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(54) Title: HEAT-RECOVERABLE COMPOSITION AND ARTICLE 		

(57) Abstract

An adhesive composition suitable for sealing to polypropylene. The composition comprises 10 % to 90 % by weight ethylene polymer, e.g. an ethylene homopolymer such as polyethylene or an ethylene copolymer, 10 % to 90 % by weight modified polypropylene, 0 % to 30 % by weight rubber, and 0 % to 25 % by weight tackifier. The composition is useful when it is part of a heat-recoverable article (2) which is used to provide a protective coating onto a polypropylene-coated steel pipeline (4), particularly at a joint or weld (12) in the pipe.

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HEAT-RECOVERABLE COMPOSITION AND ARTICLE

BACKGROUND OF THE INVENTION

5 Field of the Invention

This invention relates to dimensionally recoverable articles, particularly heat-recoverable articles, and to an adhesive suitable for use with such articles.

10 Introduction to the Invention

Pipelines composed of steel pipe are commonly used to transport a variety of liquids and gases. Depending on the application and the environment, the pipe may be used above the ground or it may be buried. In order to protect the pipe from abrasion, corrosion, and degradation due to exposure to sun, soil, moisture, and other elements, it is often necessary to coat the exterior of the pipe with a protective layer. The nature of this protective layer depends on the environment to which the pipe is exposed, but, for many applications, the protective layer is polymeric. The protective layer may comprise a polymer tape which is coated with a mastic layer and is then applied to the pipe, or it may comprise an epoxy which is sprayed or painted onto the pipe. Another type of effective coating is a fusion bonded epoxy coating in which the epoxy powder is sprayed onto the pipe and is then cured to form a pinhole-free layer which is suitable for use up to about 60°C. Frequently the protective coating comprises a number of layers, for example an epoxy layer which is immediately adjacent the pipe and an outer polymer layer such as polyethylene. Such coatings provide the advantages of the epoxy and the polymer and are useful up to a temperature of about 110°C.

Recently a number of manufacturers have introduced coated steel pipe which is designed to withstand exposure temperatures of up to 110°C. Such pipe generally has a coating which comprises an inner layer of fusion bonded epoxy, an optional adhesive layer, and an outer layer of polypropylene. These layers provide excellent protection to the steel pipe because they combine the excellent adhesion and cathodic disbonding resistance of the epoxy with the low moisture absorption, low moisture transmission, and abrasion resistance of polypropylene. The difficulty with such pipe is that there are currently no easily installable coatings for the pipe joints or welds that are created when pipe is repaired or retrofitted, e.g. when two pieces of pipe are attached to one another. Therefore, when a joint or a weld must be made to the polypropylene-coated pipe, difficult and time-consuming procedures must be followed to ensure that the pipe joint

or weld is adequately protected. For example, one technique requires preheating the weld region to about 240°C by induction heating, then applying a layer of fusion bonded epoxy powder followed by a layer of polypropylene. To ensure adequate adhesion, the polypropylene sheet is heated with a torch and smoothed out with a spatula. The procedure, which requires a skilled craftsman, is especially difficult to carry out in the field where the conditions are not easily controlled.

One technique for supplying a protective coating layer to a pipe joint or weld in the field is by the use of a heat-recoverable polymeric article, i.e. a heat-shrinkable polymeric article such as a sleeve, sheet, or tape, in combination with a heat-activatable sealant. The polymeric material of the article has been crosslinked during the production process so as to enhance the desired dimensional recovery. One method of producing a heat-recoverable article comprises shaping the polymeric material into the desired heat-stable form, subsequently crosslinking the polymeric material, heating the article to a temperature above the crystalline melting point of the polymer (or, for amorphous materials, the softening point of the polymer), deforming the article, and cooling the article while in the deformed state so that the deformed state of the article is retained. In use, because the deformed state of the article is heat-unstable, application of heat, by means of a torch or other heat source, will cause the article to assume its original heat-stable shape. For many applications, the article is designed to shrink down onto the substrate.

To enhance adhesion to the substrate, such heat-recoverable articles generally comprise a layer of a heat-activatable sealant which is positioned adjacent the substrate. When the article is heated, the temperature of the heat-activatable sealant rises above its activation temperature so that a strong bond is formed between the polymeric article and the substrate. Suitable sealants include hotmelt adhesives and mastics. Good adhesion of the coating to the substrate is particularly important to avoid cathodic disbonding. Cathodic disbonding occurs as a result of the impressed electric current that is applied to the pipe to prevent corrosion of the iron in the steel pipe. Many adhesive compositions which are used to bond a protective coating onto a pipe are adversely affected by the impressed electric current. As a result, the bond weakens and the adhesive pulls away from the pipe, leaving segments of the pipe surface exposed to the corrosive conditions of the environment.

For pipe protection, conventional heat-recoverable articles are sleeves which comprise a backing layer, generally polyethylene or a copolymer comprising ethylene, in contact with a hotmelt adhesive, which is often a polyethylene-based adhesive. The

hotmelt adhesive is selected to have adequate adhesion both to the backing layer and to the substrate. Most conventional polyethylene-based heat-recoverable sleeves do not adhere well to a polypropylene-coated pipe, and those sleeves which do have good adhesion cannot be used for pipelines which are exposed to high temperatures, e.g. more than 110°C, because they contain adhesives or mastics which soften and disbond from the pipe at high temperatures. Although there are a number of commercial polypropylenes and modified polypropylenes which can be used in adhesives which stick well to polypropylene-coated pipes, these materials do not have good adhesion to polyethylene backing layers. Furthermore, because polypropylene degrades when crosslinked by means of electron beam irradiation, a heat-recoverable sleeve comprising a polypropylene backing layer is not practical.

SUMMARY OF THE INVENTION

We have now discovered that a heat-recoverable article which has good adhesion to steel, polyethylene, and polypropylene, has good cathodic disbonding resistance, and is suitable for use at temperatures up to 110°C can be made if the adhesive layer comprises both an ethylene polymer and polypropylene. In a first aspect, this invention provides an adhesive composition suitable for sealing to a substrate which comprises polypropylene, said composition comprising

- (a) 10% to 90% by weight ethylene polymer which is an ethylene homopolymer, an ethylene copolymer, or a modified ethylene polymer in which a chemical moiety has been grafted onto a polyethylene backbone;
- (b) 10% to 90% by weight modified polypropylene which
 - (i) comprises a chemical moiety which is an unsaturated carboxylic acid or acid derivative and which has been grafted onto a polypropylene backbone, and
 - (ii) has a 2% secant modulus of less than 690 MPa (100,000 psi); and
- (c) 0% to 30% by weight rubber; and
- (d) 0% to 25% by weight tackifier.

In a second aspect, this invention provides a heat-recoverable article comprising a heat-recoverable polymeric element, said element having coated on at least a part of a surface thereof an adhesive composition according to the first aspect of the invention.

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In a third aspect, this invention provides an assembly which comprises

- (1) a substrate which comprises polypropylene; and
- 10 (2) an adhesive according to the first aspect of the invention which is in contact with and seals to the substrate.

BRIEF DESCRIPTION OF THE DRAWING

15 The invention is illustrated in the drawing in which Figure 1 shows a perspective view of a heat-recoverable article of the invention positioned on a substrate;

Figure 2 shows a cross-sectional view of the article of the invention along line 2-2 of Figure 1; and

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Figure 3 shows a cross-sectional view of an article of the invention covering a weld between two pipes.

DETAILED DESCRIPTION OF THE INVENTION

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The adhesive composition of the invention is particularly useful in adhering to polypropylene. Particularly preferred compositions of the invention adhere to steel and/or to polyethylene, in addition to polypropylene. In this specification, a composition is said to have adhesive character if the peel strength of the composition to the substrate, as measured by ASTM D-1000, is greater than 0 N/mm at 23°C.

30 Adhesives of the invention preferably have a peel strength to polypropylene of at least 0.9 N/mm (5 pli), particularly at least 1.2 N/mm (7 pli), especially at least 1.8 N/mm (10 pli) at 23°C. In addition, the adhesives of the invention exhibit adhesive character at elevated temperature, e.g. 110°C or 120°C. When the peel strength of an adhesive of the invention is measured at 110°C, the adhesives preferably have a peel strength of at least 0.02 N/mm (0.1 pli), particularly at least 0.05 N/mm (0.3 pli), especially at least 0.09 N/mm (0.5 pli). The disclosure of ASTM D-1000 is incorporated herein by reference. It is preferred that adhesives of the invention have similar peel strengths at

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23°C and 110°C as those described for polypropylene for substrates comprising steel and substrates comprising polyethylene. The polypropylene to which the adhesive composition adheres may be a film, sheet, or article of polypropylene which has sufficient thickness and integrity to stand alone, or it may be in the form of a coating over a part or all of a substrate such as a pipe. The compositions of the invention are particularly useful in adhering to polypropylene-coated steel pipe.

The polypropylene present in the substrate, i.e. the material to which the adhesive composition adheres, may be either a crystalline isotactic polypropylene or an amorphous polypropylene, depending on the specific application. The polypropylene may be conventional, unmodified polypropylene which comprises at least 75% by weight of the polypropylene homopolymer, i.e. at least 75% of the polymer has a polymer backbone $-(CH-CH(CH_3))-$. Alternatively, the polymer may be modified polypropylene. In this specification, the term "modified polypropylene" is used to mean any polypropylene in which the backbone of the polymer has been chemically changed or otherwise altered to enhance the physical or chemical properties of the polymer. Such modification can be achieved during the polymerization process or in a post-polymerization step, for example by grafting a chemical moiety such as an unsaturated carboxylic acid or acid derivative onto the polymer backbone, by inserting a monomer to form a block copolymer, by incorporating a specific chain-blocking agent, or by any other suitable means. In addition, the term "modified polypropylene" includes those polymer alloys and blends, either reacted or unreacted, which comprise polypropylene and which have different chemical and/or physical properties from conventional unmodified polypropylene. Alloys and blends include those materials in which polypropylene is mixed with rubber such as ethylene propylene diene rubber (EPDM).

The polypropylene of the adhesive is a modified polypropylene as described above. Particularly preferred are polypropylenes in which a chemical moiety such as an unsaturated carboxylic acid or acid derivative has been grafted onto the polymer backbone. Among suitable chemical moieties are acrylic acid, methacrylic acid, and maleic acid. Polymers in which the chemical moiety is an anhydride, especially maleic anhydride, are particularly preferred. When an anhydride is present, it is preferred that there be at least 0.1% by weight of the polymer of anhydride grafted onto the polypropylene backbone. It is preferred that the modified polymer contain less than 10%, preferably less than 8%, particularly less than 6% by weight of acid (present as an acid moiety), as determined by titration. Commercially available modified polypropylenes which can be used in this invention include anhydride-modified

polypropylenes such as Orevac™ PP-M, Orevac™ PP-CA100, and Orevac™ PP-C (also known as Orevac M, Orevac CA100, and Orevac C, respectively), available from Atochem; Admer™ QF500E and Admer™ QB540E, available from Mitsui; Fusabond™ 108, Fusabond™ 109, and Fusabond™ 203, available from DuPont; Plexar™ 420, available from Quantum; Qestron™ EP 2070G, available from Himont; and Polybond™ 3002, available from BP Performance Polymers. Other modified polypropylenes which may be suitable for applications in which good cathodic disbondment performance is not required include acrylic acid-grafted polypropylenes such as Polybond™ 1001, Polybond™ 2005, Polybond™ 2015, available from BP Performance Polymers.

We have found that in order for the adhesive of the invention to have good cathodic disbondment performance, it is necessary that the modified polypropylene of the adhesive have a 2% secant modulus, as measured in accordance with ASTM D-882-91, Test Method A, described hereinafter, of less than 690 MPa (100,000 psi), preferably less than 620 MPa (90,000 psi), particularly less than 552 MPa (80,000 psi), especially less than 483 MPa (70,000 psi).

Adhesive compositions of the invention comprise 10 to 90% by weight modified polypropylene, preferably 15 to 85% by weight modified polypropylene, particularly 20 to 80% by weight modified polypropylene, especially 20 to 75% by weight modified polypropylene, the weight percent being measured in terms of the total composition. In addition, conventional, unmodified polypropylene may be present.

The adhesive composition also comprises 10 to 90% by weight of an ethylene polymer, preferably 15 to 85% by weight of an ethylene polymer, particularly 20 to 80% by weight of an ethylene polymer, especially 20 to 75% by weight of an ethylene polymer, the weight percent being measured in terms of the total composition. The ethylene polymer may be an ethylene homopolymer, e.g. very low density polyethylene, low density polyethylene, linear low density polyethylene, medium density polyethylene, or high density polyethylene; an ethylene copolymer, e.g. copolymers of ethylene and vinyl acetate, ethyl acrylate, methyl acrylate, or acrylic acid; an ethylene terpolymer; or blends thereof. The ethylene polymer may be any conventional ethylene polymer in which the chemical properties are not changed. The exact type and formulation of the conventional ethylene polymer is selected based on the identity of the material to which the adhesive is to be adhered and the required exposure temperature of the final product during normal operation. Alternatively, the ethylene polymer may be a modified ethylene polymer, i.e. any ethylene polymer which

has been chemically changed or otherwise altered to enhance its physical or chemical properties. As with polypropylene, such modification can be achieved by grafting a chemical moiety such as an unsaturated carboxylic acid or acid derivative, e.g. acrylic acid, maleic acid, or maleic anhydride, onto the polymer backbone, by inserting a monomer to form a block copolymer, or by any other suitable means. Commercially available modified polyethylenes which can be used in this invention include polyethylenes sold by Quantum under the tradename Plexar, e.g. Plexar™ 013 or Plexar™ 206; those sold by DuPont under the tradename Fusabond, e.g. Fusabond™ D110, Fusabond™ D158, and Fusabond™ D185; those sold by BP Performance Polymers under the tradename Polybond, e.g. Polybond™ 1009 and Polybond™ 2021; and those sold by Mitsui under the tradename Admer, e.g. Admer™ L1000, and Admer™ L2000.

In many adhesive compositions of the invention, it is desirable that rubber be present to increase the flexibility of the composition and to enhance the adhesive nature of the composition. Among those rubbers which may be used are natural and synthetic rubbers, particularly ethylene propylene rubbers, ethylene-propylene-diene rubbers (EPDM), butyl rubbers, polyisobutylene rubbers, and thermoplastic elastomers such as those based on styrene-butadiene-styrene or styrene-isoprene-styrene linear or radical block copolymers. The rubber is optional in the adhesive composition. Rubber may comprise 0 to 30% by weight of the total composition, preferably 5 to 30% by weight, particularly 10 to 30% by weight, especially 15 to 25% by weight. A single rubber or two or more different types of rubber may be present in order to achieve different physical and adhesive properties. When more than one rubber is present, the rubber component reflects the total weight percent of all the rubbers.

Also present in many compositions of the invention is a tackifier. The term "tackifier" is used in adhesive art to denote a material which, when added to an adhesive composition, promotes its adhesion to a substrate by increasing its ability to wet the substrate. It is often preferred that the tackifier be a low molecular weight polymer of monomers which contain ethylenic unsaturation and are free of polar groups. Suitable tackifiers include Nevprene™ 9500, available from Neville Chemical, which is believed to be a copolymer of a mixture of aromatically and aliphatically substituted ethylenes, Piccotex™ 75, available from Hercules, which is believed to be a copolymer of vinyl toluene and α -methylstyrene, and Escorez™ 5320, available from Exxon. The tackifier is optional in the adhesive composition. Therefore, the tackifier comprises 0 to 25% by weight of the total composition, preferably 5 to 20% by weight, particularly 10 to 18% by weight.

The adhesive composition can also contain additional additives such as stabilizers, pigments, flame retardants, fillers, waxes, and crosslinking agents. If present, these components generally comprise at most about 20% by weight of the total composition, preferably at most about 15% by weight, particularly at most about 10% by weight.

The components of the composition can be mixed in any convenient manner, for example by using conventional mixing equipment such as Brabender™ or Banbury™ mixers, extruders, or mills. Following mixing, the composition can be shaped appropriately for the desired use. For example, the composition can be formed into a sheet, e.g. by extrusion, which can be wrapped or arranged around a substrate, or the composition can be coated onto a backing layer, e.g. by extrusion, spraying, painting, or other type of coating application.

The adhesive compositions of the invention can be used for any application. In one particular application, the adhesive is used as part of a heat-recoverable article which is used to provide a covering on a pipe. A heat-recoverable article is an article, the dimensional configuration of which may be changed by subjecting the article to heat treatment. In their most common form, such articles comprise a heat-shrinkable sleeve made from a polymeric material exhibiting the property of elastic or plastic memory. Alternatively, heat-recoverable articles can be molded into shapes intended for specific applications. Articles comprising such elastic or plastic memory are described, for example, in U.S. Patents Nos. 2,027,962 (Currie); 3,086,242 (Cook et al); and 3,597,372 (Cook), the disclosures of which are incorporated herein by reference.

Conventional heat-recoverable sleeves used to provide a protective coating to pipes have either a tubular elongate configuration or a flat configuration. Where the diameter of the pipe or other substrate is very large, thus making extrusion of a sufficiently large tubular sleeve difficult, or where no free end of the substrate is available, thus preventing positioning of a tubular sleeve, it is common to use a wrap-around article. A wrap-around article is an article, typically in the form of a sheet, that is installed by wrapping it around the object to be covered so that opposed longitudinal edges overlap. A closure means is applied to secure together the opposed longitudinal edges. Such articles are described in U.S. Patent Nos. 4,200,676 (Caponigro et al) and 4,803,104 (Peigneur et al), the disclosures of which are incorporated herein by reference.

The adhesive of the invention is particularly suitable for use in making a bond between a polypropylene-coated steel pipe and a polyethylene-based heat-recoverable sleeve. The adhesive can be applied to the sleeve prior to installation on the pipe or other substrate, it can be applied directly to the pipe or other substrate prior to
5 installation of the sleeve, e.g. as a coating applied in the factory, or it can be used in the form of a sheet which is inserted between the pipe or other substrate and the heat-recoverable sleeve. In any case, the heat-recoverable sleeve may have one or more coating layers which are applied before the adhesive of the invention. For example, many conventional heat-recoverable sleeves are coated with a layer of polyamide which
10 lies between the backing layer of the sleeve and the adhesive of the composition. When the adhesive composition is applied to the heat-recoverable sleeve, it generally has a thickness of 0.025 to 1.0 mm (0.001 to 0.040 inch). It is not necessary that the adhesive composition cover an entire surface of the heat-recoverable sleeve; often strips of adhesive at the edges of the sleeve or wraparound article are sufficient to make
15 adequate connection to the substrate. When adhesives of the invention are used with heat-recoverable articles, if there is an adhesive failure, the preferred failure mechanism is between the adhesive and the backing, i.e. the heat-recoverable article, rather than between the adhesive and the substrate, e.g. the polypropylene-coated pipe. It is particularly important that the adhesive failure be uniform, i.e. that all of the adhesive
20 stick to the pipe. A "mixed" failure, in which there is partial adhesion to both the backing and the pipe, indicates that the strength of the bond to the substrate is less than desirable.

Adhesives of the invention have good performance for cathodic disbondment at
25 elevated temperature, e.g. 80 to 95°C or hotter, when tested according to ASTM G-42, described below. The cathodic disbonding radius at 95°C after 30 days is less than 35 mm, preferably less than 30 mm, particularly less than 25 mm, especially less than 20 mm. In addition to the good cathodic disbondment performance, the adhesive retains its adhesive character at the elevated temperature.

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The adhesive of the composition is also useful for making a seal over a component, around one or more components, or between two components which are designed to survive exposure to relatively high temperatures. For example, the adhesive composition can be used to seal a fiber optic splice case outlet or to make a
35 seal between the base plate and the dome-shaped cover of a fiber optic splice case such as that disclosed in U.S. Patent No. 4,913,522 (Nolf et al), the disclosure of which is incorporated herein by reference. Fiber optic splice closure systems in which the

adhesive of the invention can be used are sold by Raychem Corporation of Menlo Park, California under the tradename FOSC™.

5 The adhesive of the invention is also useful as part of an assembly in which a substrate which comprises polypropylene is in contact with the adhesive. The polypropylene of the substrate may comprise all or part of a surface coating of the substrate, e.g. a pipe, or the entire substrate may be made of polypropylene, e.g. a molded part or component. For many applications it is preferred that the polypropylene of the substrate be in the form of a layer which surrounds the substrate.

10

The adhesive of the invention may also be used as part of a method for making a connection between a layer or an article which comprises polypropylene, e.g. a polypropylene-coated pipe, and a layer or an article which comprises polyethylene, e.g. a polyethylene-containing backing layer of a heat-recoverable article. In such a method, 15 the adhesive layer is positioned in contact with the substrate which comprises polypropylene, heat is applied to allow the adhesive to melt and flow while in contact with the substrate, and the adhesive is then allowed to cool, producing a bond between the adhesive (and any backing or carrier to which it is attached) and the substrate.

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The invention is illustrated by the drawing in which Figure 1 shows a heat-recoverable article 2 in the form of a polymeric tube recovered onto substrate 4 which is a pipe. Not shown in Figure 1 is the polypropylene layer 6 which coats pipe 4. Adhesive layer 8 which is part of the heat-recoverable article 2 lies between the pipe 4 and the backing layer 10 of heat-recoverable article 2.

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Shown in Figure 2 is a cross-sectional view along line 2-2 of Figure 1. Visible in this view is the polypropylene coating layer 6 and the adhesive layer 8.

Figure 3 shows a cross-sectional view of a weld 12 between two pipes, 4, 14. 30 Adhesive layer 8 bonds to the backing layer 10 of the polymeric heat-recoverable sleeve 2, the polypropylene coating 6, 16 of the two pipes, and to the weld 12 itself.

The invention is illustrated by the following examples.

35 Example 1 (Comparative Example)

The ingredients of Adhesive A, listed in Table I, were mixed and applied by extrusion to a 0.75 mm (0.030 inch) thick high density polyethylene backing layer

which had been crosslinked and expanded about 28% prior to the application of the adhesive. The adhesion of the adhesive to various substrates was then measured at room temperature (approximately 23°C) and at 120°C following the peel strength test procedure of ASTM D-1000, the disclosure of which is incorporated herein by reference. In that test, the adhesive-coated backing was recovered onto a pipe and was cut on the pipe into test specimens with a width of 25 mm (1 inch). Each specimen was cut parallel to the direction of the pipe to create a free end which was clamped in the jaw of an Instron™ tester. After allowing the sample to equilibrate to the desired temperature (either 23°C or 120°C) in the thermal chamber of the tester, the jaw separation speed of the Instron tester was set at 51 mm/minute (2 inches/minute). The amount of force required to peel the layer from the pipe was recorded as pounds/linear inch. To determine the adhesion to steel, the adhesive-coated backing was recovered onto a steel pipe with an outer diameter (OD) of 60 mm (2.36 inch) which had been preheated to 170-180°C. To determine the adhesion to polypropylene, the adhesive-coated backing was recovered onto a polypropylene-coated steel pipe which had been preheated to a temperature of 170-180°C. Three different polypropylene-coated pipes were tested, pipe with an OD of 0.10 m (4 inch) from Atochem, pipe with an OD of 0.25 m (10 inch) from Himont, and pipe with an OD of 0.41 m (16 inch) from Duval. The coating on the Duval pipe was modified polypropylene. There was no significant difference in the results depending on the specific pipe used. The adhesion of the adhesive to the polyethylene backing was also monitored during the test.

The results of the testing are shown in Table II. Adhesive A showed no adhesion to the polypropylene-coated pipe, but had good adhesion to the polyethylene backing and to uncoated steel.

Also tested was the performance of Adhesive A under cathodic disbonding. The resistance of the adhesive to cathodic disbonding was measured following the procedure of ASTM G-42, the disclosure of which is incorporated herein by reference. In the cathodic disbonding test, a slab of the adhesive was attached to a polyethylene backing layer and was then recovered onto a shot-blasted steel pipe with an outer diameter of 51 mm (2 inches). The end of the pipe which was to be immersed was sealed with a watertight end cap. A hole (holiday) was drilled through the backing and the adhesive (but not through the pipe) in the center of the pipe to expose the metal surface of the pipe at that point. The pipe was then immersed in an electrolyte solution comprising water and 1% by weight of each of sodium chloride, sodium sulfate, and sodium carbonate. A potential of 1.5 volts was applied to the pipe, thus making the pipe a cathode in the electrolyte solution which also contained a sacrificial anode. The

sample and electrolyte solution were maintained at 95°C for 30 days. The pipe was then removed and the area around the holiday was inspected to determine the extent of disbondment. The approximate radius of the disbondment area surrounding the holiday was measured in millimeters (mm) and recorded. Adhesive A had a cathodic
5 disbonding radius of 10 to 15 mm.

Example 2 (Comparative Example)

Following the procedure of Example 1, Adhesive B was prepared and tested.
10 This adhesive showed good adhesion to polyethylene and steel but low adhesion to polypropylene-coated steel. Adhesive B had a cathodic disbonding radius of 22 mm.

Example 3

15 Following the procedure of Example 1, Adhesive C was prepared and tested. This adhesive showed good adhesion to polyethylene, steel, and polypropylene-coated steel. Tests of peel strength for this adhesive were conducted on Atochem polypropylene-coated pipe (2.59 N/mm (14.8 pli) at 23°C, 0.16 N/mm (0.9 pli) at 110°C), Himont polypropylene-coated pipe (2.24 N/mm (12.8 pli) at 23°C, 0.12 N/mm
20 (0.7 pli) at 110°C), and Duval polypropylene-coated pipe (3.85 N/mm (22.0 pli) at 23°C). The cathodic disbonding radius, when tested following the procedure of Example 1, was 14 mm.

Example 4

25 Using Adhesive C, a film with a thickness of 0.25 mm (0.010 inch) was prepared and installed on both the steel pipe and the polypropylene-coated steel pipe which had been preheated to a temperature of 230°C. On top of Adhesive C, a backing layer coated with Adhesive A (as described in Example 1) was installed. The
30 composite device was then tested as in Example 1. It exhibited good adhesion to polyethylene, steel, and polypropylene-coated steel.

TABLE I
Adhesive Compositions (Weight %)

Component	A (Comparative)	B (Comparative)	C
Modified HDPE	55.6		27.8
Modified PP		55.6	27.8
PIB	13.9	13.9	13.9
EPDM	10.0	10.0	10.0
Tackifier	15.0	15.0	15.0
Pigment	3.0	3.0	3.0
Stabilizers	2.5	2.5	2.5

5 Notes to Table I:

Modified HDPE is Plexar™ 013, a modified high density polyethylene available from Quantum.

10 Modified PP is Orevac™ C, a polypropylene modified by the addition of more than 0.1% by weight anhydride, and having a 2% secant modulus of about 426 MPa (61,800 psi), available from Atochem.

PIB is Vistanex™ L-80, solid polyisobutylene rubber available from Exxon.

EPDM is Dutral™ 044, ethylene propylene diene rubber available from Montedison.

15 Tackifier is Nevprene™ 9500, a tackifier available from Neville Chemicals.

Pigment is a color concentrate containing carbon black and ethylene/ethyl acrylate copolymer.

Stabilizers include antioxidant and a metal deactivator such as that described in U.S. Patent No. 4,997,685.

TABLE II
Adhesion to Various Substrates
(Peel Strength in Newtons/mm (Pounds/linear inch))

<u>Example</u>	<u>Adhesive</u>	<u>Temperature</u> (°C)	<u>Substrate</u>		
			<u>Polyethylene</u>	<u>Steel</u>	<u>PP-coated Steel*</u>
1	A	23	7.88 (45)	>7.88 (>45)	()
	A	120	0.88 (5)	>0.88 (>5)	NT
2	B	23	1.66 (9.5)	>1.66 (>9.5)	Low
	B	120	0.18 (1.0)	>0.18 (>1.0)	NT
3	C	23	3.40 (19.4)	>3.40 (>19.4)	Good
	C	120	0.21 (1.2)	>0.21 (>1.2)	NT
4	C	23	3.71 (21.2)	>3.71 (>21.2)	Good
	C	120	0.40 (2.3)	>0.40 (>2.3)	NT

5

* PP-coated Steel was a polypropylene-coated steel pipe available from Atochem (conventional polypropylene) or Duval (modified polypropylene). "NT" indicates that no test was conducted for that condition. "Low" indicates that the adhesion was 0.35 to 0.52 N/mm (2 to 3 pli) at 23°C and that there was adhesive failure to the polypropylene coating, i.e. between the adhesive and the polypropylene coating. "Good" indicates that the adhesion was in the range of 3.68 N/mm (20 pli) or greater at 23°C and that any failure occurred between the adhesive and the backing.

10

15 Examples 5 to 13

Following the procedure of Example 1, a number of formulations were prepared using the components listed for Adhesive C, but using different grades of modified polypropylene at 27.8% by weight of the composition. The peel strength at 23°C and 120°C was measured as in Example 1 after the adhesives were recovered onto a polypropylene-coated steel pipe. Also measured was the melt index of each adhesive, following the procedure in ASTM D-1238, Condition E, and the 2% secant modulus at 23°C of each polypropylene, following the procedure of ASTM D-882-91, Test Method A. In that test, a 250 mm (10 inch) strip of the polymer was clamped between the jaws of a machine with a constant rate of jaw separation. Using an initial strain rate of 0.1 mm/mm-min (0.1 in/in-min) and a rate of grip separation of 25 mm/min (1.0 in/min).

20

25

the test was conducted and the load versus extension was recorded. The test was stopped when the specified extension of 2% was reached. The secant modulus was calculated by dividing the stress at 2% strain by the 2% strain value. The reported secant modulus was the average of five samples. The results are shown in Table III.

- 5 For all adhesives, the adhesion of the adhesive to the polypropylene-coated steel was greater than that to the polyethylene backing. In addition to these tests, a cathodic disbonding test was conducted for samples 7, 8, and 13. Following the procedure described in Example 1, test samples were tested at 110°C for 30 days. The adhesive of Example 13 had a cathodic disbonding radius of 27 mm; the adhesives of Examples
- 10 7 and 8 showed complete disbondment from the substrate.

TABLE III
Peel Strength and Melt Index for Various Adhesives

<u>Example</u>	<u>Polypropylene</u>	<u>PP Supplier</u>	<u>Peel Strength N/mm (Pounds/linear inch)</u>		<u>Melt Index</u>	<u>2% Secant Modulus MPa (psi)</u>
			<u>23°C</u>	<u>120°C</u>		
5	Orevac PP-M	Atochem	1.24 (7.1)	0.14 (0.8)	11.1	512 (74,200)
6	Orevac CA100	Atochem	0.81 (4.6)	0.09 (0.5)	26.5	99 (14,300)
7	Polybond 2005	BP	2.64 (15.1)	0.11 (0.6)	6.8	721 (104,700)
8	Polybond 2015	BP	4.52 (25.8)	0.23 (1.3)	5.8	452 (65,500)
9	Fusabond 108	DuPont	0.51 (2.9)	NT*	NT*	904 (131,100)
10	Fusabond 109	DuPont	0.30 (1.7)	NT*	NT*	947 (137,400)
11	Fusabond 203	DuPont	0.53 (3.0)	NT*	NT*	714 (103,500)
12	Plexar 420	Quantum	2.03 (11.6)	0.44 (2.5)	3.3	356 (51,700)
13	Orevac PP-C	Atochem	4.10 (23.4)	0.14 (0.8)	2.1	426 (61,800)

15 NT* indicates that this property was not tested. Melt index numbers are in grams/10 minutes.

Examples 14 to 23

20 Following the procedure of Example 1, a number of formulations were prepared and tested. Each formulation contained 13.9% by weight Vistanex™ L-80, a solid polyisobutylene rubber available from Exxon, 10.0% by weight Dutral™ 044,

ethylene propylene diene rubber (EPDM) available from Montedison, 15.0% by weight
Nevpene™ 9500, a tackifier available from Neville Chemicals, 3.0% by weight of
pigment which comprised a color concentrate containing carbon black and
ethylene/ethyl acrylate copolymer, and 2.5% by weight stabilizers which included
5 antioxidant and a metal deactivator such as that described in U.S. Patent No.
4,997,685, the disclosure of which is incorporated herein by reference. The remaining
ingredients are shown in Table IV. For each adhesive composition, an adhesive-coated
polyethylene backing was recovered onto a steel pipe with an outer diameter of 51 mm
(2 inches) which had been preheated to 230°C. Peel strength of the adhesive
10 composition to the steel was then measured at 23°C, 110°C, and 120°C as in Example
1, using an Instron tester with a pull rate of 51 mm (2 inches)/minute.

Adhesion to polypropylene-coated steel was measured using pipe with an outer
diameter of 0.4 m (16 inches) which had been coated with an unmodified
15 polypropylene from Atochem. The polypropylene coating was roughened and the pipe
interior was preheated to achieve a temperature of about 110°C on the pipe surface prior
to recovering the adhesive-coated backing onto the pipe. To ensure that the adhesive
flowed adequately, additional heat was applied to the backing following recovery. The
assembly was cooled and the adhesion was measured at 23°C.

20

The melt index of the adhesive compositions was measured as in Example 5.
Softening points were measured using a thermal mechanical analyzer (TMA) with a 50
gram load. Cathodic disbonding at 95°C for 30 days was also measured. The results
of these tests are shown in Table V.

25

TABLE IV
Adhesive Compositions (Weight %)

	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>
PE1	27.8	41.6	14.0	27.8	27.8	27.8				27.8
PE2				27.8				27.8		
PE3					27.8				27.8	
PP1	13.9	14.0	41.6					27.8	27.8	27.8
PP2	13.9					27.8	55.6			

5 Notes to Table IV:

PE1 is Plexar™ 013, a modified high density polyethylene available from Quantum.

PE2 is Lotader™ 8200, a polyethylene terpolymer available from Atochem.

10 PE3 is Lotader™ 6600, a polyethylene terpolymer available from Atochem.

PP1 is Orevac™ C, a polypropylene modified by the addition of more than 1% by weight anhydride and having a 2% secant modulus of about 426 MPa (61,800 psi), available from Atochem.

15 PP2 is Qestron™ EP2070G, a polypropylene modified by the addition of more than 1% by weight anhydride and having a 2% secant modulus of about 555 MPa (80,500 psi), available from Himont.

TABLE V
Test Results for Adhesives 14 to 23

	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>
<u>PE/Steel</u>										
23°C					M				M	
N/mm	1.22	5.06	2.71	6.62	11.21	1.79	0.35	3.41	5.48	3.80
pli	7.0	28.9	15.5	37.8	64.0	10.2	2.0	19.5	30.3	21.7
110°C					M			M	M	
N/mm	0.25	0.23	0.32	0.19	0.05	0.14	0.07	0.16	0.19	0.14
pli	1.4	1.3	1.8	1.1	0.3	0.8	0.4	0.9	1.1	0.8
120°C				M						
N/mm	0.19	0.33	0.23	0.16	NT	0.14	NT	NT	NT	0.14
pli	1.1	1.9	1.3	0.9		0.8				0.8
<u>PE/PP</u>										
23°C										
N/mm	0.53	3.33	0.88	2.45	2.10	1.05	0.18	1.75	2.10	3.85
pli	3	19	5	14	12	6	1	10	12	22
Type	AFPE	AFPE	AFPE	AFPP	AFPP	AFPE	AFPE	AFPE	AFPP	AFPE
MI	18	6	2	25	22	9	20	13	16	2
Soft.Pt. (°C)	122	122	140	120	118	122	141	94, 132	132	122
CD radius (mm)	26	22	22	34	total	20	13	total	total	14

5 Notes to Table V:

PE/Steel indicates the peel strength in Newtons/mm (N/mm) and pounds/linear inch (pli) when the adhesive-coated polyethylene backing was attached to a bare steel pipe. "M" indicates that the failure was "mixed", i.e. that there was some adhesive failure to the polyethylene backing and some adhesive failure to the steel. In non-mixed failure, the adhesive failure is to the backing.

PE/PP indicates the peel strength in N/mm (pli) when the adhesive-coated polyethylene backing was attached to a polypropylene-coated steel pipe.

Type indicates the type of failure observed during the peel test. AFPE indicates that there is adhesive failure to the polyethylene. AFPP indicates that there is adhesive failure to the polypropylene.

MI is melt index in grams/10 minutes as measured according to ASTM D-1238.

Condition E.

Soft.Pt. is the softening point in °C of the adhesive composition as measured using a TMA with a 50 g weight. For adhesive 21, two softening points were measured.

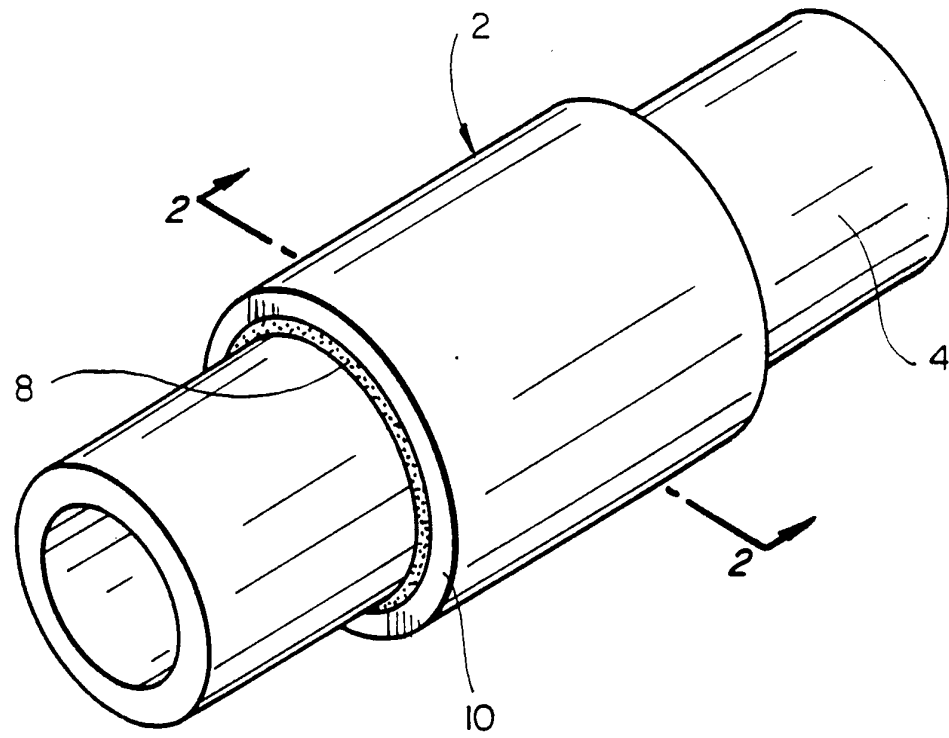
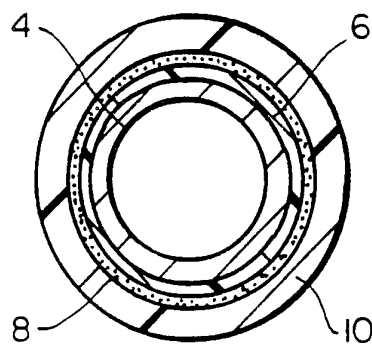
CD radius is the cathodic disbonding radius in mm measured after 30 days at 95°C.

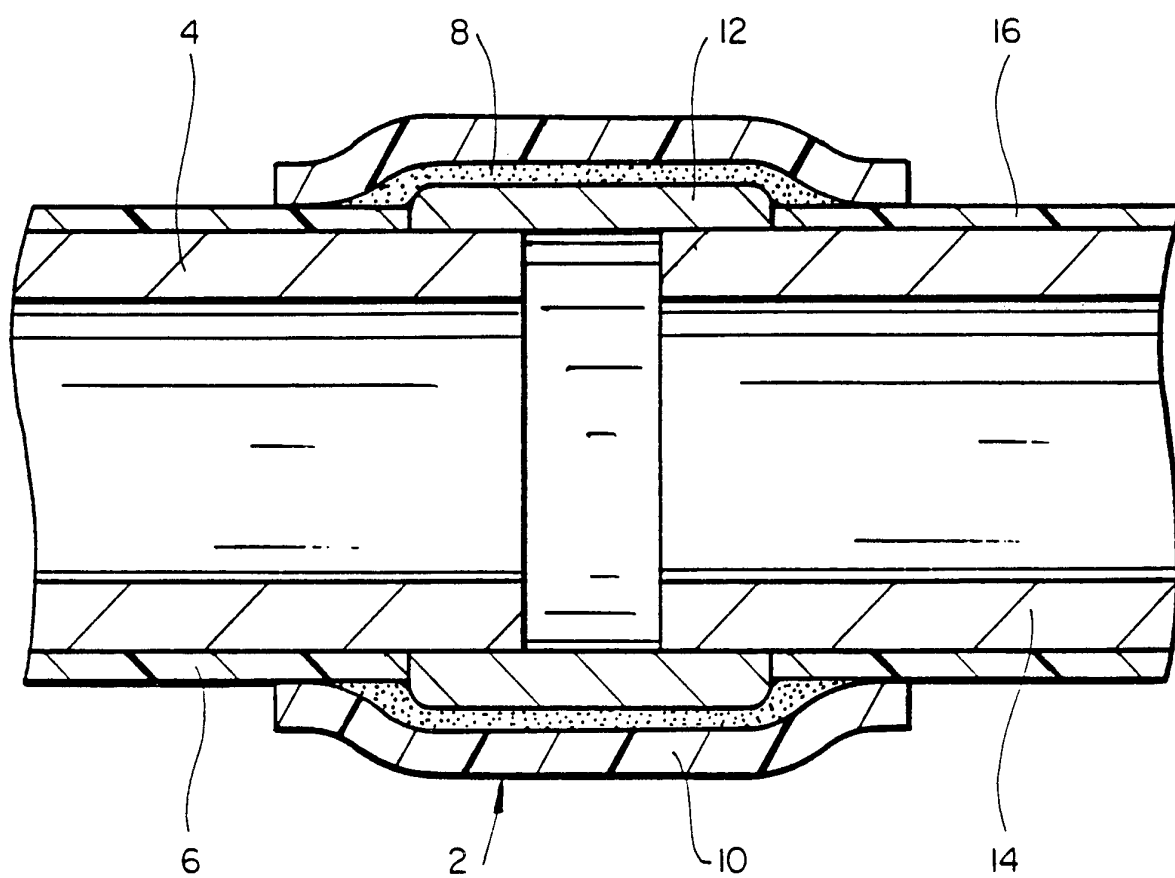
"Total" indicates that the polymer completely disbonded from the substrate.

What is claimed is:

1. An adhesive composition suitable for sealing to a substrate which comprises polypropylene, said composition comprising
 - (a) 10% to 90% by weight ethylene polymer which is an ethylene homopolymer, an ethylene copolymer, or a modified ethylene polymer in which a chemical moiety has been grafted onto a polyethylene backbone;
 - (b) 10% to 90% by weight modified polypropylene which
 - (i) comprises a chemical moiety which is an unsaturated carboxylic acid or acid derivative and which has been grafted onto a polypropylene backbone, and
 - (ii) has a 2% secant modulus of less than 690 MPa (100,000 psi); and
 - (c) 0% to 30% by weight rubber; and
 - (d) 0% to 25% by weight tackifier.
2. A composition according to claim 1 wherein the chemical moiety grafted to the polypropylene backbone is an anhydride which is present at at least 0.1% by weight.
3. A composition according to claim 2 wherein the chemical moiety is maleic anhydride.
4. A composition according to claim 1 wherein the ethylene polymer is polyethylene.
5. A composition according to any one of claims 1 to 4 which comprises 15% to 85% by weight ethylene polymer and 15% to 85% by weight modified polypropylene.
6. A composition according to any one of the preceding claims which, when tested in accordance with ASTM Test G-42, has a cathodic disbonding radius at 95°C after 30 days of less than 35 mm.

7. A heat-recoverable article comprising a heat-recoverable polymeric element, said element having coated on at least a part of a surface thereof an adhesive composition according to any one of the preceding claims, said composition being suitable for sealing to a substrate comprising polypropylene.
8. An assembly which comprises
 - (1) a substrate which comprises polypropylene; and
 - (2) an adhesive according to any one of claims 1 to 6 which is in contact with and seals to the substrate.
9. An assembly according to claim 8 wherein the substrate comprises a pipe.
10. An assembly according to claim 9 wherein the polypropylene of the substrate is in the form of a layer which surrounds the pipe.

**FIG_1****FIG_2**

**FIG_3**

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/11686

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C09D151/06 C09J151/06 C09D123/04 C09J123/04 C09J5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C09D C09J C09H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	EP,A,0 370 793 (MITSUI TOATSU) 30 May 1990 see page 3, line 24 - line 53 ---	1-6 7-10
Y	US,A,4 200 676 (D.A.CAPONIGRO ET AL) 29 April 1980 cited in the application see column 1, line 36 - line 52 see column 5, line 5 - line 32 ---	7-10
A	US,A,3 987 122 (K.W.BARTZ ET AL) 19 October 1976 see column 1, line 40 - line 50 see column 2, line 51 - line 59 see column 4, line 1 - column 5, line 23 see column 8, line 61 - line 68 --- -/--	1-10

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

6 April 1994

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/11686

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

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International Application No

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