Environmentally Friendly Protective Coatings for Metals and Alloys

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ABSTRACT

The operation and maintenance of metal structures is a costly process due to corrosion of metals and/or alloys. Corrosion severely reduces the useful lifetime and adversely affects the quality of resulting products and operational efficiency. Corrosion-resistant protective coatings are an excellent means to address the issue by creating a barrier that prevents access of fluidic substances as a corrosion-mediating electrolyte to the walls of pipes, surfaces of parts and storages causing failure of materials' integrity. Advenira's environmentally friendly SDN® coating technology has authored protective coating formulations that are in compliance with the most stringent EPA regulations. In addition to outstanding performance and being toxic-free, this technology is extremely affordable and intended to replace a plurality of conversion coatings. This paper reports the properties of these coatings for corrosion prevention in water, beverage and food processing and storage systems.

Keywords: Barrier coating, EIS, abrasion resistance, corrosion resistance, water leeching

INTRODUCTION

Metal corrosion has been a major issue for humankind since it began using metal tools thousands of years ago. Besides being unsightly, corrosion is insidious in that it slowly degrades the structural integrity of a metal object over time to the point where the object is no longer functional or useful. In order to mitigate the effects of corrosion there is a need to inspect, test, and maintain or replace corroded parts, objects and structures at regular intervals to verify that they still meet their original design specifications. This process is very costly[1-2].

In its basic form, corrosion can be described as the electrochemical oxidation of a metal when exposed to an oxidizing environment. Water is the most common corrosion-mediating electrolyte. Corrosion is often a non-uniform process, and the nature of corrosion changes with changes with water pH and chemical composition. Over the years, two distinct methods of protecting metals from corrosion have been developed: 1. specialty alloys and 2. protective/barrier coatings.

Both methods can be very effective; however, a cost/performance analysis is often the controlling factor in determining which method is implemented. Specialty alloys are much more expensive than steel or aluminum so they are typically only used in applications where those materials would rapidly fail, such as at high temperatures and unique, highly corrosive environments[3], or where specific material properties are required.

Barrier protection layers are perhaps the oldest and most widely used method of corrosion protection. By applying paint (organic), an anodic metal (Zn), a corrosion inhibitor (chromate) or other protective layer (anodization), the base metal is isolated from the surrounding environment. As long as the barrier layer remains intact, the metal is protected and corrosion will not occur. However, because a barrier must remain intact to provide corrosion resistance, a barrier layer or coating must have excellent adhesion to the base metal, as well as abrasion resistance and be defect free.

For many years, chromates have been widely used as barrier protection coatings for aluminum, zinc and other metals. Steel is typically galvanized prior to chromating. Chromate coatings work because the high oxidation state Cr(VI) causes the base metal to remain in the passive regime and since the product of oxidation of chromate is Cr_2O_3 which itself forms an inert surface film. Another advantage of chromate coatings is their ability to self-heal small imperfections, rubs or scratches. The chromium atoms can move slowly in the coating layer, and will eventually re-coat small scratches or damage. Large cuts or rubbed areas cannot self-heal and require re-treatment. However, chromate coating comes with high health and environmental costs. Hexavalent chromium [Cr(VI)] is a genotoxic carcinogen in humans and is considered an environmental toxin due to its high solubility in water. Some chromate coating baths also contain cyanide.[4]

Advenira's Solution Derived Nanocomposite (SDN®) technology is a platform technology for developing coating formulations for a wide array of applications. SDN® coating formulations based on appropriately functionalized constituents dispersed in a matrix of hydrolyzates, (metal) organic monomers and oligomers or a mixture of the above. SDN® coating formulations allow a high degree of tuning of coating properties via careful selection of major components, their ratios, and additives. We have developed two corrosion resistant formulations, F-series and H-series, with each having unique advantages. The properties of these protective coatings on metal substrates, and their potential for use and anticorrosion coatings for industrial and water distribution and storage systems will be discussed in this paper.

1 MATERIALS AND METHODS

The F-series and H-series coating formulations are proprietary liquid coating formulations. They were synthesized from standard grade precursors and solvents that were used as received. The base synthesis procedure for each formulation family is different, but both involve standard chemical synthesis, purification, and filtration methods. F-series formulations contain nanoparticles in an inorganic-organic matrix and an alcoholic solvent. H-series formulations are solvent-free, with a different composition of nanoparticles in an organic-inorganic matrix. Both formulations allow the deposition of densely cross-linked coatings, which is crucial to their performance as a physical barrier in an aqueous environment.

1.1 Materials Coated and Preparation

A variety of substrate materials were used for this study, including 6061, 6016, 5052, and 2024 aluminum alloys, 1000 series cold-rolled or mild steel (CRS), electro-galvanized CRS (EGS) and 304 and 316 stainless steel. The four grades of aluminum were selected to cover a wide range of potential applications. Cold-rolled steel is commonly used for structural applications and piping, but is readily susceptible to corrosion without a protective coating. 304 and 316 stainless steels are the most widely used austenitic stainless steels. Even though they have good overall corrosion resistance, 304 and 316 are known to be susceptible to pit corrosion when exposed to high chloride environments, especially if the pH is low.

All substrates were cleaned with a commercial alkaline cleaner/degreaser followed by rinsing with deionized water and isopropanol, and drying in clean dry air (CDA) prior to coating. The cleaner also contained additives to help prevent flash rust formation on cleaned CRS surface. In general, the metal coupons were coated immediately after cleaning.

1.2 Characterization of Coating Properties

Corrosion Testing

In terms of characterization, multiple techniques were employed to study the anti-corrosion properties of F-series and H-series coatings. Electrochemical impedance spectroscopy (EIS) measurements were taken with a Solartron 1287 Electrochemical Interface† and Solartron 1260 Impedance/Gain-Phase Analyzer†. The test cell details are as follows: 3.5 wt% NaCl electrolyte, 15 cm^2 cell, Ag/AgCl reference electrode, graphite counter electrode, and 50 mV signal amplitude. EIS data acquisition and analysis were performed using ZPlot and ZView software for Windows†.

In-house acid bubble testing was used as another method of characterizing the anti-corrosion properties of the coatings, using 1M or 11.65M HCl for coatings on Al, and 1M H_2SO_4 for coatings on CRS. The pH value for both 1M HCl and 1M H_2SO_4 is approximately 0, so all of the test solutions are highly acidic. The bubble test is quite common in the semiconductor industry and is often used as a measure of the corrosion resistance of anodized coatings.[5] For the bubble test, the coating surface is exposed to an acid solution by attaching a 25 mm diameter tube to the coating surface and filling the tube with the acid solution. When the coating starts to break down, the acid will attack the metal surface and liberate H_2 bubbles. The amount of time it takes for a continuous stream of bubbles to appear from the surface of a coating can be used to compare the corrosion resistance of one barrier coating versus another. Coatings with varying thickness can be compared by dividing the time by the total coating thickness (typically expressed in $V\mu m^{-1}$). It should be noted that defects in the coating will cause premature failure, so multiple tests (3+) are run on each sample simultaneously to verify the results.

Cyclic accelerated corrosion testing data was acquired using the GMW14872 specification up to 72 cycles and the SAE J2334 specification up to 80 cycles.[6-7] For this study, the GMW14872 test was performed on F-series coated aluminum (6016 and 5052), CRS and EGS panels, as well as and H-series coated Al (5052) and EGS panels. A single 24 h cycle consisted of the following stages: 1.) 8 h ambient stage at 25±3°C, 45±10% RH with a salt fog stress (NaCl: 0.9%, $CaCl_2$: 0.1%, $NaHCO_3$: 0.075%), 2.) 8 h humid at 49±2°C, 100% RH, and a 3.) 8 h dry stage at 60±2°C, ≤30% RH. Test panels were scribed prior to the test and the scribe creep was evaluated after 26, 48 and 72 cycles. The SAE J2334 test was performed on H-series coated CRS, zinc phosphate coated CRS, and E-coat coated CRS reference panels. A single 24 h cycle consisted of the following stages: 1.) 6 h 50°C, 100% RH, 2.) 15 min ambient stage with a salt fog stress (NaCl: 0.5%, $CaCl_2$: 0.1%, $NaHCO_3$: 0.075%), and a 3.) 17.75 h dry stage at 60°C, 50% RH.

Mechanical and Thermal Properties

Multiple techniques were also used to provide detailed information on the general properties of the coatings. Thermal cycling was performed in an environmental chamber. The test panels were subjected to 100 test cycles of -50ºC to 125ºC, with 3ºC per minute ramp rate, and 15-minute hold at the lowest and highest temperature. Abrasion resistance was measured using a Taber Industries 5135 rotary abraser† with CS-10 wheels and a 1 kg load. The abrasion testing was done in accordance to ASTM 4060.[8] A Defelsko Positest AT-A† system was used to measure pull-off adhesion strength on various substrate materials. A 0.7 $MPas^{-1}$ ramp rate and 14

† Trade name

† Trade name

mm diameter dollies were used during the pull-off tests. Microhardness measurements were taken with a Fischerscope HM 2000S† using a 5 mN max load and 10 sec loading settings. Pencil hardness measurements were performed as per ASTM D3363.[9]

Water Extraction Testing

Water extraction testing was performed according to NSF/ANSI 61[10] standard by a State of California certified water quality testing laboratory. A 24 hr. extraction (±2 hr.) of sample mass to deionized water at a 1:20 ratio was conducted at room temperature, followed by analytical testing for heavy metals (analysis methods SW6010B and SW7470A) and organic contaminants (methods SW8260B, SW8270C, 8260TPH and SW8015B(M)). Fully coated 10x10x0.3 cm polycarbonate panels were used for the water extraction test.

2 RESULTS AND DISCUSSION

1.1 Adhesion and Microhardness

Corrosion resistant coatings must be durable so that they can withstand real world handling and exposure conditions without being easily damaged. However, for many anti-corrosion coatings, there is often a trade-off between mechanical and corrosion properties. It is important to understand the limitations of any coating so that the proper coating can be selected for a given application. For this study, the properties of F-series and H-series coatings were tested using coatings that were 10-20 mm thick. Microhardness and pencil hardness data for the F-series and H-series coatings is shown in Table 1. The Martens hardness (HM) of the F coating is double that of the H coatings. F coating also has the highest Vickers hardness (HV), and the lowest plastic deformation component at indentation (n_{plast}), as well as indentation creep (C_{IT1}) that is closely related to plastic deformation. The H-series has a significantly higher plastic deformation component, which indicates a more flexible coating. It should be noted that the measured hardness values are independent of the substrate as long as the coatings are properly cured. The pencil hardness tests confirm that the F-series coating is much harder than the H-series coating (8H vs 4H).

Coating	HM (N/mm^2)	C_{IT1} (%)	n_{plast} (%)	HV (kg/mm^2)	Pencil Hardness
F-Series	450-500	< 2	16	102-114	8H
H-Series	200-240	15	60	20-27.5	4H

Table 1: Typical microhardness data of the F-series and H-series coatings

Table 2 shows a comparison of pull-off adhesion and abrasion weight loss of F and H series coatings on cold-rolled steel (CRS) and Al. Both the F and H-series coatings show excellent pull-off adhesion strength on Al and CRS. In terms of abrasion resistance there is a significant difference between the two coatings. The F-series is highly resistant to wear. In fact is performs better than sealed Type III anodized aluminum in terns of thickness loss per 1000 cycles. The H-series coating has a tenfold increase in abrasion weight loss, compared to the F-series. Although there isn't a direct correlation between hardness and wear resistance, these results are not unexpected given the much higher hardness of the F-series coating. However, it should be mentioned that the H-series coating is actually still has very good wear resistance. A comparison of typical Taber abrasion values for commercially available corrosion protection coatings based on epoxy and polyurethanes, such as 3M Scotchkote Epoxy 162PWX† and Urethane 165PW†, indicates that the H-series would have 1.5-3x better abrasion resistance (lower mass loss) if tested under the same abrasion conditions.[11-12]

Coating	Pull-off adhesion on CRS (MPa)	Pull-off adhesion on Al (MPa)	Abrasion Δmass per 1000 cycles (mg)	Abrasion Δthickness per 1000 cycles (μm)
F-Series	21	24	1.4	0.15
H-Series	16	22	13.8	4.20
Galvanized Steel	-	-	39.1	2.30
Type III Anod. Al	-	-	1.9	0.25
Electroless Ni (Hi P)	-	-	16.3	1.14

Table 2: Comparison of pull-off adhesion and abrasion weight loss of F-Series and H-series coatings

1.2 Thermall Cycling

The ability to withstand various climatic conditions is crucial for the success of protective coating. F-series were deposited Al 5052 and CRS panel and H-series coatings were deposited on Al 5052, CRS and EGS panels were cycled between -50ºC and 125ºC for 100 cycles. During the thermal cycling test, RH values oscillated between 0 and just under 40%. After the 100 cycles, the coatings were inspected for cracking, visual appearance, and changes in adhesion. The H-series panels passed the thermal cycling without changes on all substrates, and so did F-series coated aluminum and CRS. The thermal stress tolerance of the H-series coating in particular is noteworthy since, the highest temperature this coating experienced prior to testing was lower than 65ºC.

1.3 Water Extraction

National Sanitation Foundation (NSF) and Environmental Protection Agency (EPA) in the USA, and their equivavlents

† Trade name

throughout the world set the regulations for allowable concentration of inorganic and organic chemicals in drinking water. Both the F-series and H-series coatings were evaluated in a 24 h water extraction test per NSF/ANSI 61 standard for potential leaching of restricted contaminants.[10,13-14] The results are reported in Table 3.

Parameters:	H-Series	F-Series	Unit
Heavy Metals (HMS): Zn – US EPA limit is 5 mg/L	0.04	0.023	mg/L
HMS: As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mo, Ni, Se, Ag, Tl, V, Hg	ND	ND	mg/L
Halogenated compounds (chloroform etc.)	ND	ND	μg/L
Phthalates	ND	ND	μg/L
Toxic solvents (benzene, pyridine etc.)	ND	ND	μg/L
Gasoline, diesel, motor oil	ND	ND	mg/L

Table 3: Selected NSF/ANSI 61 water extraction test results for F-series and H-series coatings (ND = not detected).

CONCLUSIONS

Using Advenira's proprietary SDN™ technology, we have developed two low cost, environmentally friendly, anti-corrosion barrier coatings that can be applied to both ferrous and nonferrous metals. H-series and F-series coatings are multifunctional, nanocomposite coatings that provide anti-corrosion protection over a wide range of pH values and resistance to chloride and sulfate ion attack. When tested using field correlated cyclic accelerated corrosion testing (GMW14872 and SAE J2334), both coatings meet or exceed the corrosion resistance of chromate coatings on Al. H-series also performs very well on CRS, zinc phosphate coated CRS, and EGS. Both coatings also have excellent abrasion resistance. This unique combination of properties makes H-series and F-series useful for a wide variety of applications, ranging from automotive, industrial, and defense.

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