Environmentally Compliant Protective Coatings for Water Distribution and Storage Systems

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Abstract-The maintenance of water distribution and storage systems worldwide is a costly process due to corrosion. Corrosion severely reduces the useful lifetime of water distribution pipes and mains, and adversely affects the quality of potable water. Corrosion-resistant protective coatings are an excellent means to address the issue by creating a barrier that prevents access of water as a corrosion-mediating electrolyte to the pipe wall and the subsequent dissolution and erosion of contaminants from the pipe wall into the water. Advenira's environmentally friendly Solution Derived Nanocomposite (SDN®) coating technology has yielded two different protective coating formulations. This paper reports the properties of these coatings with particular focus on corrosion prevention in water distribution and storage systems.

Keyword- Protective Coatings; Corrosion; Water Distribution; Environmentally Friendly; Nanocomposite

I. INTRODUCTION

Ferrous metals, e.g. cast iron, ductile iron and various types of steel, form the majority of water distribution pipes installed around the globe. While iron is not known to cause any health concerns to consumers of potable water, the corrosion of ferrous metal pipes contributes to numerous problems. Consumer complaints of undesirable taste and red coloring of drinking water points to transportation of corrosion products (most commonly ferrous oxides and hydroxides) with the flow of potable water. Corrosion is often a non-uniform process, and the nature of corrosion changes with pH and chemical composition of water [1]. The growth of corrosion-induced oxide scale and tubercles can restrict the flow of water and thus decrease water pressure available to the consumer. Eventually, the loss of mass due to corrosion can lead to pipe failure.

There are several approaches to prevent and mediate corrosion in water distribution systems. These approaches can be divided in two major categories. The first is the addition of corrosion inhibitors to water, and the second is corrosion prevention of pipes and tanks by selecting materials with higher corrosion resistance, or the application of an internal liner and external wrapping or coating.

Corrosion control by means of changing the pH and introducing corrosion inhibitors can be quite specific to location; the initial pH and concentration and composition of dissolved ions varies greatly with different water sources. The optimal pH of water for minimal corrosion often depends on the presence of other solutes [2]. Thus it is not surprising if different effects are reported for a particular pH or alkalinity at specific locations [1]. Silica and silicates, as well as phosphates, are well-known corrosion inhibitors that have been used in water treatment for over a century [2].

Various alloys of stainless steel offer higher corrosion resistance as compared to cast iron and ductile iron; however, they also incur sizable increases in cost. Thermoplastic materials such as polyvinyl chloride (PVC) and polyethylene (PE) have recently been used to replace corroded < 25 cm diameter iron pipes in residential areas. Thermoplastic polymers can also be used as liners inside metal pipes. Thermoplastics offer excellent corrosion resistance, but are weakened when placed in contact with organic solvents and gasoline that can be present in soil [3].

Concrete lining is another alternative, sometimes classified as a coating. Concrete applications mainly concern large-diameter pipes and reservoirs. Galvanized iron or steel does not offer significant increases in the lifetime of a water distribution pipe, because they are subject to galvanic corrosion that results in expansive scale. In addition to zinc, they can also leach heavy metal impurities that were incorporated in the galvanization process.

Of known coatings, coal tar is the oldest [3]. Contemporary coatings that have replaced lead-based alkyd paints are based on epoxy, urethane or acrylic chemistry [4]. The recent trend to limit Volatile Organic Compound (VOC) emissions has pushed coating technology development towards solvent-free, high-solids or waterborne coating formulations.

Solution Derived Nanocomposite (SDN®) technology is a platform technology for the development of coating formulations with a wide array of applications. SDN® coating formulations are based on appropriately functionalized nanoparticle constituents dispersed in a matrix of sol-gel 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. This study has developed two families of corrosion resistant coating formulations, F-series and H-series, each with unique advantages. The properties of these protective coatings on metal substrates, and their potential for use as interior and exterior coatings in water distribution and storage systems, will be discussed in this paper.

II. MATERIALS AND METHODS

The F-series and H-series proprietary formulations were synthesized from regular grade (ACS reagent and similar) precursors that were used as received. Cold-rolled steel (CRS), electrogalvanized steel (EGS), stainless steel alloy 304, and aluminum alloys 5052, 6061, 6016 and 2024 were used as metal substrates.

A variant of the widely used alkaline cleaning protocol was used for the ferrous metals and aluminum alloys. The substrates were first wiped with isopropanol-soaked wipes to remove the majority of grease, followed by 10 minutes of ultrasonic cleaning in a Branson ultrasonic bath using a 1:10 v/v aqueous dilution of LPS Precision Cleaner (LPS Laboratories) at 50°C. After ultrasonic cleaning, the substrates were thoroughly rinsed with deionized water, followed by rinsing with isopropanol, and then dried with compressed dry air (CDA).

The cleaned substrates were coated immediately: both dip-coating and Meyer rod coating methods were used for the fabrication of test panels. The F-coated samples require 110°C thermal cure for solvent removal and cross-linking; a standard laboratory oven was used for this purpose. H-coated samples were radiation-cured in inert atmosphere conditions to obtain cross-linking. The coating thickness was measured with a Fischer FMP40 Dualscope, using a magnetic induction probe on steel and an eddy current probe on aluminum panels.

For general characterization of the coatings, pull-off adhesion was evaluated with a Defelsko Positest AT-A system, using a ramp rate of 0.7 MPa/s and dollies 14 mm in diameter. Abrasion resistance was measured using a Taber Industries 5135 rotary abraser with CS-10 wheels and a 1 kg load, in accordance with ASTM 4060. Microhardness was measured with a Fischerscope HM 2000S, using a 5 mN maximal load and 10 second loading.

Thermal cycling was performed in a CSZ ZP(H)-8 environmental chamber (Cincinnati Sub Zero Products, Inc.). The test panels were subjected to 100 test cycles of -50°C to 125°C with a ramp rate of 3°C per minute, and a 15-minute hold at the lowest and highest temperatures.

Accelerated corrosion testing according to GMW14872 was performed by Assured Testing Services (Ridgway, PA), an ISO 17025 accredited laboratory. Test panels were scribed and the scribe creep was evaluated after 26, 48 and 72 cycles according to GMW15282. E-coat reference panels were purchased from ACT Test Panel Technologies (Hillsdale, MI).

Electrochemical impedance spectroscopy (EIS) measurements were performed on a Solartron 1287 Eletrochemical Interface and Solartron 1260 Impedance/Gain-Phase Analyzer. A 15 cm^2 test cell was used, with an Ag/AgCl reference electrode, graphite counter electrode, and 3.5 wt% NaCl electrolyte. A50 mV signal amplitude was used for data acquisition. Data acquisition and analysis were performed using ZPlot and ZView for Windows software from Scribner Associates.

Water extraction test according to the ANSI 61 standard was performed by Torrent Laboratory, Inc. (Milpitas, CA), certified by the State of California. A 24-hour extraction (±2 hours) of a 1:20 sample mass to deionized water ratio was conducted at room temperature, followed by heavy metal analysis (analysis methods: SW6010B and SW7470A) and analysis of organic contaminants (methods: SW8260B, SW8270C, 8260TPH and SW8015B (M)). Fully-coated 0.1 × 0.1 × 0.003 m polycarbonate panels were used for the water extraction test.

III. RESULTS AND DISCUSSION

F-series formulations contained nanoparticles in an inorganic-organic matrix and an alcoholic solvent, whereas H-series formulations were solvent-free, with a different composition of nanoparticles in an organic-inorganic matrix. Both formulations allowed the deposition of densely cross-linked coatings, which is crucial to their performance as physical barrier in aqueous environments. Another prerequisite for a good protective coating is excellent adhesion to the substrate material. The F and H coatings were deposited directly onto the alkaline-cleaned metal surfaces. Both F and H formulations yielded clear and translucent coatings, with a smooth, glossy surface. Fig. 1 shows a steel pipe that has been coated with F coating half-way on both the internal and external walls, and subsequently exposed to corrosive conditions. Red rust tubercles cover the uncoated half of the pipe, whereas the coated half maintains its original glossy appearance.

Fig. 1 A photograph of a 10 cm steel pipe, half-coated with F coating internally and externally, and subjected to accelerated corrosion

The properties of the F and H coatings were typically tested in a thickness range of 10-20 μm. Table I shows a comparison of the pull-off adhesion and abrasion weight loss of F and H coatings on cold-rolled steel (CRS) and commercial 3M Scotchkote coatings on grit blasted steel, as reported by 3M [5, 6]. The first iteration of H coating, formulation H1, demonstrated abrasion resistance equivalent to the F coating, but a lower pull-off adhesion. The H1 formulation also showed lower cross-hatch adhesion due to its brittleness. The improved H coating, formulation HD, demonstrated pull-off adhesion strength equivalent to the F coating, but a tenfold increase in abrasion weight loss. In-house testing at Advenira has shown that abrasion weight loss with CS-17 wheels is approximately twice that of CS-10 wheels when an identical load is used. 3M reports a difference factor of 2.0625 in their datasheet for a different coating, fusion bonded epoxy 226N [7]. Taking the twofold difference into account, Advenira's HD would be comparable to the 3M epoxy and more abrasion resistant than the 3M urethane coating. 3M Scotchkote urethane demonstrates a similar pull-off adhesion as the Advenira coatings, but 3M Scotchkote epoxy demonstrates the lowest pull-off adhesion on steel.

TABLE 1 COMPARISON OF PULL-OFF ADHESION AND ABRASION WEIGHT LOSS OF ADVENIRA'S F- AND H-COATINGS AND 3M SCOTCHKOTE COATINGS CS-10 WHEELS WITH 1 KG LOAD WERE USED AT ADVENIRA. *3M ABRASION TEST IS REPORTED WITH 1KG LOAD, CS-17 WHEELS

Coating	Pull-off adhesion (ASTM D4541) on steel, MPa	Abrasion weight loss, 1000 cycles, mg
Advenira F	17.9-20.7	1.4
Advenira H1	15.5-16.6	1.4
Advenira HD	18.4-19.65	13.8
3M Scotchkote Epoxy 162PWX	12	40*
3M Scotchkote Urethane 165PW	20	90*

The ability to withstand various climatic conditions is crucial to the success of protective coating. The F coating on aluminum 5052 and CRS, and the H1 coating on Al 5052, CRS and EGS panels were cycled between -50ºC and 125ºC temperature extremes for 100 cycles. During the thermal cycling test, RH values oscillated between 0 and just under 40%. H1-coated panels passed the thermal cycling without observed changes on all substrates, as did F coated aluminum and CRS. The thermal stress tolerance of the H1 coating in particular is noteworthy because due to its radiation cure, the maximal temperature this coating experienced prior to testing was lower than 65ºC. The test demonstrated that the H1 coating shows great promise for withstanding freeze/thaw cycles in the real world.

The ability of the F and H coatings to withstand corrosion was evaluated with a GMW14872 accelerated cyclic corrosion test. This test includes an ambient stage at 25±3°C, RH 45±10% for 8 hours, followed by a humid stage at 49±2°C, ~100% RH for 8 hours and a dry stage at 60±2°C, ≤ 30% RH for 8 hours. A stress factor is applied throughout the test; this study used salt spray. The F and H1 coatings were tested alongside automotive industry standard E-coat on chromate or phosphate conversion coating. The thickness of the F coating was 8-9.5μm, H1 coating 17-19μm and E-coat reference coating 17-17.5μm. No conversion coating was applied under Advenira coatings, which were applied directly to the metal. Sixty cycles of the GMW14872 test is correlated to 10 years of outdoor exposure. The passing criterion in the automotive industry is scribe creep ≤ 6 mm. On aluminum 5052, both F and H1 coatings passed 72 test cycles alongside the E-coat references. The F coating failed the test on ferrous substrates (EGS and CRS), suggesting that interfacial modification (an alternative cleaning protocol or conversion/primer layer) is required for direct-to-metal application to ferrous substrates, in spite of the favorable pull-off adhesion test results (Table 1). The H1 coating passed the test on EGS, showing comparable performance with the E-coat reference coatings. On CRS, the H1 coating did not meet the ≤ 6 mm requirement. The formation of corrosion products on iron

is known to result in large volume expansion. Visual and microscopic observations revealed that the brittleness of the coating led to the aggressive creep of the corrosion from the scribe.

To combat this issue, the HD coating formulation was developed with reduced brittleness, confirmed by microhardness measurements. Typical microhardness data for the coatings is shown in Table II. Martens hardness of the F coating is double that of the H coatings. The F coating also has the highest Vickers hardness and the lowest plastic deformation component at indentation (n_{plast}). H1 and HD demonstrate similar ranges of Martens hardness values, but HD has a significantly higher plastic deformation component, which confirms the visual and microscopic observations of its lower brittleness.

TABLE I TYPICAL MICROHARDNESS DATA OF THE F AND H COATINGS: HM − MARTENS HARDNESS, CIT1 − CREEP AT MAXIMUM LOAD, NPLAST − PLASTIC DEFORMATION COMPONENT OF THE INDENDATION, HV − VICKERS HARDNESS

Coating	HM (N/mm^2)	C_{IT1} (%)	n_{plast} (%)	HV (kg/mm^2)
F	450-500	< 2	16	102-114
H1	220-250	5-7.5	40	32-38
HD	200-240	10-15	60	20-27.5

As shown in Fig. 2, the initial scribe width of H1 on CRS was wider (~1 mm) than that of HD, which was less brittle and shows ≤ 0.2 mm initial scribe width. After fourteen days of immersion in 3.5% NaCl solution at room temperature, scribe creep in H1 was highly noticeable while in HD, the creep extended very little from the original scribe. A SAE J2334 accelerated cyclic corrosion test is currently underway for comparison of the H1 and HD coatings on CRS. After 20 cycles, no blistering was observed on either sample, with a red rust rating of 8-9G for H1, and 9G for HD according to ASTM D610.
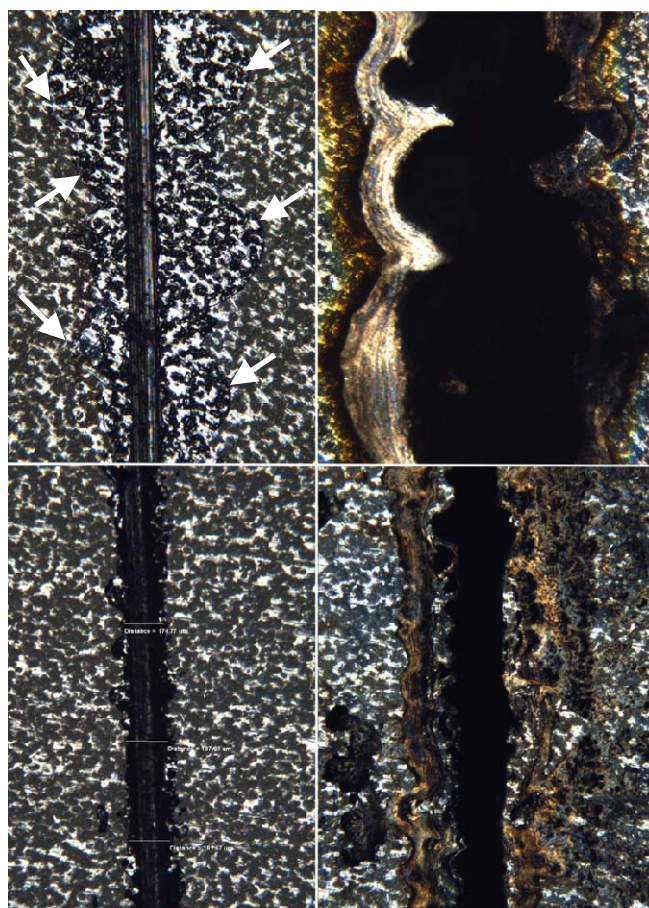

Fig. 2 Optical micrographs at 50 ✕ magnification of the scribed line in H coatings on CRS before and after two weeks of immersion in 3.5% NaCl solution. Top left: H1 before immersion (white arrows are added as a visual guide to show the scribe width). Top right: H1 after immersion. Lower left: HD before immersion. Lower right: HD after immersion

Electrochemical Impedance Spectroscopy (EIS) is a sensitive method for the detection corrosion events prior to the appearance of visual signs [8]. EIS data was acquired for ~20μm thick F and HD coatings on SS 304 substrate for a time period of over 500 hours.
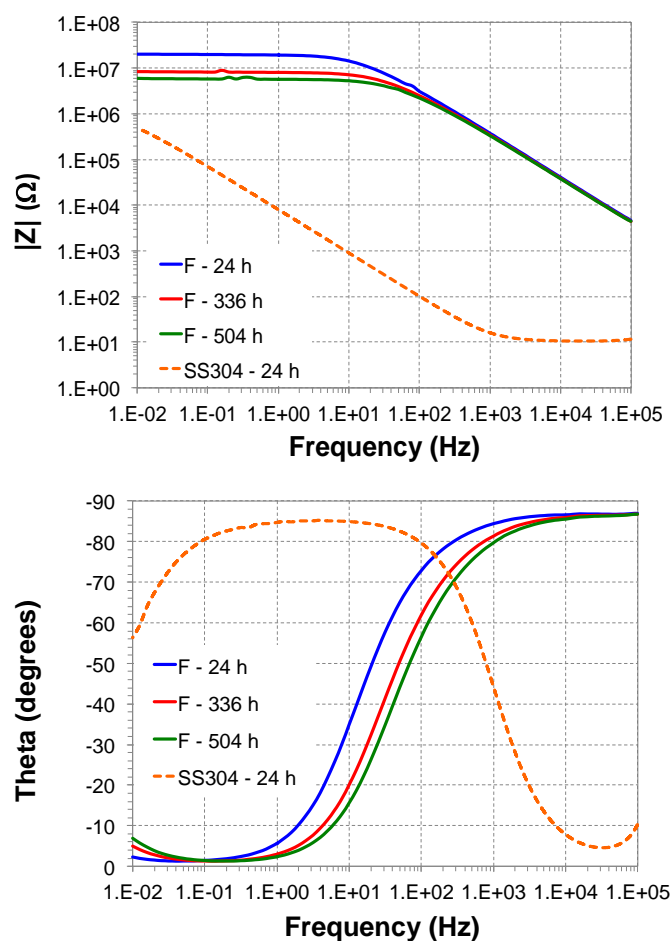
Fig. 3 EIS Bode plots of F coating

The Bode plots in Fig. 3 depict the frequency dependence of impedance modulus |Z| and the phase angle (Theta) for the F coating. The high impedance modulus values of the F coating as compared to bare SS 304 change very little over 504 hours of continuous exposure to salt solution. The absolute value of phase angle is < 80 degrees for most of the frequency range, an indication of dielectric behavior. Thus, the F coating shows good barrier performance against the passage of corrosive species. This is further confirmed by the circuit analysis according to an equivalent circuit as depicted in Fig. 4. The equivalent circuit assumes that corrosion proceeds by the same mechanism as on bare steel, but with a significantly reduced surface area. Coating capacitance, pore resistance and water uptake are calculated from fitting the raw data to the equivalent circuit. Table 3 summarizes the values obtained for the F coating at three points in time. An increase in the coating capacitance and decrease in pore resistance suggest a low water uptake of 2.7% after 504 hours.
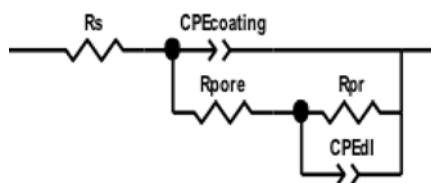

Fig. 4 Equivalent circuit used for EIS analysis

TABLE 3 F COATING PARAMETERS FROM EIS CIRCUIT ANALYSIS

Time (h)	$|Z|_{10mHz}$ (MΩ)	$C_{Coating}$ (pF)	R_{pore} (MΩ)	Water uptake (%)
24	20.2	572	8.3	0.0
336	8.4	624	3.0	2.0
504	5.9	645	2.0	2.7

Bode plots of the HD coating are displayed in Fig. 5. It was observed that the |Z| of the HD coating starts at higher values (~$10^{10}\,\Omega$) than that of the F coating (~$10^{7}\,\Omega$). Very little change is observed in |Z| over 672 hours of exposure, suggesting that HD maintains excellent barrier performance throughout this time.
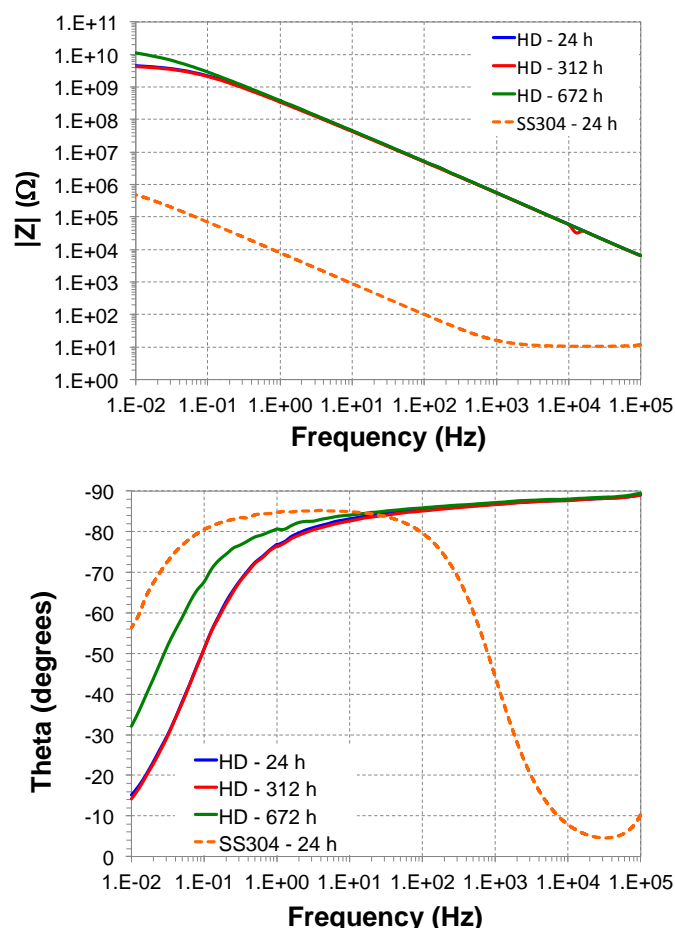
- 247 -

Fig. 5 EIS Bode plots of HD coating

Equivalent circuit analysis for the HD coating (Table IV) displays opposite pore resistance behaviour as compared to the F coating. The increase in pore resistance suggests that an active corrosion inhibition mechanism is present. Water uptake obtained for the HD coating from the EIS analysis is less than that of the F coating at 1.5% after 672 hours.

TABLE 4 HD COATING PARAMETERS FROM EIS CIRCUIT ANALYSIS

Time (h)	$|Z|_{10mHz}$ (GΩ)	$C_{Coating}$ (pF)	R_{pore} (MΩ)	Water uptake (%)
24	4.5	323	5.0	0
312	4.3	326	5.5	0.2
672	11.1	342	27	1.5

The National Sanitation Foundation (NSF) and Environmental Protection Agency (EPA) in the USA, and their equivalents throughout the world, set the regulations for allowable concentrations of inorganic and organic chemicals in drinking water. Both the F coating and HD coating were evaluated in a 24-hour water extraction test per the ANSI 61 standard for potential leaching of restricted contaminants [9].

Some of the parameters analyzed are reported in Table V. No heavy metals and toxic elements (As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mo, Ni, Se, Ag, Tl, V, Hg) were detected in water that was in contact with either the F or the H coating. The 0.04 mg/L level of Zn from the H coating and 0.023 mg/L Zn from the F coating are both well below the 5 mg/L EPA national secondary drinking water regulations. The blank contained 0.0129 mg/L Zn. Water in contact with the F and HD coatings was also tested for 139 different organic contaminants, including benzene, styrene, aniline, phthalates and halogenated compounds, as well as for the presence of gasoline, diesel and motor oil. None of these contaminants were detected in the water that was in contact with the F coating, suggesting that the F coating has potential for use with potable water, provided that additional testing will be performed for NSF approval. From water in contact with the H coating, 2.1µg/L toluene was detected. The Method Detection Limit (MDL) for toluene is 0.14 µg/L, and the Practical Quantitation Limit (PQL) is 0.5µg/L. EPA total allowable concentration for drinking water is 1 mg/L, or 1000 µg/L, over two orders of magnitude higher than the trace quantity detected. Only one other organic contaminant was detected from the water in contact with HD coating: phenol in a concentration of 67 µg/L; PQL for phenol is 14 µg/L. ANSI 61 does not state any official regulatory limits for phenol, but the San Francisco Bay Basin Water Quality Control Plan suggests a risk-based drinking water standard of 1µg/L. Additionally, the Federal Environmental Agency of Germany recommends the same, 1µg/L aesthetic guide value of phenol in drinking water, in order to guarantee the option to

chlorinate water if necessary without deteriorating its aesthetic quality with respect to taste and odour [10]. Further analytical testing of the HD coating would be required to confirm whether the phenol originates from the coating or the polycarbonate substrate. Nevertheless, the lack of other known organic contaminants suggests that the HD coating is not far from meeting the above requirements.

TABLE 5 SELECTED ANSI 61 WATER EXTRACTION TEST RESULTS FOR HD AND F COATINGS. ND – NOT DETECTED

Parameters:	HD	F	Unit
Arsenic	ND	ND	mg/L
Beryllium	ND	ND	mg/L
Cadmium	ND	ND	mg/L
Chromium	ND	ND	mg/L
Copper	ND	ND	mg/L
Lead	ND	ND	mg/L
Mercury	ND	ND	mg/L
Thallium	ND	ND	mg/L
Vanadium	ND	ND	mg/L
Zinc	0.04	0.023	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

IV. CONCLUSIONS

Advenira has developed two protective coatings for corrosion protection in water distribution and storage systems. In terms of their mechanical properties, both coatings compare favorably to competing commercially available products. Between the two proposed coatings, the F coating demonstrates higher hardness and higher abrasion resistance than the H coatings, and it passed the ANSI 61 water extraction test without leaching any toxic contaminants; thus, the F coating would be a good candidate for internal coating of water distribution systems. The HD coating is well suited for corrosion protection of external walls, where it could be applied at higher thickness without the risk of cracking. Both the F and H coating are environmentally compliant as they do not contain toxic solvents, and are phthalate and isocyanate-free.

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She is the CEO, CTO and Founder of Advenira Enterprises, located in Sunnyvale, California, in the United States. She acquired her extensive experience working with novel materials and methods during her tenures at a number of start-ups and corporations in Silicon Valley, among them Xerocoat, Fidelica Microsystems, UltraDots and Applied Materials. She has worked with sol-gels and their derivatives for more than 20 years, and has developed many unique inventions as well as acquired broad experience and in-depth knowledge of the chemistry, processes and hardware necessary to utilize sol-gels for photovoltaic manufacturing.

Dr. Ryabova has more than 30 years of experience, over 25 scientific and technical papers and presentations, and more than 15 patents.