(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 October 2011 (13.10.2011)

PCT

(10) International Publication Number
WO 2011/126683 A2

(51) International Patent Classification:
C09D 5/08 (2006.01)

(21) International Application Number:
PCT/US2011/028469

(22) International Filing Date:
15 March 2011 (15.03.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/318,838 30 March 2010 (30.03.2010) US
61/367,641 26 July 2010 (26.07.2010) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2011/126683 A2

(54) Title: ANTICORROSION COATINGS WITH REACTIVE POLYELECTROLYTE COMPLEX SYSTEM

(57) Abstract: The present application is directed to anticorrosion coatings on metal substrates. In particular the coatings are especially suitable for metal containing medical devices and implants. The anticorrosion coatings comprise a combination of anionic and cationic polyelectrolytes which when applied to a metal substrate form a complex. In addition to cationic and anionic functionality, the polyelectrolytes also possess additional functionality which allows for further reacting to form covalent bonds between the anionic and cationic polyelectrolytes. The formed complex once applied to the metal substrate surface provides improved corrosion resistance, protection from metal ion release and improved mechanical properties.

Anticorrosion coatings with reactive polyelectrolyte complex system

This application claims the benefit of U.S. Provisional Application Nos. 61/367,641, filed July 26, 2010 and 61/318,838, filed March 30, 2010 herein incorporated entirely by reference.

Field of the Invention

The present invention relates to anticorrosion coatings on metal substrates. In particular the coatings are especially suitable for metal containing medical devices and implants. The anticorrosion coatings comprise a combination of anionic and cationic polyelectrolytes which when applied to a metal substrate form a complex. In addition to cationic and anionic functionality, the polyelectrolytes also possess additional functionality which allows for further reacting to form covalent bonds between the anionic and cationic polyelectrolytes. The formed complex once applied to the metal substrate surface provides improved corrosion resistance, protection from metal ion release and improved mechanical properties.

Background

Metals are important materials widely used in various applications covering automotive, marine and medical devices and implants. Metal corrosion is a serious problem as it affects and eventually destroys integrity of metal structures. It has been estimated that the total annual direct cost of corrosion in the United States is about $276 billion, about 3.1% of the gross domestic product [Koch, G. D., Brongers, M. P. H., Thompson, N. G., Virmani, Y. P. and Payer, J. H., “Corrosion Cost and Preventive Strategies in the United State”, Perform. 7 (suppl.), 2-11 (2002)].

Corrosion resistant metals used in medical devices or implants present particular challenges. According to literature (Black, J., in “Biological Performance of Materials: Fundamentals of Biocompatibility”, Mercel Decker Inc, New York, 1992), the electrical potential of metallic biomaterial can range from -1 to 1.2 V vs. SCE (saturated calomel reference) in the human body. The high potential in the human body can cause localized pitting corrosion and crevice corrosion even for well known corrosion resistant metals

such type 316L stainless steels (SS316L) which show a pitting breakdown potential ranging from 0.4 to 0.8 V vs. SCE . See "An assessment of ASTM F2129 Electrochemical testing of small medical implants – lessons learned", S. N. Rosenboom and R. A. Corbett, NACE Corrosion 2007 Conference & Expo, Paper No. 07674 and "Pitting corrosion behavior of austentic steels – combining effects of Mn and Mo additions", A. Pardo et. al, Corrosion Science 50 (2008) 1796-1806.

Most anticorrosion coatings in the prior art act as electrical barrier for electronic and ionic migration at the metal surface. Protection of metals from corrosion is much more difficult when they are used in highly aggressive environments such as sea water and human body which consist of aqueous electrolyte solutions containing large amount of highly corrosive species such as chloride ions. Small defects in the coating may rapidly lead to deterioration of the coating-metal interface and cause peeling and flaking of the coating.

Coatings formed from polyelectrolytes are known to provide anticorrosion protection. For example, U.S. Publication No. 2004/0265603A1 discloses an anticorrosion polyelectrolyte multilayer (PEM) coating comprising a polyelectrolyte complex of two oppositely charged strong polyelectrolytes.

The disclosed PEM coatings are made by layer-by-layer (LbL) alternative deposition of poly(diallyldimethylammonium chloride) (PDAD), a strong cationic (positively charged) polyelectrolyte, and poly(styrene sulfonate) (PSS), a strong anionic (negatively charged) polyelectrolyte. Although the PEM coatings disclosed in U.S. Publication No.-2004/0265603A1 suppress localized pitting corrosion of stainless steel, additional improvement for controlling general corrosion below E_b is desired.

There are a number of references which teach various PEM systems but do not suggest their use as corrosion protective coatings. For example, Kharlampieva, E. et al. *Macromolecules* **2003**, 36, 9950 disclose PEM deposition onto hydrophilic Si crystals. The PEM system taught is a cationic copolymer of acrylamide and dimethyldiallylammonium chloride, a strong cationic polyelectrolyte and poly(methacrylic acid), a weak anionic polyelectrolyte.

Regine v. Klitzing, *Phys. Chem. Chem. Phys.*, 2006, 8, 5012–5033 discloses deposited multilayers assembled from a copolymer of poly(4-styrenesulfonic acid-co-maleic acid), a strong anionic and weak anionic polyelectrolyte deposited in alternation with poly(allylamine hydrochloride), a weak cationic polyelectrolyte onto silicon wafers.

Tjipto et. al, *Langmuir* **2005,** *21,* 8785-8792 teaches Poly(styrenesulfonate acid-co-maleic acid) assembled into multilayer thin films with polyallylamine hydrochloride (a weak cationic polyelectrolyte) on silicon wafers, quartz and glass

It has been found, however, that there is still a need for greater corrosion protection of metal, especially at the free corrosion near the open circuit potential (OCP) or the corrosion potential (E_{cor}) and to accomplish this safely, conveniently and economically without deterioration of mechanical stability. There is also a need for anticorrosion coating on metallic medical devices and implants which reduce metal ion release to surrounding body environment which release, ultimately causing pain to the patient.

Summary of the Invention

Accordingly the object of the present invention is to provide compositions which when applied onto metal give a coating which is characterized by improved corrosion protection. A further objective of the invention is to control corrosion at potential lower than the pitting breakdown potential (E_b) and especially the free corrosion near the open circuit potential (OCP) or the corrosion potential (E_{cor}).

Additional objectives of the present invention are to provide coating compositions which are mechanically stable and do not blister or peel when exposed to severe environments; to provide coatings which display some self-assembly characteristics which give even, smooth, organic coatings which are easily applied via layer by layer alternative dipping, spraying or coating without intervening drying steps; to reduce the number of deposition layers in PEM systems while still maintaining sufficient corrosion protection and finally to provide uniform, excellent adhesion which follow the contours and irregularities of the substrate, properties which are particularly valuable in coatings for medial devices and implants.

Accordingly the invention described below:

The invention encompasses several embodiments elaborated below:

A polyelectrolyte complex, a coated metal substrate comprising the polyelectrolyte complex, a method of protecting a metal substrate from corrosion, a kit of parts for the making or manufacture of an anticorrosion coating on a metal substrate and the use of the polyelectrolyte complex as an anticorrosion coating for a metal substrate, especially in medical devices and implants

Accordingly the polyelectrolyte complex comprises polyelectrolytes (A) and (B), wherein polyelectrolyte (A) is an anionic polyelectrolyte containing strongly and negatively charged groups (A_s) and weak acid groups (A_w) and
polyelectrolye (B) is a cationic polyelectrolyte containing strongly and positively charged groups (B_s) and weak base groups (B_w),
wherein groups (A_w) and groups (B_w) are reactible with each other to form covalent bonds.

The coated metal substrate comprises a

a) metal substrate and

b) a coating on said substrate comprising a polyelectrolyte complex which complex comprises polyelectrolytes (A) and (B), wherein polyelectrolyte (A) is an anionic polyelectrolyte containing strongly and negatively charged groups (A_s) and weak acid groups (A_w) and
polyelectrolye (B) is a cationic polyelectrolyte containing strongly and positively charged groups (B_s) and weak base groups (B_w),
groups (A_w) and groups (B_w) are reactible with each other to form covalent bonds and

c) optionally, further comprising an antimicrobial agent.

The invention also embodies a method of protecting a metal substrate from corrosion wherein the method of protecting the metal substrate from corrosion comprises

i.) applying to the substrate a polyelectrolyte (A) and a polyelectrolyte (B) to form complex, wherein
(A) is an anionic polyelectrolyte containing strongly and negatively charged groups (A_s) and weak acid groups (A_w) and
(B) is a cationic polyelectrolyte containing strongly and positively charged groups (B_s) and weak base groups (B_w), wherein
A_w) and (B_w) are reactible with each other to form covalent bonds;

ii.) optionally, applying an after-treatment of the applied complex to form covalent bonds between groups (A_w) and groups (B_w),

and

iii.) optionally, contacting the metal substrate, incorporating into or onto either the polyelectrolyte (A) and/or polyelectrolyte (B) or
contacting the applied complex with an antimicrobial agent.

A kit of parts is further envisioned for the manufacture or making of the coated corrosion resistant metal substrate, comprising
a first part (A) comprising an anionic polyelectrolyte containing strongly and negatively charged groups (A_s) and weak acid groups (A_w) and a second part (B) comprising a cationic polyelectrolyte containing strongly and positively charged groups (B_s) and weak base groups (B_w),
wherein groups (A_w) and groups (B_w) are reactible with each other to form covalent bonds,
and
an optional third part comprising an antimicrobial agent,
which parts when applied to the metal substrate form a coated metal substrate as described above.

The corrosion resistant coatings of the invention have numerous applications. Envisioned applications are any metal surface needing protection from corrosion. However, some specific application that especially come to mind are steel pipes carrying

petroleum and natural gas which must be protected from catastrophic corrosion failure, metal surfaces exposed to very corrosive environments such as desalination plants. Metallic medical device and implants are especially envisioned. Further, uses of the corrosion resistant coating of the invention are electronic equipments and devices, printed circuit boards, batteries, jewelry and automotive coatings.

Detailed Description of the Invention

The term "comprising" for purposes of the invention is open ended, that is other components may be included. Comprising is synonymous with terms such as including and containing.

Metal substrate

The metal substrate includes any materials which have a tendency to corrode. For example, the metals selected from the groups I A, IIA, IIIA, IVA, VA, VIA, IIIB, IVB, VB, VIB, VIIB, VIII B, IB, IIB, of the periodic table. Metal includes alloys.

Typical metal substrates may be selected from the group consisting of iron, aluminum, magnesium, copper, titanium, beryllium, silicon, chromium, manganese, cobalt, nickel, palladium, lead, cerium, cadmium, molybdenum, hafnium, antimony, tungsten, tantalum, vanadium, mixtures and alloys thereof.

Preferably the metal substrate is steel, aluminum, titanium, chromium cobalt, chromium, mixtures or alloys thereof. Most preferably the metal substrate is a steel alloy such as stainless steel (316L), aluminum, titanium, titanium alloy or chromium-cobalt alloy.

The metal substrate may be any shape or form. The substrate of course, includes not only planar surfaces but three-dimensional substrates. For example, the substrate may be a flake, tube, pipe or metal parts.

Preferably the metal substrate is at least a part of a medial device or implant.

The metal coating, method of protecting the metal substrate or kit of parts are especially suitable for metal substrates which comprise at least a part of a medical devices or implant.

Polyelectrolyte

Polyelectrolytes are known to be polymeric substances. The polyelectrolytes may be either natural (protein, starches, celluloses, polypeptides), modified natural or synthetically derived polymers. The natural polymers may be modified natural polymers such as cationically modified starch or cationically modified cellulose. The polyelectrolytes bear a plurality of charged units arranged in a spatially regular or irregular manner. The charged units may be either anionic or cationic.

Preferrably the polyelectrolytes are synthetically derived.

The synthetically derived polyelectrolyes may be homopolymers or copolymers formed from monomers, condensants or oligomers.

The monomers are generally ethylenically unsaturated molecules capable of polymerization. The monomers once polymerized give repeat units that are charged but may additionally contain neutral repeat units (e.g. positive and neutral; negative and neutral; positive and negative; or positive, negative and neutral).

Copolymers are defined as macromolecules or polymers having a combination of two or more repeat units.

The present polyelectrolytes may be virtually any type of molecular architecture. They may be linear, random, grafted, branched, dentritic, star, block or gradient polymers.

Polyelectrolytes can be described in terms of charge density (meg/g). Suitable polyelectrolytes can have a total charge density (q) of from 0.5 to 60 meq/g, preferably from 1.0 to 40 meq/g, more preferably from 2 to 30, and most preferably from 3.0 to 20.

The total charge density includes contribution from the charged groups as well as potentially chargeable groups of the weak electrolyte groups which become charged depending on pH. Thus, the total charge density is the sum of charge density (q_s) contributed from strong electrolyte groups and the charge density (q_s) contributed from the weak electrolyte groups : $q = q_s + q_w$. Suitable polyelectrolytes containing both strong and weak electrolyte groups for our invention can have a q_w/q_s ratio of from 1/99 to 99/1, preferably from 5/95 to 95/5, more preferably from 10/90 to 90/10, and the most preferably from 20/80 to 80/20.

The molecular weight of the synthetic or natural polyelectrolyte (A) or (B) (either the cationic or anionic (A) and (B)) is typically 1,000 to 10,000,000 Daltons, preferably 100,000 to 3,000,000, most preferably 5,000 to 1,000,000.

The molecular weight specified is a preferably weight average molecular weight (M_w) which can be determined by a typical light scattering method or a GPC (gel permeation chromatography) method.

Polyelectrolyte (A) containing groups A_s and A_w

(A) is an anionically charged polyelectrolyte. (A) contains both strongly and negatively charged groups (A_s) and weak acid groups (A_w).

While (A) may contain other nonionic repeat units formed from nonionic monomers, the charged repeat units on (A) will preferably not include cationic repeat units.

A_s

A_s for purposes of the invention means groups which are part of a repeat unit of the polyelectrolyte (A) which are both negatively charged and strongly charged. Strong means the A_s groups are ones which dissociate completely in solution to give a charge density substantially independent of pH. Thus these groups will substantially retain their negative charge regardless of the pH of solution they may be dissolved or dispersed within.

Strong anionic electrolyte groups (A_s) are anionic groups of a dissociated strong acid. Strong anionic electrolyte groups (As) are preferably anionic groups characterized by a pK_a value less than 2.5.

A_s groups are preferably sulfate, sulfonate, phosphate, hydrogen phosphite, phosphoric acid, mixtures or salts thereof. Accordingly, a synthetic polyelectrolyte (A) may be formed from monomers containing a sulfate, sulfonic acid, phosphate, hydrogen phosphite, phosphoric acid and phosphonic acid groups which when polymerized will give repeat units containing these moieties.

Preferably A_s has a pK_a of its conjugated acid less than 2.5, most preferably less than 2.0 and especially less than 1.0.

The A_s groups on the polyelectrolyte (A) most preferably are repeat units formed from monomers selected from the group consisting of styrene sulfonic acids , vinylsulfonic acid, allyl sulfonic acid, (meth)acrylamidopropyl sulfonic acid, vinyl phosphonic acid and salts thereof, especially styrene sulfonic acids and (meth)acrylamidopropyl sulfonic acid and salts thereof.

Strongly and anionically charged natural polymers are also envisioned as the (A) polyelectrolyte. For example, sulfonated polysaccharides may be produced by reacting a cyclic sultone such as 1,3-propane sultone with a polysaccharide. Phosphonated polysaccharides may be produced by reacting a polysaccharide with a cyclic phosphoric acid.

In contrast to the A_s groups, the term weak means A_w groups are not fully charged but dissociate partially in solution depending on the pH of the solution or dispersion containing the polyelectrolyte (A) containing the A_w moieties. The charge density of the weak anionic group is therefore pH dependent. For example, an A_w group will normally be more completely dissociated (ionized) at a high pH. The A_w group will typically be a carboxylic acid. The carboxylic group is located on the repeat units of polyelectrolyte (A) and the repeat units may be formed from monomers containing a carboxylic acid.

Preferably A_w has a pK_a value ranges from 2.0 to 7.0, most preferably from 3 to 6. At a pH of the pK_a value, half of the A_w will become charged. The amount of A_w become deprotonated or negatively charged will increase with increasing pH.

Preferably, the A_w group of the polyelectrolyte (A) will be part of a repeat unit formed from a monomer selected from the group consisting of (meth)acrylic acid, maleic acid or anhydride, itaconic acid or anhydride, crotonic acid and mixtures and salts thereof. (Meth) acrylic acid includes methacrylic acid and acrylic acid.

Alternatively the A_w on the polyelectrolyte (A) may be a carboxylated natural polymer such as a carboxylated polysaccharide.

The preferred polyelectrolyte (A) having both A_s and A_w groups are polyelectrolytes wherein the A_s group is a sulfonic, sulfate, phosphate, hydrogen phosphate or phosphoric acid groups , most preferably sulfonic or sulfate groups and the A_w group is a carboxylic acid group.

Synthetic polyelectrolytes (A) may be obtained from homopolymerization of an anionic monomer containing both groups (A_s) and A_w groups. However, most typically, a synthetic polyelectrolyte (A) will be formed from a first anionic and second anionic monomer. The first monomer will contain strongly and negatively charged groups (A_s) and the second monomer will contain weak acid groups (A_w).

Preferably the polyelectrolyte (A) is a synthetic polymer and contains repeat units formed from a first anionic monomer containing an A_s group wherein the first monomers are selected from the group consisting of styrene sulfonic acids , vinylsulfonic acid, allyl sulfonic acid, (meth)acrylamidopropyl sulfonic acid, vinyl phosphonic acid and salts thereof, especially styrene sulfonic acids and (meth)acrylamidopropyl sulfonic acid and salts thereof

and

a second anionic monomer containing A_w groups are selected from (meth)acrylic acid, maleic acid or anhydride, itaconic acid or anhydride, crotonic acid and mixtures and salts thereof, especially (meth) acrylic acid, maleic acid, itaconic acid.

Preferred synthetic polyelectrolytes (A) are poly(styrenesulfonate-co-maleic acid), poly(styrenesulfonate-co-methacrylic acid), poly(styrenesulfonate-co-acrylic acid), and poly(styrenesulfonate-co-itaconic acid).

The anionic monomers used in the polymerization may be in the acid or salt form. Polymers obtained from the acid monomer may be converted to anionic polymer salts by neutralization with a suitable base. For example, the salts of the sulfonic acids and carboxylic acids may be neutralized with an ammonium cation or a metal cation selected from the group consisting of Groups IA, IIA, IB and IIB of the Periodic Table of Elements. Preferably the salts of the sulfonic acids and carboxylic acids are salts of ammonium cations such as $[NH_4]^+$ and $[N(CH_3)_4]^+$, or K+ or Na+.

Polyelectrolyte (B) containing groups B_s and B_w

The Cationic polyelectrolyte (B) is analogous to polyelectrolyte (A) but oppositely charged.

(B) is an cationically charged polyelectrolyte. (B) contains both strongly and positively charged groups (B_s) and weak base groups (B_w).

While (B) may contain other nonionic repeat units formed from nonionic monomers, the charged repeat units on (B) will preferably not include anionic repeat units.

B_s

B_s for purposes of the invention means groups which are part of a repeat unit of the polyelectrolyte (B) which are both positively charged and strongly charged. These groups are permanent cationic groups independent of pH.

B_s groups are preferably quaternary ammonium, sulfonium, phosphonium, mixtures thereof or salts thereof. Accordingly, a synthetic polyelectrolyte (B) may be formed from monomers containing a quaternary ammonium, sulfonium, phosphonium groups which when polymerized will give repeat units containing these moieties.

Suitable monomers which carry B_s groups are for example phenyl methacrylate dimethylsulfonium nonaflate, allyl sulfonium (e.g., dimethylallyl sulfonium bromide, diallylmethyl sulfonium bromide, 2-ethoxycarbonyl-2-propenylthiophenium hexafluoroantimonate), allyl phosphonium (e.g., allyl triphenyl phosphonium bromide), diallyldimethyl ammonium chloride (DADMAC), diallyldimethyl ammonium bromide, diallyldimethyl ammonium sulfate, diallyldimethyl ammonium phosphates, diethylallyl dimethyl ammonium chloride, diallyl di(beta-hydroxyethyl) ammonium chloride, and diallyl di(beta-ethoxyethyl) ammonium chloride, dimethallyldimethyl ammonium chloride, dimethylaminoethyl (meth)acrylate methyl chloride quaternary, diethylaminoethyl (meth)acrylate methyl chloride quaternary, dimethylaminoethyl (meth)acrylate dimethylsulfate quaternary and dimethylaminoethyl (meth)acrylate benzyl chloride quaternary.

The B_s groups on the polyelectrolyte (B) are preferably repeat units formed from monomers selected from the group consisting diallyldimethyl ammonium chloride (DADMAC), diallyldimethyl ammonium bromide, diallyldimethyl ammonium sulfate, diallyldimethyl ammonium phosphates, diethylallyl dimethyl ammonium chloride, diallyl di(beta-hydroxyethyl) ammonium chloride, and diallyl di(beta-ethoxyethyl) ammonium chloride, dimethallyldimethyl ammonium chloride, dimethylaminoethyl (meth)acrylate methyl chloride quaternary, diethylaminoethyl (meth)acrylate methyl chloride quaternary, dimethylaminoethyl (meth)acrylate dimethylsulfate quaternary, dimethylaminoethyl (meth)acrylate benzyl chloride quaternary.

The B polyelectrolyte may be a natural polymer containing strong and cationically charged B_s groups. For example, quaternized chitosan and cationic starch are well known in the art.

In contrast to the B_s groups, the term weak in reference to B_w groups means these groups are not fully charged but dissociate partially in solution depending on the pH of the solution or dispersion containing the polyelectrolyte (B). The charge density of the weak base group is therefore pH dependent. For example, an B_w group will normally be more completely dissociated (ionized) at a low pH. The B_w group will typically be a primary, secondary or tertiary amine. The amine is located on the repeat unit of the

polyelectrolyte (B) and the repeat units may be formed from monomers containing the primary, secondary, tertiary amine or acid addition salts thereof.

B_w can become positively charged when it associated with a positively charged proton H^+ and thus the pH will affect the amount of the protonated B_w. The amount of B_w become protonated or positively charged will increase with decreasing pH.

Suitable pK_a for the B_w may range from 3 to 14, preferably from 5 to 12, and more preferably from 6 to 11.

Preferably, the B_w group of the polyelectrolyte (B) will be part of a repeat unit formed from a monomer selected from the group consisting of diallylamine, methyldiallylamine, allylamine, methylallylamine, dimethylallylamine, and their salts, aminoalkyl (meth)acrylates such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, and 7-amino-3,7-dimethyloctyl (meth)acrylate, and their salts including their alkyl and benzyl quaternized salts; N,N'-dimethylaminopropyl acrylamide and its salts, vinylimidazole and its salts, and vinyl pyridine and its salts, vinylamine (obtained by hydrolysis of vinyl alkylamide polymers) and its salts.

Most preferably, the B_w group will be part of a repeat unit formed from a monomer selected from the groups consisting of diallyamine, vinylimidazole, vinyl pyridine, vinyl amine (obtained by hydrolysis of vinyl alkylamide polymers), dimethylaminoethyl (meth)acrylate and salts thereof.

Natural polymers of interest having amine functionality are for example chitosan and polylysine.

The preferred polyelectrolyte (B) having both B_s and B_w groups are polyelectrolytes wherein the B_s group is a quaternized ammonium, sulfonium or phosphonium group, most preferably a quaternized ammonium group and the B_w group is a primary, secondary or tertiary amine group.

Synthetic polyelectrolytes (B) may be obtained from homopolymerization of an cationic monomer containing both groups (B_s) and B_w groups, for example, an amine

and a quaternary ammonium groups. However, most typically, a synthetic polyelectrolyte (B) will be formed from a first and second monomer. The first monomer will contain strongly and cationically charged groups (B_s) and the second monomer will contain weak base groups (B_w).

Preferably the polyelectrolyte (B) is a synthetic polymer and contains repeat units formed from a first cationic monomer containing a B_s group wherein the first monomers are selected from the group consisting of diallyldimethyl ammonium chloride (DADMAC), diallyldimethyl ammonium bromide, diallyldimethyl ammonium sulfate, diallyldimethyl ammonium phosphates, diethylallyl dimethyl ammonium chloride, diallyl di(beta-hydroxyethyl) ammonium chloride, and diallyl di(beta-ethoxyethyl) ammonium chloride, dimethallyldimethyl ammonium chloride, dimethylaminoethyl (meth)acrylate methyl chloride quaternary, diethylaminoethyl (meth)acrylate methyl chloride quaternary, dimethylaminoethyl (meth)acrylate dimethylsulfate quaternary, dimethylaminoethyl (meth)acrylate benzyl chloride quaternary.

and

a second cationic monomer containing B_w groups and the second monomers are selected from diallyamine, vinylimidazole, vinyl pyridine, vinyl amine (obtained by hydrolysis of vinylalkylamide polymers), dimethylaminoethyl (meth)acrylate and salts thereof.

Preferred synthetic cationic polyelectrolytes (B) of the present invention are copolymers of DADMAC with diallylamine.

The polyelectrolyte (B) preferably comprises at least 1 to 99 weight percent, most preferably 5 to 80 weight percent, and especially 20 to 60 weight percent, of B_s repeat units and 1 to 99 weight percent, preferably 5 to 80 weight percent, and most preferably 20 to 60 weight percent, one or more weak B_w repeat units and optionally, 0 to 90 weight percent of nonionic repeat units, all weights based on the total weight of polyelectrolyte (B).

The polyelectrolytes (A) and (B) are at least partially soluble in water. Partially soluble in water means 1 gram of solute is soluble per liter, preferably > 10, and most preferably > 50, g solute in one liter is considered as water soluble.

The complex of polyelectrolytes (A) and (B) will form an insoluble complex in water.

The layered coatings may be prepared by any means know in the art such as brushing, spraying, drop casting, spin coating, draw down, substrate immersion. However, immersion or dipping the substrate for a period of time is a simple and reproducible process providing excellent results and is a good approach for layer by layer deposition.

Thus polyelectrolyte multilayers (PEM) can be formed by a sequence wherein a substrate is conveniently immersed or dipped into a solution of a cationic polymer for a selected period of time, removed, rinsed, and then immersed or dipped into a solution of an anionic polymer for a selected period of time before being removed and rinsed. The sequence may be repeated until a film of the desired thickness is prepared.

The polyelectrolyte solution comprises an appropriate solvent. The polyelectrolytes (A) and (B) are at least partially soluble in water or polar solvents. Thus the formation of a solution or dispersion of (A) and (B) is simple to implement. The application of (A) and (B) does not require drying steps in between the layer by layer deposition. Excess application of either (A) or (B) may be removed for example, by rinsing the previously (A) coated surface with water, then continuing to build up the successive layers by successive dipping and rinsing.

When applying the polyelectrolytes ((A) and (B)) via layer by layer deposition within a solution or dispersion, the concentration of the polyelectrolyte solutions may range from 0.01 to 200 grams/liter, more preferably 0.5 to 100 and most preferably 1 to 10.

Preferably the coating is applied to the metal via a layer-by-layer deposition in sequence of the cationic polymer (B) and the anionic polymer (A) in solutions forming the polyelectrolyte complex on the metal substrate.

This layer-by-layer deposition in sequence may be repeated multiple times resulting in a multilayered coating.

Post Treatment of Coating

Post heat treatment of applied complex on the metal substrate gives further improved anticorrosion and mechanical properties. The said heat treatment comprises heating the PEM coated metals at a temperature above 100 °C and below decomposition temperature of the PEM coating for a period ranging from 1 minutes to 24 hours. Preferably, the temperature for the heat treatment is from 140 to 200 °C. Preferably, the heat treatment is carried out in vacuum so as to promote the crosslink (between B_w and A_w) reaction by removing possible small molecular weight byproduct such as water from the condensation reaction.

It is believed that the weak acid A_w and weak base B_w groups provide a secondary ionic and/or hydrogen bonding interaction between (A) and (B) and potential for crosslinking. The formation of covalent bonds via crosslinking, secondary ionic and/or hydrogen bonding further contribute to the stability and corrosion resistance of the coating as well as offering higher corrosion protection with fewer multiple layers.

Antimicrobial Agent Incorporation

Suitable antimicrobial agents including antimicrobial metal agents such as silver metals, ions or complexes may further comprise the anticorrosion coating. The inventors have determined that this addition to the coating surprisingly improves corrosion protection. This corrosion protection is further elaborated in co-pending provisional application number 61/318,838, filed March 30, 2010.

The antimicrobial agent includes for example, noble metals such as silver, copper, gold, iridium, palladium and platinum. Preferably, metal ions from silver and copper with known antimicrobial activity are envisioned such as monovalent Ag(I) (or

Ag^+) and divalent Ag(II) (or Ag^{2+}), silver ions, both of which are known to be excellent antimicrobial and biocide agents.

Silver ions can be incorporated into the coatings by using inorganic and/or organic silver salts. Examples of usable silver salt compounds include but are not limited to silver nitrate, silver sulfate, silver fluoride, silver acetate, silver permanganate, silver nitrite, silver bromate, silver salicylate, silver iodate, silver dichromate, silver chromate, silver carbonate, silver citrate, silver phosphate, silver chloride, silver bromide, silver iodide, silver cyanide, silver, silver sulfite, stearate, silver benzoate, and silver oxalate. Salts such as silver nitrate, silver fluoride, silver acetate, silver permanganate, silver citrate, silver salicylate have reasonable water solubility and are well suited for use in solution for treating the polymer coating on the metal substrate.

The antimicrobial agent may be selected from the group consisting of ions of silver, copper, gold, iridium, palladium and platinum. Preferably, the antimicrobial agent is a silver salt or ion.

Complex sliver ions can be prepared from a silver salt in an aqueous medium containing excessive amounts of a cationic or anionic or neutral species which are to be complexed with silver. For example, $AgCl_2^-$ complex ions can be generated by placing $AgNO_3$ salt in an aqueous solution containing excessive amount of NaCl. Similarly, the $Ag(NH_3)_2^+$ complex ions can be formed in aqueous solution by adding silver salt to excess ammonium hydroxide. The $Ag(S_2O_3)_2^{3-}$ ions may be formed in aqueous solution by adding $AgNO_3$ to excess sodium thiosulfate.

Incorporation of the antimicrobial agent into the coatings of the invention can be realized either by first applying the polyelectrolyte(s) onto the metal substrate and then treating the applied coating with a solution containing antimicrobial agent, or the antimicrobial agent can be incorporated into either one of the polyelectrolytes, followed by application of the antimicrobial agent containing polyelectrolyte to the substrate.

Alternatively, the antimicrobial agent, preferably a silver salt may be applied as a salt solution to pretreat the metal substrate before application of the polyelectrolytes (A) and (B).

Examples

Film thickness, morphology and layer-by-layer film buildup is measured using AFM and ATR-FTIR. Electrochemical methods are used to evaluate corrosion of uncoated and coated samples.

The raw materials used for the preparation of polyelectrolyte multilayer coatings are shown in Table A.

Table A. raw materials used for the preparation of polyelectrolyte multilayer coatings

	Chemical name and composition	Abbreviation	source
A1	poly(styrenesulfonate-co-maleic acid) sodium salt; **(3:1)** 4-styrenesulfonic acid:maleic acid mole ratio, powder, M_w ~20,000	PSSMA25	Aldrich
A2	Poly(styrenesulfonate sodium), M_W 70,000	PSS70	Aldrich
A6a	Poly(acrylic acid), M_w ~15,000	PAA	
A13	Dextran sulfate	DXS	Aldrich
A14	Poly(galacturonic acid)	PGA	Aldrich
B2	Poly(diallylamine-co-DADMAC), 25/75 mole, 30.6% active (11zs8C6), M_w ~ 300,000	DAA25	CIBA
B5	Poly(allylamine)hydrochloride, M_w ~ 15,000	PAH	
B7	Poly(diallyldimethylammonium chloride), pDADMAC, Alcofix 111 M_w ~ 450,000	pDAD	CIBA
B8	Chitosan	CTS	
D1	Phytic acid	PY	Fisher
	silver nitrate in water	AG	

Layer-by-layer (LbL) deposition of polyelectrolyte multilayers (PEM)

Layer-by-layer (LbL) assembled polyelectrolyte multilayer (PEM) films are prepared by cyclic sequential dipping of a metal substrate into a cationic polyelectrolyte solution (polymer B) and an anionic polyelectrolyte solution (polymer A) with deionized water rinses in between as shown by the following general procedure:

1. Dip in Polymer **B** solution for 10 minute;
2. Rinse in DIW for 3 minutes;
3. Dip in Polymer **A** solution for 10 minute;
4. Rinse in DIW for 3 minutes; record $(B/A)_i$ double layer number, i
5. Stop if coated double layer number i equal to the desired number, n ; otherwise go back to step 1

If n is a whole number such as n = 20, the PEM coating has 20 double layers and ends with anionic polymer A as the outmost layer. If n is a whole and half number such as n = 20.5, the PEM coating has 20.5 double layers and ends with cationic polymer B as the outmost layer.

Electrochemical corrosion tests

A modified ASTM G5-94 reference test method for making potentialstatic and potentiodynamic polarization measurements as described below. Similar potential dynamic and potentialstatic polarization using 0.7M NaCl electrolyte solution was also used in US patent 2004/0256503A1.

The wire to be tested is placed as working electrode in an electrochemical cell containing testing electrolyte solution (0.7M NaCl in deionized water with a pH of about 6.0 or phosphate buffered saline (PBS) with a pH of 7.4), a Ag/AgCl (3M NaCl) reference electrode and a platinum wire counter electrode. The electrolyte solution in the cell is purged with high purity nitrogen gas before starting the electrochemical testing. The area of the wire dipped in the electrolyte solution is 1.0 cm^2. Open circuit potential (OCP) monitoring, anodic polarization scans and chronoamperometric scans are obtained using a Solartron 1287A Electrochemical Interfacer (ECI) with CorrWare software. The Electrochemical Impedance Spectroscopy (EIS) is carried out using a Solartron 1252A Frequency Response Analyzer (FRA) with a ZPlot software over the frequency (f) of 300,000 to 0.05 Hz with 5 mV AC amplitude. A series of electrochemical tests are carried out continuously in the sequence listed in Table B to test anticorrosion properties of the uncoated (also referred to as bare) and coated wires.

Table B. Electrochemical corrosion tests and testing conditions

Step	Measurements

OCP-1	Open circuit potential (OCP) monitoring 5000 sec
Zplot-1	Impedance spectroscopy: AC amplitude 5 mV vs OCP frequency scan from 300k to 0.05 Hz
PD-1	Potentiodynamic polarization: sweep from -100 mV (vs OCP) to +900 mV (vs ref) at 0.1667 mV/s scan rate
PS-1	Potentiostatic polarization: +600 mV/300 sec
OCP-2	OCP monitoring 3000 sec
PS-2	Potentiostatic polarization: +700 mV/14 h
OCP-3	OCP monitoring 3000 sec
Zplot-2	Impedance spectroscopy: AC amplitude 5 mV vs OCP frequency scan from 300k to 0.05 Hz

The PD-1 measurement provide most information about anticorrosion properties including corrosion potential, E_{corr}, corrosion current, I_{corr}, and polarization resistance, R_p, of free corrosion near OCP, pitting and breakdown corrosion potential, E_b. The PS-2 measurement tests long term durability of the coatings to withstand long term (14 hours) testing of static anodic polarization at pitting breakdown potential (700 mV) of bare type 316 stainless steel. In case the pitting breakdown occurs during the PS-2 test, the time it begins (t_b) is reported.

The traditional Tafel fit of the polarization scans near E_{oc} using CorrView software yields data of corrosion current (I_{corr}, $\mu A/cm^2$), corrosion potential (E_{corr}, mV), and beta Tafel constants Ba and Bc. The polarization resistance can then be calculated using Stern-Geary relationship:

$$R_p = (Ba*Bc)/[2.303*(Ba+Bc)*I_{corr}]$$

In general, the corrosion potential (E_{corr}) is slightly lower than, but close to, the open circuit potential (E_{oc}).

The EIS analysis (Zplot-1) just before the PD-1 measurement gives information about free corrosion properties near the open circuit potential (OCP). The polarization resistance is given by the difference of measured impedance (Z) at sufficiently low and

high frequencies (f). (Impedance Spectrosopcpy: Theory, Experiment, and Applications, Edited by E. Barsoukov and J. R. MacDonald, published by John Wiley & Sons, New Jersey in 2005, page 344)

$R_p = Z(f \rightarrow 0) - Z(f \rightarrow \infty)$

As the value of the impedance at high frequency is usually negligible compared to that of the impedance at low frequency, the value of the polarization resistance is close to the impedance at low frequency. In the present study, data of the impedance at 0.05 Hz, Z(0.05Hz) measured in Zplot-1 testing, is used to compare corrosion resistance of different samples. Similar to R_p, a high Z(0.05Hz) value indicate high corrosion resistance.

Example 1: PEM2 coatings with 20 double layers of polymer A1 and Polymer B2 (16zs200DWH)

Vacuum arc remelted stainless steel 316LVM (ASTM F138 chemistry) wires (1.25 mm in diameter) purchased from Smallparts.com were abraded with SiC (1200 grit) sand paper purchased from Fisher Scientific Co., degreased with isopropanol, and then washed with deionized water (DIW) in an ultrasonic bath for 10 minutes. Some of such cleaned wires are tested as uncoated and served as a control for comparison. Some of the cleaned wires are coated with anticorrosion polymers and tested in the same conditions.

Polyelectrolyte multilayer coatings of 20 double layers $(PEM2)_{20}$ of polymer A1 (poly(styrenesulfonate-co-maleic acid) sodium salt) and polymer B2 (Poly(diallylamine-co-DADMAC)) are deposited on freshly abraded and ultrasonically cleaned 316LVM stainless steel (SS316LVM) wires using the above stated layer-by-layer deposition method. The PEM2 coatings are obtained from Polymer A solution made of 10 mM poly(styrenesulfonate-co-maleic acid) sodium salt (A1) in 0.25M NaCl aqueous solution and Polymer B solution made of 10 mM Poly(diallylamine-co-DADMAC) (B2) in 0.25M NaCl aqueous solution.

PEM2-H coatings of the heat treatment are obtained by treating PEM2 coated SS316LVM wires in a 170 ^{o}C vacuum oven for 17 hours. The treated wires are rinsed

with deionized water (DIW) and dried with a nitrogen stream. Uncoated SS316LVM wires are also treated in the same conditions (16zs223H) for comparison in corrosion testing.

Electrochemical corrosion tests are carried out on coated and uncoated SS316LVM wires in 0.7M NaCl solution. The potentiodynamic polarization curves from the PD-1 testing are compared in Figure 1 for bare SS316L wire (C curve), SS316L wire coated with 20 double layer PEM-2 polymers (B curve), and SS316L wire coated with 20 double layers of PEM-2 polymers and heat treated in 170 ^{o}C vacuum oven for 3 hrs (A curve). Bare SS316L wires show significant pitting corrosion with a breakdown potential E_b of 700 mV, beyond which a sustained corrosion current occurs. The plot for bare wire also contains random current spikes indicating meta-stable pitting before pitting breakdown at 700 mV. Wires coated with 20 double layer of PEM-2 coatings exhibit significant improvement in corrosion resistance. The meta-stable pitting is suppressed and there is no pitting breakdown up to the 900 mV potential observed. The heat treatment (170 C/3 hrs) of the PEM-2 coated wires provides significantly further improvement in corrosion resistance. The anodic polarization current for $(PEM\text{-}2)_{20}$ coatings with the heat treatment is significantly lower than that for $(PEM\text{-}2)_{20}$ coatings without the heat treatment (Figure Ex1). The free corrosion properties near OCP are also improved significantly as shown by the data in Table Ex1. With the heat treatment on the PEM-2 coated SS316LVM wires, the corrosion potential, E_{corr}, increased from 21 to 118 mV, corrosion current, I_{corr}, decreased about 5 times from about 30 to 6 nA/cm^2, and the polarization resistance, R_p, increased about 5 times from 714 to 3500 k Ω*cm^2.

For comparison (see comparative example 1 for more details), the heat treated (170 ^{o}C vacuum oven for 3 hours) and bare SS316LVM wires are subjected to the same electrochemical corrosion tests. The heat treatment of SS316LVM treated raised significantly the corrosion potential, E_{corr}, but did not suppress pitting corrosion breakdown. The heat treated wire had a pitting corrosion breakdown potential (780 mV) slightly higher than that (700 mV) for untreated wire.

This example demonstrated benefit of the heat treatment with polyelectrolyte multilayer coatings for anti-corrosion improvement on medical grade SS316LVM stainless steel. Significant improvement in anti-corrosion properties can be achieved by

heat treatment of coated SS316LVM to promote crosslink and thus improving the coatings' protective properties.

Table Ex1. Data from Zplot-1, PD-1 and PS-2 tests for SS316L wires uncoated and coated with PEM-2.

Wire ID	coatings	Z(0.05Hz)	E_{corr}	I_{corr}	R_p	E_b	t_b(700mV)
		$K\Omega*cm^2$	mV	$\mu A/cm^2$	$k\Omega*cm^2$	mV	Hr
Bare SS316L	No	30	-128	0.093	285	700	0
16zs200DW	$(PEM-2)_{20}$	60	21	0.029	714	No	> 14
16zs200DWH	$(PEM-2)_{20}$ + heat*	107	118	0.006	3500	No	> 14

*heat in 170 °C vacuum oven for 17 hours

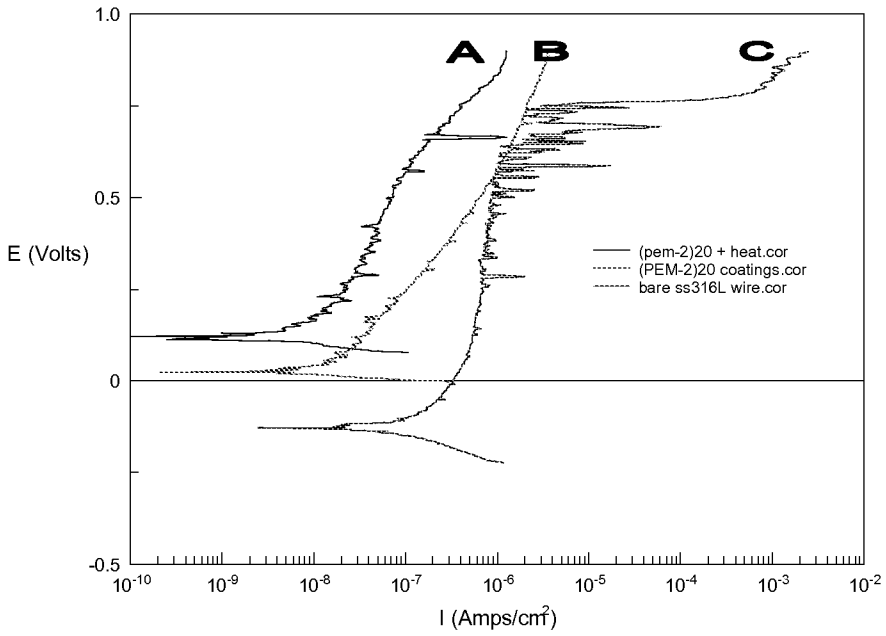

Figure Ex1: Potentiodynamic polarization curves from the PD-1 testing, bare SS316L wire (A curve), SS316L wire coated with 20 double layer PEM-2 polymers (B curve), and SS316L wire coated with 20 double layers of PEM-2 polymers and heat treated at 170 °C for 3 hours (C curve)

Comparative Example 1: (heat treated SS316L**)** (16zs223H)

Uncoated bare SS316LVM wires are heat treated in a vacuum oven at 170 °C for 3 hours. For comparison, the heat treated and bare SS316LVM wires are subjected to the same electrochemical corrosion tests as in Example 1. As can be seen from Figure C1 and Table C1, The heat treatment of SS316LVM treated raised significantly the corrosion potential, E_{corr}, but did not suppress pitting corrosion breakdown. The heat treated wire had a pitting corrosion breakdown potential (780 mV) slightly higher than that (700 mV) for untreated wire.

Table C1 Data from Zplot-1, PD-1 and PS-2 tests for heat treated and untreated SS316L wires.

Wire ID	reference	E_{corr}	I_{corr}	R_p	E_b	t_b(700mV)
		mV	$\mu A/cm^2$	$k\Omega/cm^2$	mv	hr
Bare SS316L	Bare 316	-128	0.093	285	700	0
SS316L heat treated	16zs223H	198	0.016	1610	780	0

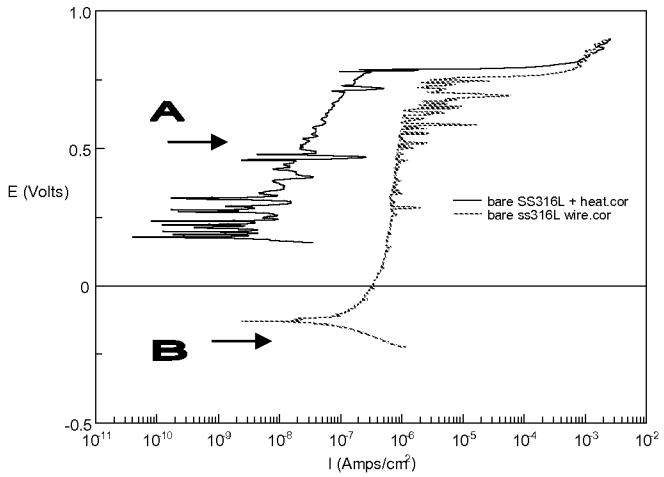

Figure C1: Potentiodynamic polarization curves from the PD-1 testing, bare SS316L wire (B curve), SS316L wire treated in 170 C vacuum oven for 3 hour (A curve)

Example 2: PEM2 coatings with 20 double layers of polymer A1 and Polymer B2 on phytic acid treated SS316LVM wires (16zs200PWH)

Freshly abraded and ultrasonically cleaned 316LVM stainless steel (SS316LVM) wires were immersed in a solution of 10 mM of phytic acid and 0.25 NaCl for 40 minutes, rinsed with deionized water for 1 minute and dried with nitrogen stream flow. Such phytic acid treated wires are identified by symbol Py for the phytic acid monolayer coating.

Polyelectrolyte multilayer coatings of 20 double layers $(PEM2)_{20}$ of polymer A1 (poly(styrenesulfonate-co-maleic acid) sodium salt) and polymer B2 (Poly(diallylamine-co-DADMAC)) are deposited on the phytic acid treated 316LVM stainless steel (SS316LVM) wires using the same layer-by-layer deposition method as described in Example 1. PEM2-H coatings of the heat treatment are obtained by treating PEM2 coated SS316LVM wires in a 170 ^{o}C vacuum oven for 17 hours. The treated wires are rinsed with deionized water (DIW) and dried with a nitrogen stream.

The PD-1 electrochemical corrosion testing results are shown in Figure Ex2 and Table Ex2. The treatment of phytic acid on SS316L fairly improved anticorrosion properties. Adding a 20 double layer PEM2 coatings on the Py treated SS316L greatly improved the anticorrosion properties. The heat treated PEM2 coatings $(Py/(PEM\text{-}2)_{20}$ + heat) gave lowest corrosion current density (I_{corr}), highest corrosion potential (E_{corr}) and highest polarization resistance (R_p). The benefit of improved anticorrosion properties from heating the reactive PEM2 coatings can thus also be seen on phytic acid treated SS316LVM substrate.

Table Ex2. Data from Zplot-1, PD-1 and PS-2 tests for SS316L wires uncoated and coated with PEM-2.

Wire ID	coatings	E_{corr}	I_{corr}	R_p	E_b	t_b(700mV)
		mV	$\mu A/cm^2$	$k\Omega*cm^2$	mV	hr
Bare SS316L	no	-128	0.093	285	700	0
16zs212PY	PY	-203	0.026	670	No	4 h
16zs200PW	$Py/(PEM\text{-}2)_{20}$	42	0.011	3650	No	>14

16zs200PWH	Py/(PEM-2)$_{20}$ + heat*	210	0.005	6180	No	> 14

*heat in 170 °C vacuum oven for 17 hours

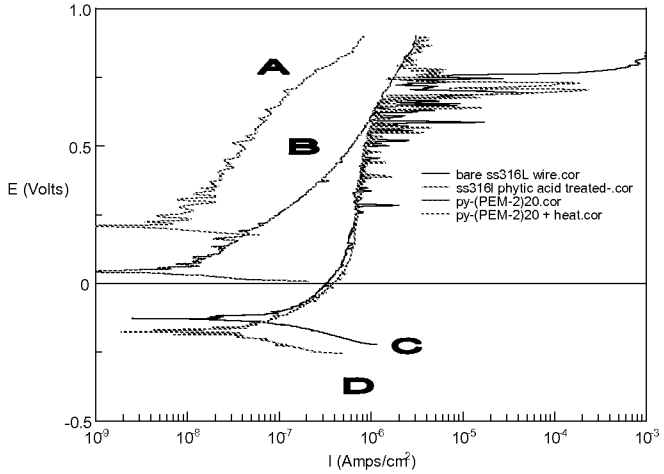

Figure Ex2: Potentiodynamic polarization curves from the PD-1 testing, bare SS316L wire (C curve), Py treated SS316L wire (D curve), Py treated SS316L wire coated with 20 double layer PEM-2 polymers (B curve), and Py treated SS316L wire coated with 20 double layers of PEM-2 polymers and heat treated at 170 °C for 3 hours (A curve)

Example 3: PEM2 coatings with 12 double layers of polymer A1 and Polymer B2 (16zs238PEM2W12AH)

Polyelectrolyte multilayer coatings comprising 12 instead of 20 double layers of polymer A1 and polymer B2 $(PEM2)_{12}$ were prepared on SS316LVM wires in the same ways as described in Example 1 $(PEM-2)_{12}$.. Some of the $(PEM-2)_{12}$ coated SS316L wires were heat treated in vacuum oven at 170 °C for 3 hours ($(PEM-2)_{12}$+Heat). The PD-1 electrochemical corrosion testing results are shown in Figure Ex3 and Table Ex3. The heat treated PEM2 coatings gave low corrosion current density ($\underline{\mathbf{I}_{corr}}$) and high corrosion potential ($\underline{\mathbf{E}_{corr}}$) and polarization resistance (R_p). The benefit of improved anticorrosion properties from heat treatment in the PEM2 coatings can also be seen with reduced double layers number (12) and thus decreased coating film thickness.

Table Ex4. Data from PD-1 testing for PEM2 coatings with 12 double layers of polymer A1 and Polymer B2

Wire ID	Coatings	E_{corr}	I_{corr}	R_p	E_b
		mV	$\mu A/cm^2$	$k\Omega*cm^2$	mV
Bare SS316L	No	-128	0.093	285	**700**
PEM2W12	$(PEM\text{-}2)_{12}$	65	0.004	2270	no
PEM2W12AH	/$(PEM\text{-}2)_{12}$+Heat	171	0.003	3790	no

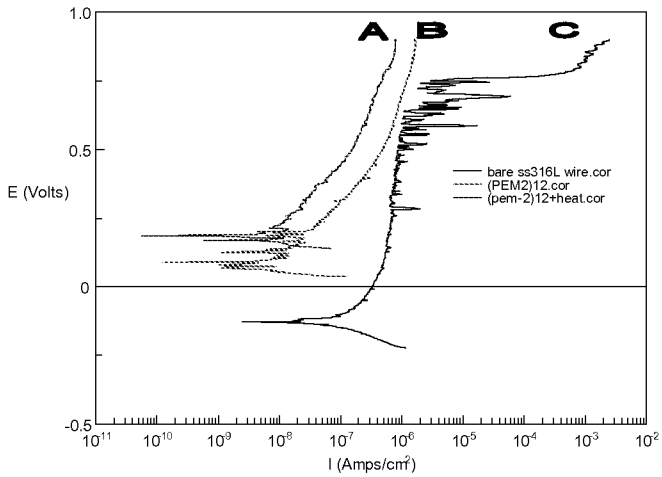

Figure Ex4: Potentiodynamic polarization curves from the PD-1 testing, bare SS316L wire (C curve), SS316L wire coated with 12 double layer PEM-2 polymers (B curve), and SS316L wire coated with 12 double layers of PEM-2 polymers and treated in vacuum oven at 170 C for 3 hours (A curve).

Example 4: PEM2 coatings with 12 double layers of polymer A1 and Polymer B2 with phytic acid pre-treatment (16zs238PEM2W12BH)

Polyelectrolyte multilayer coatings comprising 12 instead of 20 double layers of polymer A1 and polymer B2 $(PEM2)_{12}$ were prepared on Py pre-treated SS316LVM wires in the same ways as described in Example 2 (Py/$(PEM\text{-}2)_{12}$). Some of the $(PEM\text{-}2)_{12}$ coated SS316L wires were heat treated in vacuum oven at 170 ^oC for 3 hours (Py$(PEM\text{-}2)_{12}$+Heat). The PD-1 electrochemical corrosion testing results are shown in

Figure Ex4 and Table Ex4. The heat treated PEM2 coatings gave low corrosion current density (I_{corr}) and high corrosion potential (E_{corr}) and polarization resistance (R_p). The benefit of improved anticorrosion properties from heating the reactive PEM2 coatings can also be seen with reduced double layers number (12) and thus decreased coating film thickness.

Table Ex4. Data from PD-1 testing for PEM2 coatings with 12 double layers of polymer A1 and Polymer B2

Wire ID	coatings	E_{corr}	I_{corr}	R_p	E_b
		mV	$\mu A/cm^2$	$k\Omega*cm^2$	mV
Bare SS316L	No	-128	0.093	285	700
PEM12W12B	$Py/(PEM\text{-}2)_{12}$	87	0.019	1261	no
PEM12W12BH	$Py/(PEM\text{-}2)_{12}$+Heat	152	0.002	8060	no

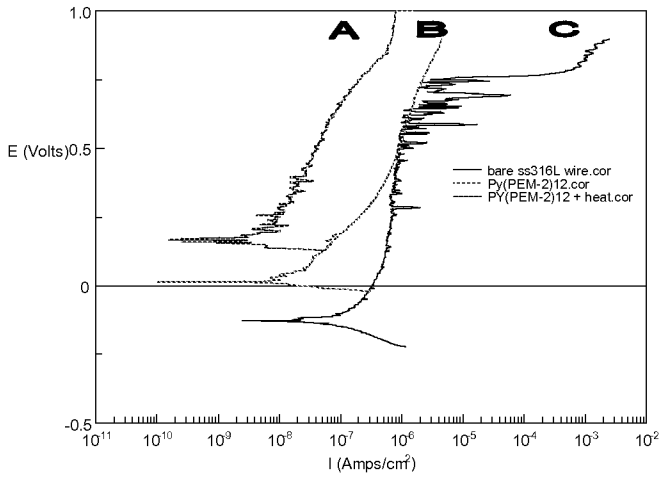

Figure Ex4: Potentiodynamic polarization curves from the PD-1 testing, bare SS316L wire (C curve), SS316L wire coated with 12 double layer PEM-2 polymers (B curve), and SS316L wire coated with 12 double layers of PEM-2 polymers and treated in vacuum oven at 170 C for 3 hours (A curve)

Example 5: PEM2 coatings with 2 double layers of polymer A1 and Polymer B2 (16zs233PEM2W6A)

Polyelectrolyte multilayer coatings comprising 6 instead of 20 double layers of polymer A1 and polymer B2 $(PEM2)_6$ are prepared on SS316LVM wires in the same ways as described in Example 1 $(PEM\text{-}2)_6$. Some of the $(PEM\text{-}2)_6$ coated SS316L wires are heat treated in vacuum oven at 170 °C for 3 hours ($(PEM\text{-}2)_6$+Heat). The PD-1 electrochemical corrosion testing results are shown in Figure Ex5 and Table Ex5. The heat treated PEM2 coatings gave low corrosion current density (I_{corr}) and high corrosion potential (E_{corr}) and polarization resistance (R_p). The benefit of improved anticorrosion properties from heating the reactive PEM2 coatings can also be seen with reduced double layers number (6) and thus decreased coating film thickness.

Table Ex5. Data from PD-1 testing

Wire ID	coatings	E_{corr}	I_{corr}	R_p	E_b
		mV	$\mu A/cm^2$	$k\Omega*cm^2$	mV
Bare SS316L	No	-128	0.093	285	700
PEM2W6	$(PEM\text{-}2)_6$	112	0.008	3400	No
PEM2W6 +heat	$(PEM\text{-}2)_6$ + heat	148	0.003	4240	No

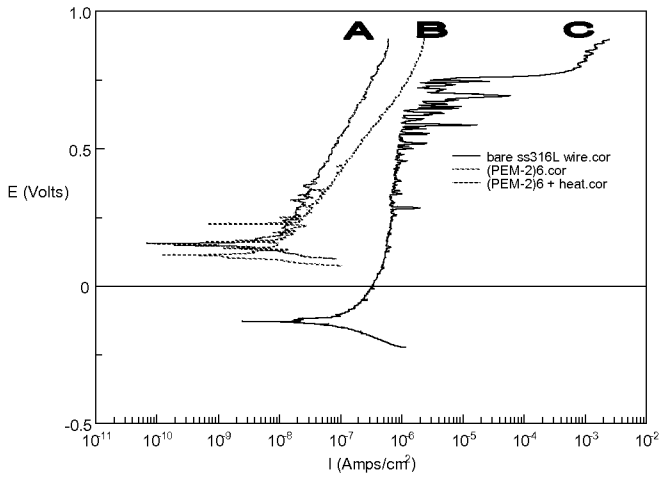

Figure Ex5: Potentiodynamic polarization curves from the PD-1 testing, bare SS316L wire (C curve), SS316L wire coated with 6 double layer PEM-2 polymers (B curve), and

SS316L wire coated with 6 double layers of PEM-2 polymers and treated in vacuum oven at 170 C for 3 hours (A curve)

Example 6: PEM2 coatings with 2 double layers of polymer A1 and Polymer B2 (16zs233PEM2W2A)

Polyelectrolyte multilayer coatings comprising 2 instead of 20 double layers of polymer A1 and polymer B2 $(PEM2)_2$ were prepared on SS316LVM wires in the same ways as described in Example 1 $(PEM-2)_2$. Some of the $(PEM-2)_2$ coated SS316L wires were heat treated in vacuum oven at 170 °C for 3 hours ($(PEM-2)_2$+Heat). The PD-1 electrochemical corrosion testing results are shown in Figure Ex6 and Table Ex6. The heat treated PEM2 coatings gave low corrosion current density (I_{corr}) and high corrosion potential (E_{corr}) and polarization resistance (R_p). The benefit of improved anticorrosion properties from heating the reactive PEM2 coatings can also be seen with reduced double layers number (2) and thus decreased coating film thickness.

Table Ex6. Data from PD-1 testing

Wire ID	coatings	E_{corr}	I_{corr}	R_p	E_b
		mV	$\mu A/cm^2$	$k\Omega*cm^2$	mV
Bare SS316L	No	-128	0.093	285	700
PEM2W2	$(PEM-2)_2$	127	0.002	1140	No
PEM2W2-Heat	$(PEM-2)_2$+heat	218	0.002	5550	No

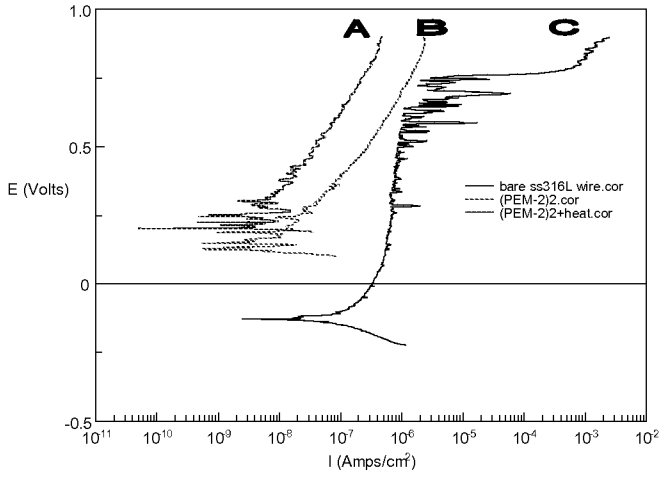

Figure 6: Potentiodynamic polarization curves from the PD-1 testing, bare SS316L wire (C curve), SS316L wire coated with 2 double layer PEM-2 polymers (B curve), and SS316L wire coated with 6 double layers of PEM-2 polymers and treated in vacuum oven at 170 C for 3 hours (A curve)

What we claim are:

1. A polyelectrolyte complex which complex comprises
polyelectrolytes (A) and (B), wherein polyelectrolyte (A) is an anionic polyelectrolyte containing strongly and negatively charged groups (A_s) and weak acid groups (A_w) and polyelectrolye (B) is a cationic polyelectrolyte containing strongly and positively charged groups (B_s) and weak base groups (B_w),
wherein groups (A_w) and groups (B_w) are reactible with each other to form covalent bonds.

2. The polyelectrolyte complex according to claim 1, wherein the polyelectrolyte (B) is a polyelectrolyte (B) having both B_s and B_w groups wherein the B_s group is a quaternized ammonium, sulfonium or phosphonium group, most preferably a quaternized ammonium group and the B_w group is a primary, secondary or tertiary amine group.

3. The polyelectrolyte complex according to claims 1 or 2, wherein the anionic polelectrolyte A having both A_s and A_w groups are polyelectrolytes wherein the A_s group is a sulfonic, sulfate, phosphate, hydrogen phosphate or phosphoric acid groups , most preferably sulfonic or sulfate groups and the A_w group is a carboxylic acid group.

4. The polyelectrolyte complex according to any of the preceding claims , wherein the anionic polyelectrolyte (A) is poly(styrenesulfonate-co-maleic acid).

5. The polyelectrolyte complex according to any of the preceding claims, wherein the polyelectrolyte (B) is a copolymer of diallyldimethylammonium chloride (DADMAC) and diallylamine (DAA).

6. A coated metal substrate comprising a
a) metal substrate,
b) a coating on said substrate comprising a polyelectrolyte complex according to any one of claims 1 to 5 and
c) optionally, further comprising an antimicrobial agent.

7. The coated metal substrate according to claim 6, wherein the metal substrate is at least a part of a medical device or implant.

8. A method of protecting a metal substrate from corrosion comprising the steps of
i) applying to the substrate a polyelectrolyte (A) and a polyelectrolyte (B) to form a complex according to any one of claims 1 to 5,
ii.) optionally, applying an after-treatment to the applied complex to form covalent bonds between groups (A_w) and groups (B_w),
and
iii.) optionally, contacting the metal substrate, incorporation into either the polyelectrolyte (A) and/or (B) or contacting the applied complex with an antimicrobial agent.

9. The method according to any one of claims 6 to 8, wherein the polyelectrolyte (A) and polyelectrolyte (B) are applied sequentially to the substrate via layer-by-layer deposition, wherein the sequential application is optionally repeated.

10. A kit of parts for the manufacture of a corrosion resistant metal substrate, comprising a first part (A) comprising an anionic polyelectrolyte containing strongly and negatively charged groups (A_s) and weak acid groups (A_w) and a second part (B) comprising a cationic polyelectrolyte containing strongly and positively charged groups (B_s) and weak base groups (B_w)
wherein groups (A_w) and groups (B_w) are reactible with each other to form covalent bonds,
and an optional third part comprising an antimicrobial agent,
which parts when applied to the metal substrate form a coated metal substrate according to any one of claims 1 to 5.

11. The use of the polyelectrolyte complex as defined in any one of claims 1 to 5 as an anticorrosion metal coating, preferably wherein the metal coating is on at least a part of a medical device or implant.