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(71) Applicant: **THE DOW CHEMICAL COMPANY**
Dow Center 2030 Abbott Road Post Office Box 1967
Midland Michigan 48640(US)

(72) Inventor: **Brezinsky, Richard H.**
793 Golden Drive
Newark Ohio 43055(US)

(74) Representative: **Hann, Michael, Dr. et al,**
Patentanwälte Dr. Michael Hann Dr. H.-G. Sternagel
Marburger Strasse 38
D-6300 Giessen(DE)

(54) Multilayer metal/organic polymer laminate.

(57) A multilayer metal/organic polymer laminate structure is provided wherein the metal is stainless steel which has been plated with a duplex coating of a chromium containing oxide overlying a metallic chromium layer. One or more adhesive polymer layers are adhesively bonded to at least one chromium containing oxide layer. A non-adhesive polymer layer is optionally bonded to an adhesive polymer layer. Alternatively, a second metal layer may be applied to an adhesive polymer layer to form a metal/plastic/metal laminate structure. The multilayer metal/organic polymer laminate structure may be used as a cable shielding tape for electrical cables, communications cables or lightwave data transmission cables.

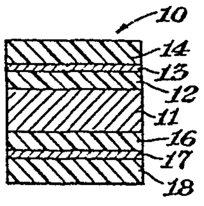

Fig.1

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Croydon Printing Company Ltd.

(E-1784)

MULTILAYER METAL/ORGANIC POLYMER LAMINATE

The present invention relates generally to a multilayer metal/organic polymer laminate structure which is suitable for use as a cable shielding or armoring tape. More particularly, the present invention relates to such a laminate structure wherein the metal is stainless steel.

In the art of designing and constructing electrical cables, especially telecommunication cables such as telephone cables, it is known to assemble insulated conductors in a core and surround it by shield and jacket components. A well known telephone cable design of such construction is referred to in the art as an "Alpeth" cable. This type of cable is more fully described by F. W. Horn et al. in the paper "Bell System Cable Sheath Problems and Designs" in A.I.E.E. Proceedings 1951, Volume 70. The shielding tape of the "Alpeth" cable is formed of a layer of bare aluminum having a thickness of about 8 mils (0.2 mm) which is usually corrugated transversely prior to being wrapped about the cable core. The corrugations impart greater flexibility to the cable and permit bending of the cable without wrinkling or rupturing of the shielding tape.

The term "shield, screen or shielding tape", as used herein, means a relatively thin layer of metal, bare or coated, which can provide mechanical protection and electrostatic and electromagnetic screening for the conductors in the core of electrical power or communication cables. Such a tape also provides suitable mechanical protection for optical fibers in a lightwave cable.

When cables are installed underground by being buried directly in soil, the outer jacket of such cables, which is formed from a polymeric resinous material such as polyethylene, is susceptible to damage. Damage to the outer jacket may result from rigors of installation, rodents, lightning, frost or dig-ins following installation. Once the outer jacket is breached, the shielding or armoring tapes are exposed to sub-surface water thereby creating a potential for corrosion, not only of the shielding or armoring tape but of the insulated conductors in the core of the cable.

Where the outer jacket of such cables is formed from a polymeric resinous material such as polyethylene, the jacket is not well adhered to the shielding or armoring tape of bare metal. The outer plastic jacket is known to slip over the shielding or armoring tape and to fold up into shoulders as the cables are pulled through ducts or placed into trenches. The shielding or armoring tape is also known to kink, curl or twist during installation causing metal fatigue in the tape and, in extreme cases, rupture of the tape because of mechanical bending stresses exerted thereon.

In order to improve the corrosion resistance of a shielding or armoring tape of bare metal, a special adhesive polyethylene coating may be applied to cover one or both sides of the metallic strip as taught in U.S. Patent Nos. 3,233,036 and 3,795,540. Such shielding or armoring tapes are widely used in the manufacture of electrical power cables and communications cables. The adhesive polyethylene used for this film contains reactive carboxyl groups which have the ability to develop firm adhesion to the metallic strip and also to the overlying polyethylene jacket. The metal component of such shielding or armoring tapes provides electrostatic screening and mechanical strength to the cable. The coating of polymeric resinous material, e.g., an ethylene/acrylic acid (EAA) copolymer, provides bondability, sealability and corrosion protection to the metal component.

When a polyethylene jacket is extruded over the metallic strip coated with the adhesive polyethylene film, the heat from the semi-molten polyethylene jacket bonds the film coated metal strip to the jacket. In this manner, a unitized construction is formed which combines the strength of the metal strip component with the elongation and fatigue resistance of the polyethylene jacket component. Such cable constructions are referred to in the art as "Bonded Jacket" cable designs.

If the heat content of the extruded polyethylene is sufficiently high, the shielding or armoring tape could become hot enough so that the overlapped portions of the shielding tape bond together at the seam, thereby forming a sealed tube or pipe around the core of the cable. The "Bonded Jacket" cable with a sealed seam has improved resistance to moisture penetration into the cable core. This cable construction also has been shown to have the greater mechanical strength necessary to withstand repeated bending of the cable . In other words, this cable construction reduces occurrences of kinking and fatigue failures of the shielding or armoring tape which result from bending stresses during installation. Further, the effects of stresses induced by temperature cycles experienced by cables under service conditions are reduced.

The thin plastic coating protects the underlying metal to some degree from corrosion either by limiting the area over which such corrosion can occur or by preventing contact between the metal and sub--surface water. The coating should be tightly bonded to the metal to resist significant delamination therefrom. A tightly bonded coating reduces corrosion and formation of metal corrosion products by restricting the path of corrosive attack to exposed metal edges of the shielding or armoring tape.

It has been found that rodents, such as gophers, will gnaw through copper and aluminum cable shielding or armoring tapes after breaching the outer jacket. They may also penetrate the insulated conductors in the core of a cable.

Even if rodents do not completely sever the shielding or armoring tape, they breach the tape and expose bare metal. Corrosion may then be accelerated due to an unfavorable ratio of anodic and cathodic areas of bare and coated metal. Corrosion which propogates circumferentially from breach sites may prematurely destroy longitudinal continuity of the shielding tape. In this manner, effectiveness of the cable from a cable shielding point of view is reduced. If the conductors are severed by rodents or are corroded by water, the cable is rendered inoperative.

It has been found that rodents generally cannot gnaw through a thickness of stainless steel in excess of about three mils (0.076 mm). An apparently simple solution to the problem posed by rodents with respect to copper and aluminum cable shielding or armoring tapes would involve substituting stainless steel for copper or aluminum.

It has been found, however, that adhesive polymer coatings readily delaminate from untreated stainless steel surfaces in the presence of water over a period of time. It has also been found that conventional stainless steel surface treatments including acid washes, immersion in alkaline or molten salt baths, and mechanical abrasion or scouring does not appreciably improve long term delamination resistance.

Cables, particularly those which are buried, are expected to have a long service life. Penetration and subsequent corrosion of shielding or armoring tapes is a serious technical and financial problem for the wire and cable industry.

In one aspect, the present invention is a multilayer metal/organic polymer laminate structure which is suitable for use as a cable shielding or armoring tape.

The laminate structure has a stainless steel substrate layer. The substrate layer has a first major planar surface and a second major planar surface. The first and second major planar surfaces are generally parallel to each other.

The laminate structure also has a first chromium metal layer and a second chromium metal layer. The first and second chromium metal layers are adhered, respectively, to the first and second major planar surfaces of the substrate layer without the use of an intermediate adhesive layer. The chromium metal layers have a minimum thickness and a maximum thickness. The minimum thickness is that which provides a generally continuous chromium metal layer. The maximum thickness is less than that which delaminates from the substrate layer when the laminate structure is flexed.

The laminate structure further has a first chromium oxide layer and a second chromium oxide layer. The first and second chromium oxide layers are intimately adhered, respectively, to the first and second chromium metal layers without the use of an intermediate adhesive layer. The chromium oxide layers have a thickness of from 0.25 to 5 milligrams of chromium metal as chromium oxide per square foot of chromium oxide layer surface area (2.69 to 53.76 mg/m^2).

At least one adhesive layer is adhered to the first chromium oxide layer, to the second chromium oxide layer, or to both chromium oxide layers. The adhesive layers are adhered to the chromium oxide layers without an intermediate adhesive layer.

In a second aspect, the present invention is a cable adapated for use in supplying electrical power or communications. The cable comprises (a) a core of at least one insulated conductor, (b) at least one shield surrounding the core, the shield comprising the multilayer metal/organic polymer laminate structure described hereinabove and (c) an outer plastic jacket.

In a third aspect, the present invention is a cable adapted for use in a lightwave data transmission system. The cable comprises (a) a core of at least one stranded unit tube and, optionally, at least one strength member, (b) a shield surrounding the core, the shield comprising the multilayer metal/organic polymer laminate structure described hereinabove and (c) an outer plastic jacket.

In a fourth aspect, the present invention is a metal/plastic/metal laminate structure. The structure comprises at least one multilayer metal/organic polymer laminate structure as described hereinabove and a second metallic substrate. The second metallic substrate is adhered to the adhesive polymer layer of the multilayer metal/organic polymer laminate structure without an intermediate adhesive layer.

The multilayer metal/organic polymer laminate structure, when used as a shield, may be used either with or without being transversely corrugated. Irrespective of whether the laminate structure is corrugated, it is desirably overlapped longitudinally and bonded so as to form a sealed tube or pipe around a cable core.

"Stranded unit tube", as used herein, designates a structure comprising a core of at least one linear strength member that is resistant to tension, at least one coated glass fiber suitable for transmitting visible light and a plastic jacket which surrounds the core and coated glass fibers. The coated glass fibers are continuous and generally parallel to the strength member.

"Adhesive layer", as used herein, means a layer of polymeric resinous materials having good bonding characteristics to chromium/chromium oxide coated stainless steel, to a second adhesive layer, and to a non-adhesive polymer layer.

The present invention is further understood by reference to the following specification taken in conjunction with the drawings. Like characters of reference designate corresponding materials and parts in each of the drawings where they appear.

Figure 1 is a partial cross-sectional view of a cable shielding tape construction in accordance with the present invention.

Figure 2A is a cutaway view of an end, and Figure 2B is a cross-section, of a typical three conductor power cable incorporating a cable shielding tape constructed in accordance with the present invention.

Figure 3A is a cutaway view of an end and Figure 3B is a cross-section, of a typical lightwave cable incorporating a multilayer metal/organic polymer laminate structure constructed in accordance with the present invention.

The stainless steel substrate layer suitably has a thickness of from 1 to 30 mils (0.0254 to 0.76 mm), beneficially from 3 to 10 mils (0.0762 to 0.254 mm). It has been found that martensitic, austenitic and ferritic stainless steels work equally well for purposes of the present invention.

The stainless steel substrate layer may be electroplated with a duplex coating of a chromium containing oxide overlying a metallic chromium layer in accordance with U.S. Patent No. 3,642,587.

Additional references which teach plating of a duplex coating of a chromium containing oxide overlying a metallic chromium layer include (a) Electroplating Engineering Handbook, A. K. Graham, editor (3rd Ed. 1971) pages 195-96; (b) "Tentative Recommended Practice for Preparation of and Electroplating on Stainless Steel," A.S.T.M. Designation B254-53, 1958 Book of A.S.T.M. Standards, Part 2, p. 982; and (c) U.S. Patent No. 3,498,892.

The first and second chromium metal layers suitably have a thickness which meets two requirements. First, the layers must be sufficiently thick to provide a generally continuous chromium metal layer. Second, the layers must be sufficiently thin to preclude delamination of the multilayer laminate structure at the stainless steel-chromium metal interface upon flexure of said laminate structure. Desirably, the first and second chromium metal layers have a thickness of from 2 to 48 milligrams per square foot of layer surface area (21.5 to 516 mg/m^2).

The first and second chromium oxide layers suitably have a thickness sufficient to provide a surface to which an adhesive layer can bond. Beneficially, the first and second chromium oxide layers have a thickness of from 0.25 to 5 milligrams of chromium as chromium oxide per square foot of layer surface area (2.69 to 53.76 mg/m^2). Desirably, the first and second chromium oxide layers have a thickness of from 0.25 to 2 milligrams of chromium as chromium oxide per square foot of layer surface area (2.69 to 21.5 mg/m^2).

The adhesive polymer layer suitably has a thickness of from 0.1 to 10 mils (0.0025 to 0.254 mm), beneficially from 0.3 to 3 mils (0.0076 to 0.076 mm). Where two or more adhesive polymer layers are used, a total adhesive polymer thickness of from 0.2 to 20 mils (0.005 to 0.51) provides satisfactory results.

The adhesive polymer layer is suitably formed from any thermoplastic polymeric resinous material which will tightly bond the chromium oxide layer to a non-adhesive polymer layer. Copolymers of ethylene and an ethylenically unsaturated carboxylic acid readily form a strong adhesive bond with metals. Such copolymers also form a strong adhesive bond with a variety of non-adhesive polymer layers. Accordingly, these copolymers are particularly suitable for purposes of the present invention.

The adhesive polymer which is beneficially used in accordance with this invention is a normally solid thermoplastic polymer of ethylene modified by monomers having reactive carboxylic acid groups. The adhesive polymer is desirably a copolymer having polymerized therein a major proportion of ethylene and a minor proportion, typically from 1 to 30 and preferably from 2 to 20 percent by weight, of an ethylenically unsaturated carboxylic acid.

As used herein, the term "ethylenically unsaturated carboxylic acid" includes mono- and polybasic acids, acid anhydrides, and partial esters of polybasic acids.

Specific examples of suitable ethylenically unsaturated carboxylic acids are acrylic acid, methacrylic acid, crotonic acid, fumaric acid, maleic acid, itaconic acid, maleic anhydride, monomethyl maleate, monoethyl maleate, monomethyl fumarate, monoethyl fumarate, tripropylene glycol monomethyl ether acid maleate, or ethylene glycol monophenyl ether acid maleate.

The carboxylic acid monomer is preferably selected from α,β-ethylenically unsaturated mono- and polycarboxylic acids and acid anhydrides having from 3 to 8 carbon atoms per molecule and partial esters of such polycarboxylic acid wherein the acid moiety has at least one carboxylic acid group and the alcohol moiety has from 1 to 20 carbon atoms.

The adhesive copolymers may consist essentially of ethylene and one or more ethylenically unsaturated acid monomers copolymerizable therewith. The adhesive copolymers may also have polymerized therein small amounts of other monomers copolymerizable with ethylene. The "other monomer" may, for example, be an ester of acrylic acid.

The comonomers of the adhesive copolymers can be combined in any way, e.g., as random copolymers, as block or sequential copolymers, or as graft copolymers, or as mixtures thereof.

Random copolymers of ethylene and monomers having a reactive carboxylic acid group are prepared in accordance with U.S. Patent No. 3,239,370 to Thompson et al. or U.S. Patent No. 4,351,931 to Armitage.

Graft copolymers of ethylene and monomers having a reactive carboxylic acid group are prepared in accordance with U.S. Patent No. 3,873,643 to Wu et al. and U.S. Patent No. 3,882,194 to Krebaum et al.

Blends of adhesive resins suitable for use in the present invention are prepared in accordance with U.S. Patent Nos. 4,087,587 and 4,087,588 to Shida et al. and U.S. Patent No. 3,298,712 to Machonis, Jr. et al.

Other methods of preparing the aforementioned types of adhesive copolymers of ethylene which are known to those skilled in the art may also be used in accordance with the present invention.

As noted hereinabove, a non-adhesive polymer layer may be intimately adhered to the adhesive polymer layer. The non-adhesive polymer layer suitably has a thickness of from 0.1 to 15 mils (0.0025 to 0.05 mm), desirably from 0.5 to 2 mils (0.0127 to 0.05 mm).

The second metallic substrate, which is needed in a metal/plastic/metal laminate structure, can be formed from a wide variety of metallic materials. It may, for example, be stainless steel which has been electroplated with a duplex coating of a chromium containing oxide overlying a metallic chromium layer. The second metallic substrate may also be formed from a metal selected from aluminum, aluminum alloys, alloy clad aluminum, copper, surface modified copper, bronze, steel, tin-free steel, tin plate steel, aluminized steel, copper-clad low carbon steel, terne-plate steel, galvanized steel, chromium plated on chromium treated steel, lead, magnesium, tin, and the like. These materials can, if desired, be surface treated or have conversion coatings on the surface thereof.

The second metallic substrate suitably has a thickness of from 2 to 35 mils (0.05 to 0.87 mm). The thickness is desirably from 4 to 15 mils (0.1 to 0.38 mm).

Suitable non-adhesive polymer materials include low, medium or high density polyethylene; copolymers of a major proportion of ethylene with a minor proportion of <u>alpha</u>-olefin monomers having 3 to 12 carbon atoms; ethylene/ethyl acrylate copolymers; ethylene/vinyl acetate copolymers; ionic olefin polymers; derivatives of polyethylene such as chlorinated polyethylene and chlorosulfonated polyethylene; polypropylene; polyamides; polyethylene terephthalates; fluoropolymers; ethylene/propylene copolymers; ethylene/propylene/diene terpolymers and the like.

In the practice of the present invention, one or more adhesive polymer layers may be applied to one or more chromium oxide layers in any convenient manner which may be desired.

Conventional extrusion coating techniques may, for example, be used to apply a single layer of an adhesive polymer to a layer of chromium oxide. Additional adhesive polymer layers may be individually applied over the single layer in separate extrusion coating operations.

If multiple adhesive polymer layers are to be applied to a chromium oxide layer in a single extrusion coating operation, existing coextrusion equipment and technology is suitably employed.

As an alternative to extrusion coating, conventional film lamination techniques may be used. Multiple lamination steps in which separate monolayer films are applied to a chromium oxide layer or to an existing adhesive polymer layer, as appropriate, may be used. A preferable, and more efficient, lamination technique involves a single lamination operation using a previously coextruded film of a desired multilayered adhesive film structure.

As another alternative, a combination of one or more extrusion or coextrusion coating operations may be combined with one or more lamination operations to provide the multilayered metal/organic polymer laminate structure of the present invention.

Referring now to the drawings, Figure 1 illustrates a multilayer metal/organic polymer laminate structure 10. The laminate structure 10 comprises a stainless steel substrate 11, a first chromium metal layer 12, a second chromium metal layer 16, a first chromium oxide layer 13, a second chromium oxide layer 17, a first adhesive polymer layer 14 and a second adhesive polymer layer 18.

The first chromium metal layer 12 and the second chromium metal layer 16 are adhered to different planar surfaces of the stainless steel substrate 11 without the use of an intermediate adhesive layer. The first chromium oxide layer 13 is adhered to the first chromium metal layer 12 without the use of an intermediate adhesive layer. The second chromium oxide layer 17 is adhered to the second chromium metal layer 16 without the use of an intermediate adhesive layer. The first adhesive polymer layer 14 and the second adhesive polymer layer 18 are adhered respectively to the first chromium oxide layer 13 and the second chromium oxide layer 17 without the use of an intermediate adhesive layer. As noted hereinabove, one of the adhesive polymer layers may be omitted.

Figures 2A and 2B show a typical three-conductor power cable 20. The conductors 21 are made of metal, usually copper or aluminum, and may be either solid (Figure 2A) or stranded (Figure 2B). The conductors are each insulated, usually with an extruded plastic cover 22 of polyvinyl chloride, polyethylene, chlorinated polyethylene, ethylene-propylene rubber, ethylene-propylene-conjugated diene terpolymer, natural rubber and the like. Space fillers 23 of hemp, foamed plastic, petroleum based components, and the like are used, in conjunction with the conductors 21, to provide a generally circular core assembly 24.

The core assembly 24 is enclosed in a laminate structure 10A which is identical to that described hereinabove except for the omission of one adhesive polymer layer. Accordingly, the laminate structure 10A comprises a stainless steel substrate layer 11A, a first chromium metal layer 12A, a second chromium metal layer 16A, a first chromium oxide layer 13A, a second chromium oxide layer 17A, and a first adhesive polymer layer 14A. The laminate structure 10A is shown with an overlap in Figure 2A and without an overlap in Figure 2B.

An outer plastic jacket 28 encloses the laminate structure 10a. The outer plastic jacket 28 is adhered to the first adhesive polymer layer 14a of the laminate structure 10a without the use of an intermediate adhesive layer.

Figures 3A and 3B show a typical cable 30 which is adapted for use in a lightwave data transmission system. The cable 30 has contained therein three stranded unit tubes 31. The stranded unit tubes 31 each comprise a fiberglass strength member 32, a number of coated glass fibers 35, space fillers 36, and an extruded plastic cover 38.

Each fiberglass strength member 32 comprises a bundle of fiberglass fibers 33 and a plastic jacket 34. The plastic jacket 34 may be formed from any of the non-adhesive polymer materials identified hereinabove. The jacket 34 is adhered to the bundle of fiberglass fibers 33 with an intermediate adhesive layer 39. The intermediate adhesive layer 39 may be omitted if desired.

The coated glass fibers 35 are oriented parallel to the fiberglass strength member 32 and are held in place against said strength member 32 by the space fillers 36. The coated glass fibers 35, the fiberglass strength member 32 and the space fillers 36, when taken together, comprise a stranded unit tube core 37.

As an alternative to a fiberglass strength member, a linear strength member may be formed from a metal such as nickel alloy steel.

The extruded plastic cover 38 encloses the stranded unit tube core 37.

Materials suitable for use as space fillers 36 include hemp, foamed plastic, petroleum based compounds and the like.

As shown in Figures 3A and 3B, a fiber-optic cable core 40 comprises three stranded unit tubes 31, three strength members 41 and space fillers 42. The three stranded unit tubes 31 are all in contact with each other for a portion of their circumference. Each of the strength members 41 is in contact with two stranded unit tubes 31 for a portion of their circumference. The space fillers 42, in conjunction with the stranded unit tubes 31 and the strength members 41, provide a generally circular cross section.

The space fillers 42 are suitably the same as the space fillers 36.

The strength members 41 may, for example, be stainless steel tubes, wire cables and the like. The material of construction is not important so long as it provides adequate tensile strength to the fiber-optic cable. Those skilled in the art will understand that the strength members 41 may be omitted if sufficient tensile strength is provided by other components of the fiber-optic cable.

The fiber optic cable core 40 is enclosed in a laminate structure 10B which is identical to the laminate structure 10A described hereinabove. Accordingly, the laminate structure 10B comprises a stainless steel substrate layer 11B, a first chromium metal layer 12,B a second chromium metal layer 16B, a first chromium oxide layer 13B, a second chromium oxide layer 17B and a first adhesive polymer layer 14B. The laminate structure 10B is shown with an overlap in Figure 3A and without an overlap in Figure 3B.

The first chromium metal layer 12B and the second chromium metal layer 16B are adhered to different surfaces of the stainless steel substrate layer 11B without the use of an intermediate adhesive layer. The first chromium oxide layer 13B and the second chromium oxide layer 17B are adhered respectively to the first chromium metal layer 12B and the second chromium metal layer 16B without the use of an intermediate adhesive layer. The first adhesive polymer layer 14B is adhered to the first chromium oxide layer 13B without the use of an intermediate adhesive layer.

An outer plastic jacket 28B encloses the laminate structure 10B. The outer plastic jacket 28B is adhered to the first adhesive polymer layer 14B of the laminate structure 10B without the use of an intermediate adhesive layer.

The following examples are illustrative of the present invention and are not intended to limit the scope thereof. In the examples, parts and percentages are by weight unless otherwise noted.

Environmental Resistance Test

A. Sample Preparation

A number of samples of stainless steel, some of which were plated with a duplex coating of chromium metal and chromium oxide, were coated with a two-layer adhesive film and tested for delamination resistance.

The samples of stainless steel had a thickness of five mils (0.127 mm) and were fully annealed by a bright annealing process to minimize surface oxidation.

A duplex coating of a chromium containing oxide overlying a metallic chromium layer was electroplated onto some of the samples of stainless steel in accordance with the process detailed in U.S. Patent No. 3,642,587 cited hereinabove. The duplex coating was a layer of about 10 milligrams per square foot (107.5 mg/m^2) of chromium metal overlaid by a layer of about 0.8 milligrams per square foot (8.6 mg/m^2) of a chromium containing oxide.

The two-layer adhesive film had a first layer of an ethylene/acrylic acid copolymer having an acrylic acid content of 6.5 percent of copolymer weight and a melt index of 2.5 decigrams per minute as measured in accordance with American Society for Testing and Materials (ASTM) Test D-1238. The first layer had a thickness of 2.0 mils (0.05 mm). The second adhesive layer was formed from a blend of 10 percent by weight of an ethylene/acrylic acid copolymer and 90 percent by weight of a high density polyethylene graft copolymer. The ethylene/acrylic acid copolymer had an acrylic acid content of 6.5 percent of copolymer weight and a melt index of 5 decigrams per minute as measured by ASTM D-1238. The high density polyethylene graft copolymer was commercially available from Chemplex Company under the trade designation Plexar® 201. The second layer had a thickness of 0.3 mils (0.0076 mm).

The samples of stainless steel were preheated in an oven set at a temperatue of 350°F (176.7°C) for a period of one minute. The preheated samples were then fed through a pair of nip rolls to laminate the two-layer adhesive film thereto. The nip rolls had previously been threaded with the two-layer adhesive film. The two-layer adhesive film had been oriented so the first layer thereof would be in contact with the preheated stainless steel samples as they passed through the nip rolls.

The laminated samples were then post-heated in an oven set at a temperature of 300°F (149°C) for a period of one minute. After post-heating, the samples were removed from the oven, cooled to about room temperature and cut into strips for testing. The strips measured 2-1/2 inches by 1 inch (6.35 x 2.54 cm).

Wrought stainless steels tested herein are identified in Table I which follows hereinafter by American Iron and Steel Institute (AISI) type Number, by generic description, and by composition.

TABLE I

Stainless Steel Description

AISI Type No.	Generic Description	Composition: Percentage Chromium	Composition: Percentage Nickel	Composition: Percentage Other Elements
304	Austenitic	18.0 to 20.0	8.0 to 11.0	Manganese 2.0 max.
305	Austenitic	17.0 to 19.0	10.0 to 13.0	Manganese 2.0 max.
434	Ferritic	16.0 to 18.0	0	Manganese 0.3-0.9, Molybdenum 0.75-1.20
201	Austenitic	17	4	Manganese 6.5

B. Testing of Laminates

The strips of laminate, prepared as hereinabove described, were immersed in 200 milliliters of a 0.1 Normal solution of hydrochloric acid at room temperature (about 25° Centigrade). The strips were then observed after 30 hours for delamination of the adhesive film by undercutting from the edges of the strip inward.

Results of delamination testing are set forth in Table II which is set forth hereinafter. The following abbreviations are used to describe the results: (a) NOD = no observable delamination; (b) CD = complete delamination.

In Table II, examples of the present invention are identified by Arabic numerals and comparative examples are identified by an alphabetic letter.

TABLE II

Environmental Resistance Test Results

Example/ Comparative Example	AISI Type No.	Stainless Steel Duplex Coated With Chromium Metal & Oxide of Chromium		Observation/ Test Results
		Yes	No	
1	304	X		NOD
A	304		X	CD
2	305	X		NOD
B	305		X	CD
3	201	X		NOD
C	201		X	CD
4	434	X		NOD
D	434		X	CD

From the results set forth in Table II above, it is readily apparent that those stainless steel samples which were plated with a duplex coating of chromium metal overlaid by a layer of a chromium containing oxide had markedly superior delamination resistance. Similar results are obtained with other adhesive polymers, either in monolayer or multilayer form.

Additional Environmental Resistance Tests

In a second series of environmental resistance tests, polymer coatings were varied while keeping the type of stainless steel constant. The type of stainless steel used was AISI Type Number 304. The composition of AISI Type Number 304 is set forth hereinabove.

A duplex coating of a chromium containing oxide overlying a metallic chromium layer was electroplated onto one-half of the samples tested using the process set forth hereinabove. The duplex coating was a layer of about 6 milligrams per square foot (64.5 mg/m^2) of metallic chrome overlaid by a layer of about 0.4 milligrams per square foot (4.3 mg/m^2) of a chromium containing oxide. The polymer coatings were laminated to the stainless steel samples by the process described hereinabove. The polymer coatings were applied as single layers rather than as a two-layer adhesive film.

The polymer coatings tested are set forth in Table III which follows.

TABLE III

Polymer Coatings

Code	Description
A1	An ethylene/acrylic acid copolymer having an acrylic acid content of 6.5 percent by weight of copolymer and a melt index of 5 decigrams per minute (ASTM D-1238), commercially available from The Dow Chemical Company under the trade designation EAA 455.
A2	An ethylene/methacrylic acid copolymer having a methacrylic acid content of 8.5 percent by weight of copolymer and a melt index of 10

decigrams per minute (ASTM D-1238), commercially available from E.I. duPont de Nemours & Co. under the trade designation ACR 0910.

A3	An ionomer resin produced through sodium neutralization of an ethylene/methacrylic acid copolymer. The ionomer resin had a melt index of 0.9 decigrams per minute (ASTM D-1238) and was commercially available from E.I. duPont de Nemours & Company under the trade designation Surlyn® 1707.
A4	An ethylene-vinyl acetate copolymer having a vinyl acetate content 9 percent by weight of copolymer and a melt index of 7 decigrams per minute (ASTM D-1238), commercially available from E.I. duPont de Nemours & Company under the trade designation EVA 3124.
A5	An ethylene-methyl acrylate copolymer having a methacrylate content of 20 percent by weight of copolymer and a melt index of 6 decigrams per minute (ASTM D-1238), commercially available from Gulf under the trade designation EMA 2207.
A6	A rubber-modified high density polyethylene graft copolymer having a melt index of 6 decigrams per minute (ASTM D-1238) a density of 0.94 grams per cubic centimeter (ASTM D-1505), and a Vicat softening point of 123° Centigrade (ASTM D-1525), commercially available from Chemplex Company under the trade designation Plexar® 6.

A7 A thermoplastic polybutylene terephthalate polymer having a specific gravity of 1.31-164, and a melting point of about 221°C commercially available from GAF Corporation under the trade designation Gafite® 1400A.

The laminates were tested for delamination using the test described hereinabove. Results of the delamination testing, determined after 30 hours, are set forth in Table IV which follows. The abbreviations used to describe test results are the same as those used herein at Table II. Examples of the present invention are identified by Arabic numerals and comparative examples are identified alphabetically.

TABLE IV

Environmental Resistance Test Results

Example/ Comparative Example No.	Polymer Coating Code	Stainless Steel Plated with Duplex Coating Yes	No	Observation/ Test Results
5	A1	X		NOD
E	A1		X	CD
6	A2	X		NOD
F	A2		X	CD
7	A3	X		NOD
G	A3		X	CD
8	A4	X		NOD
H	A4		X	CD
9	A5	X		NOD
I	A5		X	CD
10	A6	X		NOD
J	A6		X	CD
11	A7	X		NOD
K	A7		X	CD

From the results set forth in Table IV above, it is readily apparent that electroplating a duplex coating of chromium metal overlaid by a chromium oxide coating onto stainless steel substrate markedly improves adhesion of an adhesive polymer thereto. Similar results are obtained with other adhesive polymer such as those described hereinabove.

Jacket Bond Testing

A. Preparation of Samples

Using the procedure hereinabove described for preparation of Environmental Resistance Test samples, samples of stainless steel, some of which were electroplated with the duplex coating of chromium metal and a chromium containing oxide, were coated with an adhesive polymer layer. The adhesive polymer layer had a thickness of 2.3 mils (0.058 mm). Adhesive polymer layer compositions are set forth hereinafter at Table V.

Each of the adhesive polymer coated stainless steel samples was then laminated to a premolded plaque of a jacketing resin. The plaque measured 8 by 6 inches (20.3 x 15.2 cm) and had a thickness of 70 mils (1.78 mm). The jacketing resin was an admixture of a low density polyethylene resin having a melt index of 0.45 decigrams per minute (ASTM D-1238) and a density of 0.932 grams per cubic centimeter with 2.6 weight percent carbon black, based on admixture weight. A narrow strip of polyester film of 3 mil (0.076 mm) thickness was placed between the plaque of jacketing resin and the adhesive polymer coated stainless steel sample along one edge of the plaque. The polyester film prevented bonding between the jacketing resin and the adhesive polymer, thereby forming a "tab" for use in a tensile strength testing machine.

The plaque of jacketing resin was bonded to the adhesive polymer coating on the stainless steel using a compression molding press. The press had a molding temperature of 230° C. The molding pressure was 4500 pounds per square inch (315 kg/cm^2). A molding dwell time of 1.5 minutes was used.

The laminates were cooled by immersion in tap water which had a temperature of about 30°C. After cooling, the laminates were cut into one inch by six-inch (2.54 x 15.2 cm) strips for bonding strength testing. The strips were cut so as to leave the aforementioned "tab" at one end thereof.

B. Test Method Description

A tensile testing apparatus, commercially available from Instron Corporation as model number 1123, was used to measure bond strength. A crosshead speed of two inches (5.1 cm) per minute was used during testing.

The "tab" of jacketing resin was placed in an upper jaw of the apparatus. That portion of the adhesive polymer coated stainless steel which did not adhere to the jacketing resin was placed in a second, or lower, jaw. The end of the sample not inserted into the jaws of the testing apparatus was allowed to float freely during testing.

The force required to separate the jacketing material from the adhesive polymer coated stainless steel was recorded as a measure of adhesive strength. Those skilled in the art understand that separation can occur at the interface between adjacent layers (adhesive failure) or within a layer (cohesive failure).

C. Test Results

Tensile strength testing was conducted initially and after aging. Aging was accomplished by placing test strips in a container of deionized water. The container was then placed into a water bath set at a temperature of 70°C. Test results set forth hereinafter in Table V were measured at room temperature (about 25°C).

TABLE V

Jacket Bond Test Results

Example/ Comparative Example No.	Adhesive Polymer Coating Code	Stainless Steel Plated with Duplex Coating		Adhesion in pounds/-inch of width (Newton/Meter)		
		Yes	No	Initial	Aged 1 Week	Aged 2 Weeks
13	A9*	X		27.0 (4725)	24.1 (4217.5)	24.0 (4200)
M	A9*		X	26.8 (4690)	16.9 (2957.5)	15.0 (2625)
14	A10**	X		18.2 (3185)	18.5 (3237.5)	18.7 (3275.5)
N	A10**		X	15.4 (2695)	13.4 (2345)	11.7 (2047.5)

* A rubber modified high density polyethylene graft copolymer having a melt index of 6 decigrams per minute (ASTM D-1238) a density of 0.94 grams per cubic centimeter (ASTM D-1505), and a Vicat softening point of 123° Centigrade (ASTM D-1525), commercially available from Chemplex Company under the trade designation Plexar® 6.

** The two-layer adhesive film used in Examples 1-4 set forth hereinabove.

A review of the data presented in Table V makes one point perfectly clear. That is, long term adhesion of an adhesive polymer to stainless steel is markedly improved when the stainless steel has been plated with a duplex coating of chromium metal overlaid by a layer of a chromium containing oxide. Similar results are obtained with other stainless steels and other adhesive resins, both of which have been set forth hereinabove.

1. A multilayer metal/organic polymer laminate structure, the structure comprising:

(a) a stainless steel substrate layer having first and second major planar surfaces;

(b) first and second chromium metal layers adhered respectively to the first and second major planar surfaces of the substrate layer without the use of an intermediate adhesive layer, the chromium metal layers having a thickness sufficient to provide, as a minimum, a generally continuous chromium metal layer, the thickness also being less than that which inherently delaminates from the substrate layer when the laminate structure is flexed;

(c) first and second chromium oxide layers adhered respectively to the first and second chromium metal layers without use of an intermediate adhesive layer, said chromium oxide layers having a thickness of from 2.69 to 53.76 mg of chromium metal as chromium oxide per square meter of layer surface area; and

(d) at least one adhesive polymer film layer adhered, without use of an intermediate adhesive, to the first or second chromium oxide layer or to both chromium oxide layers.

2. The laminate structure of Claim 1 wherein the thickness of the first and second chromium metal

layers is from 21.5 to 516 milligrams per square meter of layer surface area.

3. The laminate structure of Claim 1 wherein the stainless steel substrate layer has a thickness of from 0.0254 to 0.76 mm.

4. The laminate structure of Claim 1 wherein the stainless steel substrate layer has a thickness of from 0.0762 to 0.254 mm.

5. The laminate structure of Claim 1 wherein the first and second chromium metal layers and the first and second chromium oxide layers are electroplated onto the stainless steel substrate.

6. The laminate structure of Claim 1 wherein the adhesive polymer film layer has a thickness of from 0.00254 to 0.254 mm.

7. The laminate structure of Claim 1 wherein the adhesive polymer film layer has a thickness of from 0.0076 to 0.076 mm.

8. The laminate structure of Claim 1 wherein the adhesive polymer film layer is formed from a normally solid thermoplastic polymer of ethylene modified by one or more monomers having reactive carboxylic acid groups.

9. The laminate structure of Claim 8 wherein the thermoplastic polymer of ethylene is a copolymer of ethylene and from 1.0 to 30 percent by weight of copolymer of an ethylenically unsaturated carboxylic acid.

10. The laminate structure of Claim 9 wherein the ethylenically unsaturated carboxylic acid is selected from acrylic acid, methacrylic acid, crotonic acid, fumaric acid, maleic acid, itaconic acid, or maleic anhydride.

11. The laminate structure of Claim 1 including a non-adhesive polymer layer adhered to the adhesive polymer film layer without use of an intermediate adhesive layer.

12. The laminate structure of Claim 11 wherein the non-adhesive polymer layer has a thickness of from 0.00254 to 0.38 mm.

13. The laminate structure of Claim 11 wherein the non-adhesive polymer layer is formed from a polymer material selected from low density polyethylene, medium density polyethylene, high density polyethylene; ethylene/ethyl acrylate copolymers; ethylene/vinyl acetate copolymers; ionic olefin polymers; chlorinated polyethylene; chlorosulfonated polyethylene; polypropylene; polyamides; polyethylene terephthalate; fluoropolymers; or ethylene/propylene/diene/terpolymers.

14. An improved cable adapted for use in supplying electrical power or communications, the cable comprising a core of at least one insulated conductor, a shield surrounding said core and an outer plastic jacket, wherein the improvement comprises providing as the shield, the multilayer metal/organic polymer laminate structure of Claim 1.

15. A metal/plastic/metal laminate structure comprising a first metal substrate layer, a second metal substrate layer, and at least one adhesive polymer layer, the adhesive polymer layer being disposed between and adhesively bonded to the first metal substrate layer and the second metal substrate layer, wherein the improvement comprises providing, as the first metal substrate layer, the multilayer metal laminate structure of Claim 1.

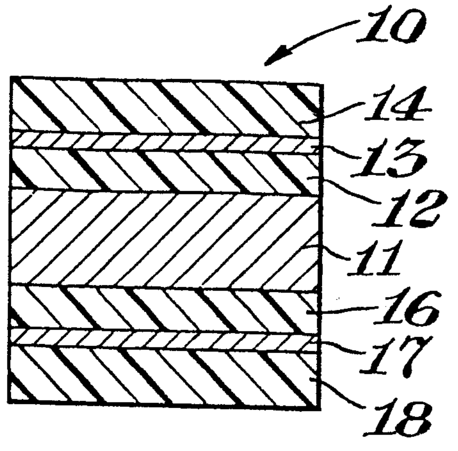

Fig. 1

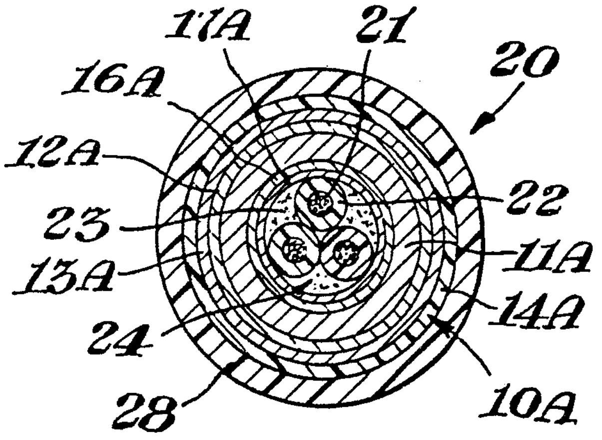

Fig. 2B

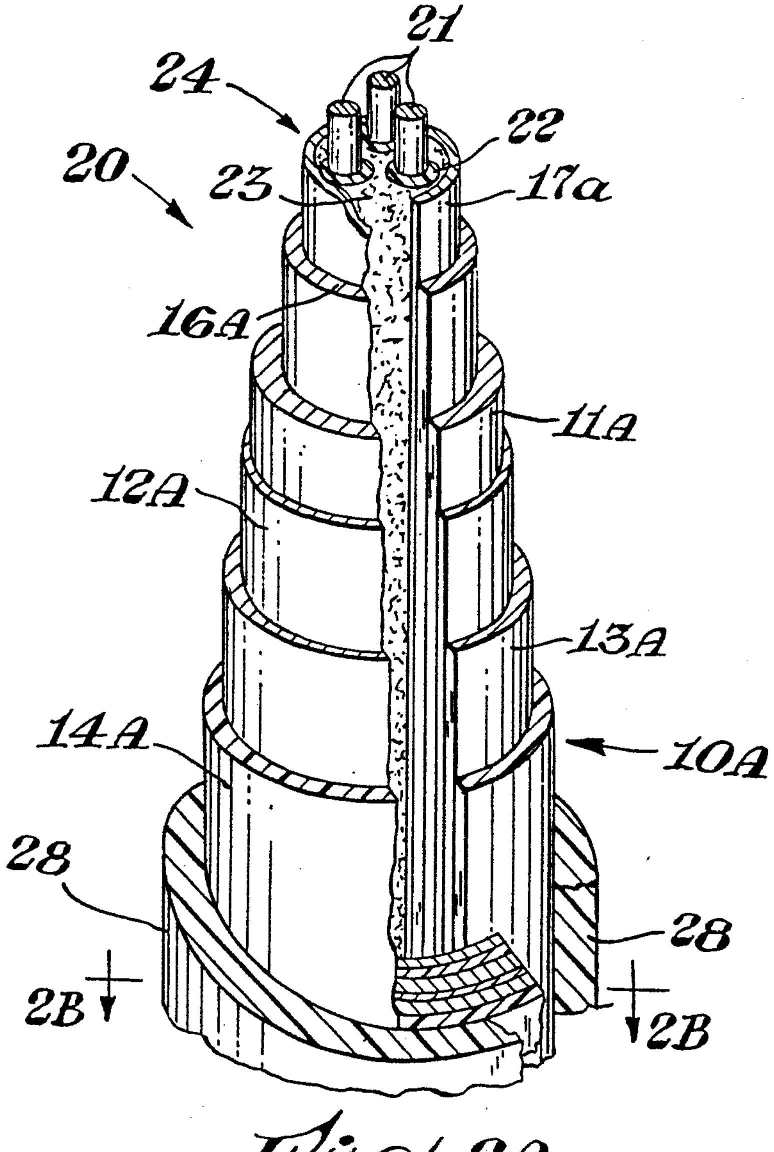

Fig. 2A

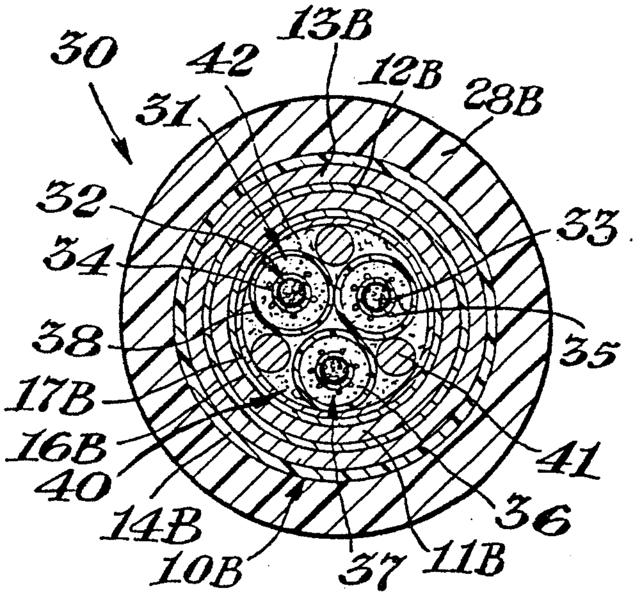
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Fig. 3B

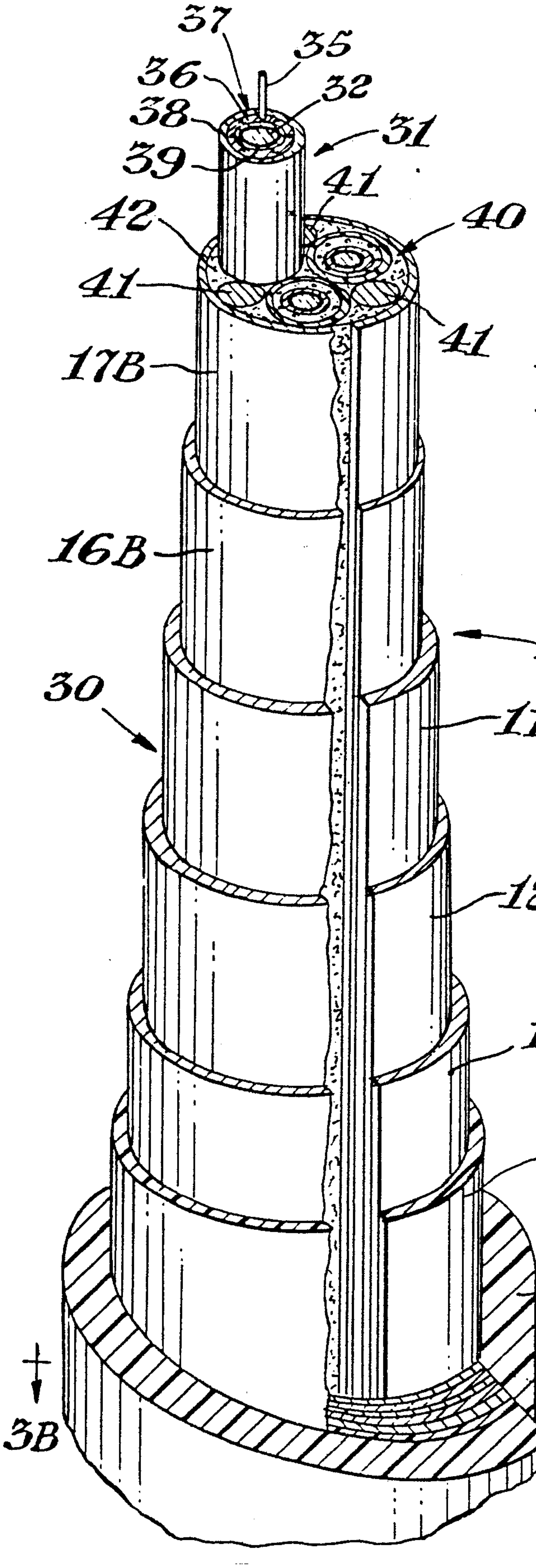
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Fig. 3A