5 to about 10 mils). During the coating process, the syrup is further exposed to a bank of low intensity UV lights to complete the polymerization and crosslink the adhesive.

- Alternatively, a polymerization method which yields an adhesive which is
20 capable of being coated by an extruder may be used. In this method, a plastic vessel is filled with monomers and photoinitiators (i.e., precursor) and optionally tackifier, crosslinker, and plasticizer, with the addition of chain transfer agents to keep the molecular weight low enough after polymerization so that the polymer can be extruded. The vessel material typically is selected from the group
25 consisting of ethylene-vinyl acetate, ethylene-acrylic acid, polypropylene, polyethylene, polybutadiene, and ionomeric films. The filled vessel is exposed to low intensity UV (radiation intensity 1-2 mW/cm²), which produces the polymerized composition inside the vessel. The vessel and contents are then fed to an extruder where the vessel is physically dispersed and other components (e.g.,
30 tackifier) may be added and melt mixed. The resulting molten composition is then hot melt coated onto a liner to yield a composition comprising a high molecular

weight PSA having a small percentage of vessel material therein, typically 3 weight percent or less. after which it is then exposed to UV or to electron beam to crosslink the adhesive.

Reactive extrusion, such as the continuous free-radical polymerization methods described in U.S. Patent Nos. 4,619,979 and 4,843,134 (both Kotnour et al.) may also be utilized to prepare PSAs useful in this invention. Reactive extrusion is a solventless technology where the polymerization is initiated by thermal means as opposed to UV radiation. The monomers along with the initiator are fed to an extruder. The temperature along the extruder is varied to control the polymerization. Chain transfer agents are added to control the molecular weight and prevent gel formation. The adhesive obtained at the end of the extruder is hot melt coated and cured either by UV light or electron beam in order to improve its cohesive strength.

15 Flexible Retroreflective Sheeting

The article of the present invention comprises flexible sheeting. This flexible sheeting may be microsphere-based or cube-corner based. Suitable flexible retroreflective sheeting is known in the art and includes, but is not limited to, U.S. Patent No. 5,066,098 (Kult et al.), U.S. Patent No. 5,069,964 (Tolliver et al.), U.S. Patent No. 5,064,272 (Bailey et al.), U.S. Patent No. 4,896,943 (Tolliver et al.), U.S. Patent No. 3,551,025 (Bingham), U.S. Patent No. 4,950,525 (Bailey), U.S. Patent No. 5,008,142 (Wilson et al.), U.S. Patent No. 5,262,225 (Wilson et al.), U.S. Patent No. 5,491,586 (Phillips), U.S. Patent No. 5,264,063 (Martin), U.S. Patent No. 5,415,911 (Zampa et al.), U.S. Patent No. 5,213,872 (Pricone et al.), EP 0714040, and U.S. Patent No. 5,514,441 (Pohto et al.).

Flexible sheeting suitable for the present invention can be applied to a post having a radius of curvature of 2.5 cm (1 inch) while maintaining good retroreflectivity.

Retroreflectivity can be measured according to the procedures set forth in ASTM E809 and ASTM E12.08.

A preferred embodiment comprises flexible retroreflective sheeting described in U.S. Patent No. 5,450,235 (Smith et al. This flexible sheeting comprises: a body portion that includes a body layer which contains a light transmissible polymeric material having an elastic modulus less than 7×10^8 pascals and a plurality of cube-corner elements projecting from a first side of the body portion. The cube-corner elements comprise a light transmissible polymeric material having an elastic modulus greater than 16×10^8 pascals. "Elastic modulus" is defined as the elastic modulus determined according to ASTM-D 882-75b using Static Weight Method A with a 12.7 cm (5 inch) initial grip separation, a 2.54 cm (1 inch) sample width, and a 2.54 cm / minute (1 inch / minute) rate of grip separation.

This flexible cube-corner sheeting comprises a multitude of cube-corner elements and a body portion. The body portion can include a land layer and a body layer. The body layer typically functions to protect the sheeting from environmental elements and/or to provide significant mechanical integrity to the sheeting. The land layer is the layer immediately adjacent to the base of the cube-corner elements. The cube-corner elements project from a first or rear side of the body portion. The land layer typically has a thickness in the range of about 0 to about 150 micrometers. The body layer typically has a thickness in the range of about 20 to about 1000 micrometers. The cube-corner elements typically have a height in the range of about 20 to about 500 micrometers.

A sealing layer preferably is applied to the backside of the cube-corner elements to maintain an air interface at the backside of the cubes to enhance retroreflectivity. Preferably the sealing layer comprises a polymeric material having an elastic modulus less than 7×10^8 pascals. Alternatively, a metallic vapor coat (e.g., aluminum) may be used. The adhesive layer is then applied to secure the sheeting to the curved substrate.

Examples of thermoplastic polymers suitable for the cube-corner elements include acrylic polymers (e.g., polymethylmethacrylate; polycarbonates; cellulose (e.g., cellulose acetate, cellulose(acetate-co-butyrate), cellulose nitrate); epoxies; polyesters (e.g., poly(butylene terephthalate) and poly(ethylene terephthalate));

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fluoropolymers; polyamides; polyetherketones; poly(etherimide); polyolefins; poly(phenylene sulfide); polystyrene and polystyrene copolymers; polysulfone; silicone modified polymers; fluorine modified polymers; and mixtures thereof.

5 Polymer materials suitable for the land layer include those suitable for the cube-corner elements. The land layer may also be made from softer polymers such as those used in the body layer. Suitable polymers for the land layer include, but are not limited to, fluorinated polymers, ionomeric ethylene copolymers, low density polyethylenes, plasticized vinyl halide polymers, polyethylene copolymers, aliphatic and aromatic polyurethanes, and mixtures thereof.

10 Colorants, UV absorbers, light stabilizers, free radical scavengers or antioxidants, processing aids such as anti-blocking agents, releasing agents, lubricants, and other additives may be added to the body portion of the cube-corner elements.

Another preferred embodiment of the present invention incorporates the
15 sheeting described in U.S. Patent No. 5,805,338 (Janovec). The sheeting disclosed is capable of accommodating the expansion and contraction of the underlying polymeric substrate. The sheeting has a pillowed or curved microstructured member bonded in a regular pattern to a sealing member. The sheeting comprises: (a) a microstructured retroreflective member having a body
20 portion and a plurality of cube-corner elements projecting from a first side of said body portion; (b) a sealing member; and (c) a network of intersecting lines bonding said first side of said body portion and said sealing member to each other in a regular pattern of cells whereby said sheeting comprises: (i) a normal state wherein said microstructured member is curved and is substantially parallel to said
25 sealing member; and (ii) a compressed state wherein said microstructured member is arched and said sealing member is substantially flat. The cube-corner elements are preferably selected from the group consisting of acrylic, polycarbonate, polyester, polyurethane, and crosslinked acrylates. The sealing member is preferably selected from the group consisting of polyurethane, poly(ethylene
30 terephthalate), polyethylene copolymers, ethylene methyl acrylate copolymer,

ethylene ethyl acrylate copolymer, ethylene vinyl acetate copolymer, and polyvinyl chloride containing a polymeric plasticizer.

Another preferred embodiment of the present invention incorporates the sheeting described in WO 95/11464 (Benson et al). The ultra-flexible sheeting disclosed comprises: (a) a retroreflective layer of a two-dimensional array of independent cube-corner elements, wherein the retroreflective layer is comprised of a first polymeric material; and (b) an overlay layer comprised of a second polymeric material. The composite material is comprised of cube-corner elements directly bonded to the overlay layer substantially without an intervening land structure. The first polymeric material has an elastic modulus greater than about 25×10^8 pascals. Preferably, the first polymeric material is selected from the group consisting of polycarbonate, polymethylmethacrylate, poly(ethylene terephthalate), and crosslinked polymers of multifunctional acrylate monomers. The second polymeric material is a thermoplastic having an elastic modulus less than about 13×10^8 pascals. Preferably the second polymeric material is selected from the group consisting of ionomeric ethylene copolymers, aliphatic polyurethanes, aromatic polyurethanes, and combinations thereof.

Curved Low Energy Substrates

The flexible retroreflective sheeting may be adhered to a variety of curved low energy surfaces. Illustrative examples include, but are not limited to a vehicle body (e.g., a bumper), mud flaps, and traffic control devices (e.g., posts, cones, barrels).

A wide variety of polymers may be used to fabricate these low energy surfaces. For example, mud flaps tend to be rubber-based while traffic control elements typically are comprised of low density polyethylene, high density polyethylene, polypropylene, plasticized polyvinyl chloride, and their copolymers.

Preferably the radius of curvature of these substrates ranges from about 2.5 cm (1 inch) to about 1.5 meters (5 feet).

A single piece of sheeting or multiple pieces of sheeting may be applied to the curved substrate. The sheeting may be a "closed loop" or may have a gap.

Further, the sheeting may be overlapped or be applied so that the edges meet, but do not overlap.

The retroreflective sheeting may be applied to the these substrates manually or through mechanical means. See for example U.S. Patent No.

5 5,047,107 (Keller et al.) which discloses a mechanical means for applying sheeting to a traffic control device.

Examples

The present invention will be further described with reference to the
10 following nonlimiting examples and test methods. All parts, percentages, and ratios are by weight unless otherwise specified.

Retroreflective Sheeting

The retroreflective sheeting used in the examples was prepared as follows:

15 Molten polycarbonate resin (MAKROLON™ 2407 available from Bayer Corp., Pittsburgh, PA) was cast onto a heated microstructured nickel tooling containing microcube prism recesses having a depth of approximately 86 micrometers (0.0034 inch). The microcube recesses were formed as matched pairs of cube-corner elements with the optical axis canted or tilted 8.15 degrees
20 away from the primary groove, as generally described in U.S. Patent No. 4,577,258 (Hoopman). The nickel tooling thickness was 508 micrometers (0.02 inch) and the tooling was heated to 215.6°C (420°F). The molten polycarbonate, at a temperature of 287.8°C (550°F), was cast onto the tooling at a pressure of approximately 1.03×10^7 to 1.38×10^7 pascals (1500 to 2000 psi) for 0.7 seconds
25 to replicate the microcube recesses. Simultaneously with filling the cube recesses, additional polycarbonate was deposited in a continuous land layer above the tooling with a thickness of approximately 51 micrometers (0.002 inch). A previously extruded 71 micrometer (0.0028 inch) thick aliphatic polyester urethane body layer (MORTHANE™ PNO3-214 available from Morton
30 International, Seabrook, NH) was then laminated onto the top surface of the continuous polycarbonate land layer when the surface temperature was

approximately 190.6°C (375°F). The nickel tooling and the polycarbonate and laminated polyurethane body layer were then cooled with room temperature air for 18 seconds to a temperature between 71.1 and 87.8 °C (160 and 190°F), allowing the laminate materials to solidify to form the microstructured member. This member, having a substantially flat first side and a multitude of cube-corners on the second side, was then removed from the nickel tooling.

A sealing member was made using the following method. A blend of 60% aliphatic polyester urethane (MORTHANE™ PNO3-214) and 40% aromatic polyester polyurethane (including 50% aromatic polyester urethane, ESTANE™ 58810 available from B.F. Goodrich Co., Cleveland, OH, and 50% titanium dioxide, previously compounded in a twin screw extruder and pelletized) was extruded. One side of the sealing member was protected by a 51 micrometers (0.002 in) thick PET film.

Subsequently, the microstructured and sealing members were fed into a nip at approximately the same speed between a steel embossing roll and a rubber roll having a 75 Shore A durometer. The embossing pattern on the steel roll was of rectangular configuration with dimensions of 0.86 cm by 2.54 cm (0.34 inch by 1 inch).

The PET film of the microstructured member was allowed to contact the rubber roll with the cube-cornered side exposed. The PET film of the sealing member was allowed to contact the steel embossing roll with a sealing member exposed (i.e., back face bonding). The steel embossing roll was heated to 216°C (420°F). The rolls turned at a speed of 1.52 meters/min (5 feet /min) and the force on the nip was held at 43 N/cm (25 lb/in). As the members passed through the nip, bonds were created between the exposed sealing member and the cube-corners of the microstructured member. Both PET protective films were then removed.

Adhesive

Each of the adhesive compositions set forth in the examples (about 63 micrometers (0.0025 inch) in thickness) was then laminated to the unbonded side
5 of the sealing member.

Curved Substrate

The sheeting was applied manually onto either a traffic control barrel or post as generally described in U.S. Patent No. 5,026,204 (Kulp et al.).

10 The low density polyethylene barrels (from Traffix Devices Inc., San Clemente, CA) were about 1.2 meters (4 feet) tall and had 5 tapered rings each slightly larger than the next and was molded into one piece. The barrels had a radius of curvature ranging from about 20 to 25 cm (8 to 10 inches). The base of the barrel was molded separately.

15 The posts (from Bent Manufacturing, Huntington Beach, CA) were about 1.2 meters (4 feet) tall and had a radius of curvature ranging from about 2.4 to 5 cm (1 to 2 inches).

The barrels or posts were placed onto a mandrel rotating at 1.52 meters/minute (0.5 revolutions/minute). They were then heated to a surface
20 temperature of 49°C (120°F). This heating simulated operating conditions used by some manufacturers who apply retroreflective sheeting after flame-treating the barrels or posts. Immediately after heating, the sheetings were applied manually to either the barrels or the posts.

The barrels or the posts were then cooled to room temperature.
25

Example 1.

The following adhesive chemistries were evaluated using thermal cycling testing and cold impact testing:

Sample 1: Rubber-based Adhesive - (comparative)

A 50/50 butadiene rubber (TAKTENE™ 220, Bayer Corp., Orange, TX) and PICCOLYTE™ A 135 tackifier (Hercules, Wilmington, DE) mixture was crosslinked using e-beam. The dose levels ranged from 2 Mrad to 7 Mrad at a voltage of 225 KeV yielding gel fraction values of 0.2 to 0.35.

Gel fraction was obtained using the following method. The adhesive sample weighing about 0.3 grams was placed on a stainless steel fine mesh wire screen. The screen was folded and immersed in about 100 ml of THF for 3 days at room temperature. On removal from the solvent, the adhesive samples were dried at about 93°C (200°F) for 30 minutes and re-weighed. The uncrosslinked portions of the adhesive were extracted by the solvent. The gel fraction is the ratio of the final adhesive weight to its original weight. This method was also used for other samples.

This adhesive had a Tg of about -20°C as measured from the maximum tan delta in dynamic mechanical measurements using a Bohlin VOR rheometer.

Sample 2: Tackified Block Copolymer - (comparative)

A mixture of 39 weight percent SOLPRENE™ 411 (Fina, Dallas, TX), an SBS copolymer, 9 weight percent FINAPRENE™ 502 (Fina), an SBS copolymer, and 52 weight percent of PICCOLYTE™ A 135 tackifier (Hercules) was blended in solvent and coated. This adhesive is physically crosslinked through the polystyrene phase.

Sample 3: Tackified Non-polar Acrylate

The following components were mixed together:

95 parts IOA (isooctyl acrylate), available from CPS Chemical, Old Bridge, NJ

4.75 parts IBA (isobornyl acrylate), available from Sartomer Co., West Chester, PA

0.25 part AA (acrylic acid), available from BASF Corp., Charlotte, NC

A plastic vessel (ethylene-vinyl acetate) was filled with this mixture. The filled vessel was exposed to a UV blacklight to completely polymerize the adhesive. The vessel and contents were then fed to a counter-rotating 34 millimeter twin-screw extruder (Leistritz, Somerset, NJ) at 149°C (300°F) where
5 about 15 to about 30 parts of tackifier (REGALREZ™ 6108 available from Hercules) were added and the resulting composition was hot melt coated onto a liner. Then, the extruded coating was exposed to electron beam (about 5 to about 8 Mrad dosage at a voltage of 225 KeV) to crosslink the adhesive. The gel fraction ranged from 0.45 to 0.62.

10

Sample 4: Lightly Tackified Non-polar Acrylates - (comparative)

The following components were mixed together:

75 parts IOA

24.5 parts IBA

15 0.5 part AA

and polymerized using the method described in Sample 3 except 5 pph of tackifier was added. The e-beam dose levels varied from 3 to 6 Mrad at a voltage of 225 KeV yielding gel fractions ranging from 0.35 to 0.65.

20 Sample 5: Tackified Acrylates

The following components were mixed together:

97 parts IOA

3 parts AA

and polymerized using the method described in Sample 3 except from about 20 to
25 about 40 pph of tackifier (FORAL™ 85, available from Hercules) were added. The e-beam dose level ranged from 4 to 7 Mrad at a voltage of 225 KeV yielding gel fraction values from 0.36 to 0.61.

Sample 6: Tackified Acrylate

The following components were mixed together:

98 parts IOA

2 parts AA

5 and polymerized as described in Sample 5.

Sample 7: Tackified polyalphaolefins - (comparative)

Polyoctene and tackifier were mixed together in the following ratio:

70 parts polyoctene (available from Eastman Chemical, Kingsport, TN)

10 30 parts REGALREZ™ 1126 (available from Hercules).

Then, 0.12 weight percent of t-butyl anthraquinone (Aldrich, Milwaukee, WI) was added as the UV crosslinker and each composition was crosslinked at a UV energy of 800 mJ/cm². The resulting gel fractions ranged from about 0.45 to about 0.6.

15

Sample 8: Untackified Acrylic - comparative

The following components were mixed together:

93 parts IOA

7 parts AA

20 and polymerized in the presence of a solvent (ethyl acetate). Crosslinker (0.05 pph bisamide) was then added and the resulting adhesive was coated onto a liner.

These samples were laminated to traffic control barrels as described above and evaluated using both the thermal cycling and cold impact tests.

25

Thermal Cycling

Samples of the sheeting, approximately 1.5 to 1.8 meters (5 to 6 feet) long and about 0.14 meter (5.5 inches) wide were placed on the heated barrel. These sheets were completely wrapped around the barrel and overlapped about 5 to 8 cm (2 to 3 inches).

30

After remaining one day at room temperature, each barrel was inspected for lifting of the sheeting. Subsequently, each barrel was placed in a cold truck at about -1°C (30°F). After 2 to 3 days, the barrel was again inspected for further lifting of the sheeting from the barrel.

5

Rating System

A rating was assigned for each delamination or buckling that was observed on the barrel. Values of 2 through 5 were assigned as follows:

- | | | |
|----|---|---|
| 10 | 5 | Delamination throughout the width (5.5 inches (0.14 meter) of the sheeting and 2 to 3 cm along the length of the sheeting |
| | 4 | Delamination throughout the sheeting width but narrow in length (about 1 cm) |
| | 3 | Delamination to $> 50\%$ of the sheeting width (greater than about 2.75 inches (0.07 meter)) |
| 15 | 2 | Delamination to $< 50\%$ of the sheeting width (less than about 2.75 inches (0.07 meter)) |

Cold Impact Test

- 20 After the thermal cycling test was performed, the barrels were impacted with a truck driven at 88.5 km/hr (55 mph). The samples found in Table 1 were impacted at about -11°C (12°F) and the samples found in Table 2 were impacted at -18°C (0°F). The barrels were then visually inspected and either "passed" or "failed" based on whether the sheeting came off of the barrel. Results are set forth in Tables 1 and 2.

Table 1

Sample	# Failures on cooling from 49°C (120°F) to R.T. at rating:				# Failures on cooling from R.T. to -1°C (30°F) at rating:				Total with rating >3	Cold Impact at -11°C (12°F)
	5	4	3	2	5	4	3	2		
1	4	0	0	0	0	0	0	1	4	Passed
2	0	0	3	2	0	1	5	23	9	Failed
3	0	0	0	2	0	0	2	2	2	Passed
4	1	1	4	3	0	0	0	3	6	Failed
7	0	1	2	5	0	0	1	1	4	Failed
8	0	1	2	4	0	0	3	4	6	Failed

Table 2

Sample	Tackifier Level (pph)	E-beam Dose (Mrad)	Gel Fraction	# Failures on cooling from 49°C (120°F) to -1°C (30°F) at rating:		Buckling at overlap splice*	Cold Impact at -18°C (0°F)
				3	2		
3	19	4	0.37	1	8	Yes	Passed
3	19	5	0.49	2	1	Yes	Passed
3	19	6	0.54	0	1	Yes	Passed
3	19	7	0.61	1	7	Yes	Passed
3	25	5	0.41	0	3	Yes	Passed
3	25	6	0.50	0	3	Yes	Passed
3	25	7	0.55	0	1	Yes	Passed
3	25	8	0.61	0	7	Yes	Passed
3	29	6	0.55	0	3	Yes	Passed
3	29	8	0.62	1	7	Yes	Passed
5	39	5	0.56	0	1	No	Passed
5	30	5	0.62	1	2	No**	Passed

* Buckling throughout the width of the sheeting

5 ** Some buckling, but not throughout entire width of sheeting

Example 2.

The flexible sheeting described above was applied at room temperature to polyethylene barrels using the adhesive compositions set out in Table 3. The barrels were placed in an oven at about 49°C (120°F) for 3 days.

- 5 The barrels were then removed from the oven and kept at room temperature for around 24 hours.

The barrels were then placed in a cold truck at about -1°C (30°F) for about 1 week.

- 10 The barrels were then analyzed for delamination and buckling. The above-defined ratings were used to evaluate the adhesive performance.

Table 3

Sample	Tackifier Level FORAL 85, pph	E-beam Dose Level (Mrad)	# of Failures at Each Rating:				Buckling at Overlap Splice
			5	4	3	2	
6	30	4	0	0	0	0	0
6	30	5	0	1	0	0	3
6	30	6	0	0	0	2	0
6	30	7	0	0	0	1	2
6	30	8	0	0	1	1	4
6	39	4	0	0	0	0	0
6	39	5	0	0	0	0	0
6	39	6	0	0	0	0	0
6	39	7	0	0	0	0	3
6	39	8	0	0	0	0	4
5	30	4	0	0	0	0	0
5	30	5	0	0	0	0	0
5	30	6	0	0	0	0	3
5	30	7	0	1	0	0	4
5	30	8	0	0	0	1	4
5	39	4	0	0	0	0	0
5	39	5	0	0	0	1	0
5	39	6	0	0	0	1	3
5	39	7	0	0	0	0	1
5	39	8	0	0	0	0	0

In general, a higher tackifier level and a lower e-beam dosage level are preferred.

Example 3.

5 Adhesive composition sample 6 (23 weight percent tackifier (30 pph), e-beam treated at 8 Mrad) laminated to the above-described retroreflective sheeting was applied to a barrel using the method described above. The sheeting was cut to different lengths and then applied to the barrel as follows:

- 10
- A) a single piece of sheeting (about 1.5 meter (5 foot) in length) with one 2.5 to 5 cm (1 to 2 inch) overlap splice
 - B) 2 pieces of sheeting, each 0.75 meter (2.5 feet) in length, with two 2.5 to 5 cm (1 to 2 inch) overlap splices
 - C) 3 pieces of sheeting, each about 0.6 meter (2 feet) in length, with three 2.5 cm (1 inch) overlap splices.

15 A thermal cycling test was then used to evaluate the sheeting: After the
sheeting was applied to the barrel at room temperature, the barrel was placed in an
oven at about 49°C (120°F) for 24 hours. The barrel was then kept at room
temperature for 48 hours and inspected for delamination of the sheeting. The
barrel was then placed in a cold truck at -1°C (30°F) for an additional 48 hours
20 and again inspected for delamination. The above-defined rating system was used
to evaluate the adhesives. Results may be found in Table 4.

Table 4

Sample	R.T. after being heated to 49°C (120°F)	At -1°C (30°F)
A	5 - at overlap splice	5 - at overlap splice 2 places with 3 rating
B	4 - at both overlap splices	4 - at overlap splice 2 places with 2 rating
C	4 - at all overlap splices	5 - at all overlap splices

Example 4.

The adhesive composition of Sample 5 (with 39 pph tackifier and 4 Mrad e-beam dose) was laminated to a 40 cm (16 inch) piece of retroreflective sheeting and then placed around a traffic cone having a 2 inch radius of curvature using the method described above. After the thermal cycling test (set forth in Example 3) no delamination was observed.

Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows.

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CLAIMS:

1. An article comprising:

(a) a curved substrate having a surface energy below 45 dynes/cm²;

5 (b) flexible retroreflective sheeting; and

(c) a crosslinked tackified pressure-sensitive adhesive adhering said sheeting to said substrate, said adhesive comprising the reaction product of:

(i) from about 65 to about 99 parts by weight of
10 at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, and mixtures thereof, the alkyl group of which comprises from 4 to 12 carbon atoms, which as a homopolymer has a glass transition temperature less
15 than -25°C;

(ii) from about 1 to about 10 part(s) by weight of a polar monomer copolymerizable with the monomer(s) of component (i);

(iii) optionally from 0 to about 25 parts by
20 weight of a non-polar ethylenically unsaturated monomer copolymerizable with components (i) and (ii) selected from the group consisting of alkyl acrylates, N-alkyl acrylamides, and combinations thereof, whose homopolymer has a solubility parameter of no greater than 10.50 and a Tg
25 greater than 15°C;

(iv) from about 1 to about 65 parts by weight of a tackifier based upon the total weight of components (i), (ii), and (iii); and

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(v) optionally from 0 to about 1 part by weight of a crosslinking agent based upon the total weight of components (i), (ii) and (iii).

2. The article of claim 1, wherein said curved
5 substrate comprises a radius of curvature ranging from about 2.5 cm to about 1.5 meters.

3. The article of claim 1, wherein said adhesive further comprises from about 1 to about 10 parts by weight of plasticizer based on 100 parts by weight of components
10 (i), (ii), and (iii).

4. The article of claim 3, wherein said plasticizer is selected from the group consisting of polyglycol ethers, polyethylene oxides, phosphate esters, aliphatic carboxylic acid esters, benzoic esters, sulfonamides, aromatic
15 carboxylic acid esters, and mixtures thereof.

5. The article of claim 1, wherein said polar monomer is selected from the group consisting of ethylenically unsaturated carboxylic acids, ethylenically unsaturated sulfonic acids, ethylenically unsaturated phosphoric acids,
20 acrylamides, N,N-dialkyl substituted acrylamides, N-vinyl lactams, N,N-dialkylaminoalkyl acrylates, and mixtures thereof.

6. The article of claim 1, wherein said non-polar ethylenically unsaturated monomer is selected from the group
25 consisting of 3,3,5-trimethylcyclohexyl acrylate, cyclohexyl acrylate, isobornyl acrylate, and N-octyl acrylamide.

7. The article of claim 1, wherein said tackifier is selected from the group consisting of rosin esters, esters of hydrogenated resins, hydrogenated C₉ aromatic resins, and
30 terpene phenolic resins.

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8. The article of claim 1, wherein said adhesive is crosslinked via electron beam, UV radiation, thermal activation, or moisture cure.

9. The article of claim 1, wherein said flexible
5 sheeting is selected from the group consisting of microsphere-based sheeting and cube-corner sheeting.

10. The article of claim 1, wherein said flexible sheeting is capable of being applied to a post having a radius of curvature of about 2.5 centimeters while
10 maintaining good retroreflectivity.

11. The article of claim 1, wherein said flexible sheeting comprises:

(a) a body portion having a body layer comprising a polymeric material having an elastic modulus less than
15 7×10^8 Pascals; and

(b) a plurality of cube-corner elements projecting from the first side of the body portion wherein said elements comprise a material having an elastic modulus greater than 16×10^8 Pascals.

20 12. The article of claim 11, wherein said flexible sheeting further comprises a sealing layer.

13. The article of claim 1, wherein said curved substrate comprises a traffic control device.

14. The article of claim 13, wherein said traffic
25 control device is selected from the group consisting of a post, a cone, a barrel, and a nose cone.

15. The article of claim 1, wherein said curved substrate comprises a vehicle part.

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16. The article of claim 15, wherein said vehicle part comprises a bumper or a mud flap.

17. The article of claim 1, wherein said curved substrate comprises low density polyethylene, high density
5 polyethylene, polypropylene, plasticized polyvinyl chloride, or a copolymer thereof.

18. A method of bonding a crosslinked tackified acrylic adhesive to a curved substrate having low surface energy, the method comprising the steps of:

10 (a) filling a vessel with a precursor comprising 100 parts by weight of components (i), (ii), (iii), (vi), and optionally (v), wherein the precursor comprises:

(i) from about 65 to about 99 parts by weight of
15 at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, and mixtures thereof, the alkyl group of which comprises from 4 to 12 carbon atoms, which as a homopolymer has a glass transition temperature less
20 than -25°C;

(ii) from about 1 to about 10 part(s) by weight of a polar monomer that is solution copolymerizable with the monomer(s) of component (i);

(iii) optionally from 0 to about 25 parts by
25 weight of a non-polar ethylenically unsaturated monomer copolymerizable with components (i) and (ii) selected from the group consisting of alkyl acrylates, N-alkyl acrylamides, and combinations thereof, whose homopolymer has a solubility parameter of no greater than 10.50 and a Tg
30 greater than 15°C;

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(iv) optionally from 0 to about 1 part by weight of a crosslinking agent based upon the total weight of components (i), (ii), and (iii); and

5 (v) from about 0.01 to about 1 parts by weight of a photoinitiator based upon the total weight of components (i), (ii), and (iii);

(b) exposing said vessel filled with said precursor to low intensity ultraviolet radiation yielding a hot melt coatable adhesive;

10 (c) adding from about 1 to about 65 parts by weight of a tackifier based upon the total weight of components (i), (ii), and (iii) and melt mixing said tackifier with said hot melt coatable adhesive in an extruder wherein the vessel is physically dispersed yielding
15 a compounded tackified hot melt coatable adhesive;

(d) extruding said compounded tackified hot melt coatable adhesive onto a liner;

(e) exposing said compounded tackified hot melt coatable adhesive to radiation yielding a crosslinked
20 adhesive;

(f) applying said crosslinked adhesive to either a curved low energy surface or a retroreflective sheeting; and

(g) joining the retroreflective sheeting to the curved low energy surface, said crosslinked adhesive
25 disposed between the retroreflective sheeting and the curved low energy surface.

19. The method of claim 18, wherein the compounded tackified hot melt coatable adhesive is first applied to flexible sheeting and then crosslinked.

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20. The method of claim 18, wherein a tackifier and an optional plasticizer are added to the vessel in step (a).

21. The method of claim 18, wherein the curved surface comprises polyethylene.

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22. The method of claim 18, comprising adding about 15 to about 50 parts by weight of tackifier based on the total weight of components (i), (ii), and (iii).

10 23. The method of claim 18, wherein the adhesive has a glass transition temperature of about 0°C to about -40°C as measured by dynamic mechanical analysis.

15 24. The method of claim 18, wherein the adhesive has a glass transition temperature of about -15°C to about -30°C as measured by dynamic mechanical analysis.

25. The method of claim 18, wherein the adhesive contains sufficient amounts of component (ii) and tackifier,
20 and is sufficiently crosslinked, to:

(I) have a glass transition temperature less than about -15°C as measured by dynamic mechanical analysis; and

(II) enable the sheeting, when wrapped around a
25 low density polyethylene barrel, to remain firmly bonded to the barrel without buckling when cooled from 49°C to -1°C.

26. The article of claim 1, wherein the curved substrate comprises polyethylene.

27. The article of claim 1, wherein the adhesive
30 contains about 15 to about 50 parts by weight of tackifier

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based on the total weight of components (i), (ii), and (iii).

28. The article of claim 1, wherein the adhesive has a glass transition temperature of about 0°C to about -40°C as
5 measured by dynamic mechanical analysis.

29. The article of claim 1, wherein the adhesive has a glass transition temperature of about -15°C to about -30°C as measured by dynamic mechanical analysis.

30. The article of claim 1, wherein the adhesive
10 contains sufficient amounts of components (ii) and (iv), and is sufficiently crosslinked, to:

(I) have a glass transition temperature less than about -15°C as measured by dynamic mechanical analysis; and

15 (II) enable the sheeting, when wrapped around a low density polyethylene barrel, to remain firmly bonded to the barrel without buckling when cooled from 49°C to -1°C.

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