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Evaluation of organic coatings for corrosion protection of condensing economizers

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Abstract

A corrosion protection of Stainless Steel (Grade 304) with low-cost commercial organic coatings (paints) was investigated in this study. Air sprayed Polyurethane (PU)-, Epoxy- and Acrylic-based commercial paints on the above substrate were tested for their anticorrosion properties in prospect of potential application for the protection of condensing economizers from industrial flue gases. PU and Epoxy coatings exhibited better corrosion protection efficiency of stainless steel than the acrylic coatings with values of 40, 39 and 28.1% respectively. This is in total agreement with corrosion current density trend calculated from potentiodynamic polarization curves. Corrosion rates of coatings in 3.5% wt NaCl aqueous solutions were calculated at 0.065, 0.067 and 0.071 mpy for Epoxy, PU and Acrylic coatings respectively. Condensation phenomena and water collection rates (WCR) at various conditions are also provided. The highest WCR exhibited on the epoxy coatings reaching 1.987 ml $m^{-1}h^{-1}$ at 40°C and 100% RH. These data provide a full dataset for the designers of condensing economizer systems willing to incorporate organic coatings either at structural components or as touch up solutions.

Peer-review under responsibility of the scientific committee of the 1st International Conference of the Greek Society of Experimental Mechanics of Materials.

Keywords: Condesning economizer; dropwise condensation; organic coating; corrosion; stainless steel

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1. Introduction

The European directive (Ecodesign) for Energy-related Products (ErP) has been activated since 26 September 2015. In this directive conventional boilers shall be gradually replaced, or modified with condensing heat exchangers, in which the latent heat of the flue gases is exploited. With such operations the energy efficiency can be increased by at least 8% compared to conventional boilers. These facilities exploiting the latent heat of the flue gases are usually referred to as condensing economizers, condensing heat exchangers etc (Attinger et al. (2014)). The condensing economizers can be either incorporated in novel energy production systems, or be attached to conventional and already operating systems. Three are the main issues that have to be addressed in order for this technology to be applied and improve the energy efficiency of novel boiling systems (Dietz et al. (2010)): i) Improve the corrosion protection of the heat exchanging surfaces on which condensation is taking place. Flue gases usually contain SO_x, NO_x, Cl etc, which upon condensation form corrosive solutions such as H_2SO_4, HCl etc (Chen et al. (2017); Duron et al. (2017); Zhuang et al. (2018)). ii) Promote the dropwise condensation (DwC) over the filmwise condensation (FwC) on the heat exchange surface. DwC can deliver heat transfer coefficients (HTC) increased by a factor of 2 compared to FwC (Preston et al. (2015)), and therefore improve the energy efficiency of the condensing economizer (Rykaczewski et al. (2014)). iii) Enhance the easy self-removal of the condensates from the heat exchange surface, which yield to increased HTC (Cai and Bhunia (2017); Ghosh et al. (2014); Hao et al. (2016)).

There are two main routes to address the corrosion issue of condensing surfaces of heat exchangers (a) either to use expensive metals as materials for the fabrication exhibiting low corrosion rates at a condensing economizer environment, or (b) to apply a special coating to protect the base material. Ceramic coatings are able to provide protection in metal substrates at extreme conditions (Stathopoulos et al. (2016); Georgiopoulos et al. (2014, 2018); Marathoniti et al. (2014); Vourdas et al. (2018)). However thermal spraying methods are not straight forward and not as cost efficient as needed for condensing economizers application. In general coatings approach is preferable in terms of cost (Koch et al. (2016)).

In this work we assess a series of low cost commercially available coating solutions (Epoxy, Polyurethane -PU and Acrylic based) easily deposit by air spraying. The substrates used for the above coatings are of Stainless Steel (SS304 Grade) which can be a common structural material for condensing economizers. Corrosion rates on acidic environments, 3-electrode open current potential (OCP) measurements, potentiodynamic polarization curves and condensation phenomena investigation are reported.

2. Experimental protocol

2.1. Preparation of substrates

Commercial SS304 sheets of 0.002 m height was cut by laser in order to provide rectangular coupons of (0.05x 0.03 m) and tubes of 0.0015 mm outside diameter and 0.09 m height were used as substrates for testing purposes in the experiments of this study. Prior organic coating deposition, the preparation of the surfaces involved grinding of the substrates with a 800-grit silicon-carbide abrasive paper with a grinding polishing apparatus (METKON FORCIPOL 1V) and further degreasing with sonochemical treatment in ethanol and acetone. Samples' edges, especially on coupons, were smoothed (Fig.1).

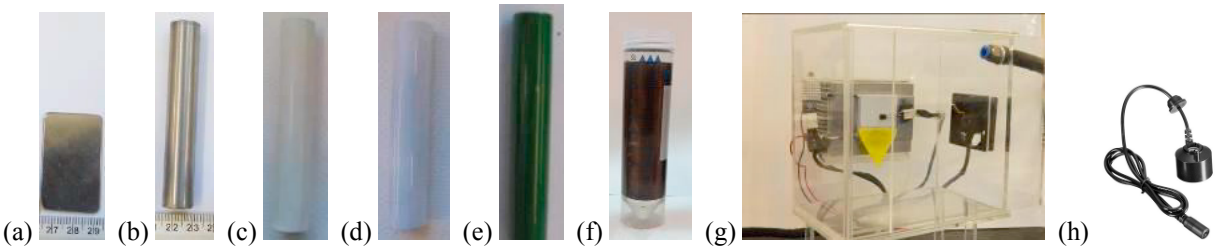

Fig. 1. Specimens used (a) SS304 coupon, (b) SS304 tube (blank), (c) Epoxy, (d) PU, (e) Acrylic, (f) Open polypropylene (PP) testing vials with specimen, (g) lab-scale chamber for droplet condensation assessment, (h) ultrasonic atomizer air humidifier.

2.2. Preparation of organic coatings

Three commercial organic coatings (paints) were used in order to evaluate their corrosion protection capabilities. Epoxy (1300 TDS), Polyurethane (PU) (BOATLAC) and Acrylic-based paints were purchased from Stancolac, Chrotex and Vivechrom respectively. For Epoxy and PU top coatings, epoxy primers were used (914 Epoxy Mastic and Novepox 915 respectively) in order to provide a suitable bond coat between the substrates (SS304) and the top coats. For acrylic coatings no primer was used. For the primer 914 EPOXY mastic, component A and B was prepared by mixing components A and B with a ratio of A:B=4. Finally, a quantity (13%wt) of an epoxy thinner (E1900) was added to the above two component mixture, in order to provide a proper rheology for air spraying. The primer coat was left to dry. The primer (NOVEPOX 951, component A and B) was prepared by mixing the two components (A and B) with a ratio of A:B=4:1 wt%. Finally, a quantity (13%wt) of an epoxy thinner (E1900) was added to the above two component mixture, in order to provide a proper rheology for air spraying. The two primers (NOVEPOX 951 and 914 MASTIC) were deposited within the limits of the suggested thicknesses provided by the datasheet of each company. For the Epoxy topcoat, component I and II was prepared by mixing the two components I and II with a ratio of 4 and a quantity (13%wt) of an epoxy thinner (E1900) was added to the above two component mixture. The top coat of BOATLAC polyurethane color was prepared by mixing components P1 and P2 with a weight ratio of 4 and has been diluted (23%wt) with a S1701 solvent. The acrylic paint was used as purchased. All the above systems showed a proper rheology for spraying gun. The coatings were successfully deposited by a CRESCENDO MODEL 175 spraying gun. The spraying air pressure was kept at 2 bar and the distance of the nozzle and SS304 sample at 20 cm. For coatings deposition ASTM D4228 – 05 was followed and adhesion tests on final coatings were performed based on EN-ISO 2409.

2.3. Corrosion studies on harsh environments

Acid corrosion tests were performed in PP airtight vials (Fig.1c) filled with 40% of H_2SO_4, HNO_3 and HCl solutions respectively. The specimens remained immersed throughout the testing duration. The specimens were weighted before introduced in the chamber, and at specific time set points. At set time specimens were taken out of the chamber, rinsed with deionized water, left to dry, visually inspected and weighed again. The test was ended if there was extensive corrosion of the coupon. As will be evidenced hereafter significant variations among the different coatings were recorded, indicating that this test may facilitate the quick assessment of the quality of the coatings. A controllable heating water bath (BUCHI) was keeping all the coupons at the desired temperature. The temperature was kept stable with ±0.5 ^{o}C throughout the experiments at elevated temperatures. The setup was capable of a maximum simultaneous load of 8 samples. Corrosion rates were estimated on harsh environments (40% of H_2SO_4, HNO_3 and HCl solutions) at room temperature (RT) and at 60 ^{o}C.

2.4. Open Current Potential (OCP) measurements- Potentiodynamic polarization curves

OCP measurements were conducted through a three electrode setup using Saturated Calomel Electrode (SCE) acting as reference and Pt as counter electrode. Experiments were conducted at uncoated (SS304) and coated samples in a borosilicate glass beaker filled with 3.5% wt NaCl aqueous solution under normal stirring and the potential was recorded at least for five days. In addition, Potentiodynamic polarization curves were acquired with a step height of 0.0002 V and potential range (-0.25 … 0.25 V) vs SCE. Data recording were achieved through an AMETEK VersaStat 3 Potentiostat/Galvanostat Station. The linear Tafel segments to the anodic and cathodic curves were extrapolated to corrosion potential in order to calculated corrosion current densities through Stern-Geary equation (Stern and Geary (1957)). The corrosion protection efficiency (% PE) of coated samples was calculated from the measured current densities of coated samples (i_{corr}) and the current density of uncoated (SS304) blank specimen (ic,b) using Eq.(1) (Bish et al. (2016)). Corrosion rates (in mpy) were calculated based on measured current densities i_{corr} of samples (in $\mu A/cm^2$), density of coatings (g/cm^3) based on factory specifications and equivalent weight (EM in g) of coatings according to Eq.(2).

$$\%PE = \frac{i_{c,b} - i_{corr}}{i_{c,b}} \cdot 100 \quad (1)$$

$$R_{corr}\,(mpy) = 0.13 \cdot \frac{i_{corr} \cdot EM}{d} \tag{2}$$

2.5. Condensation phenomena investigation

The construction of a lab-scale plexiglas chamber (box) with 15x15x17 cm dimensions was necessary for the assessment of droplet condensation on the samples of interest. The chamber was designed with controllable moisture and temperature capabilities through an Arduino automation board and sample and chamber temperature was continuously controlled and recorded. A Peltier thermoelectric cooling element was used in order to achieve sub ambient temperature on the sample and humidity was produced through a commercial DC 24V 35×28 mm Ultrasonic Atomizer Air Humidifier (Fig.1d & e). Condensation phenomena were observed for 100% RH @ 20°C and @ 40°C at 5, 7 and 10°C sample's temperature. Water collection rates were calculated out of mean values out of 3 measurements.

3. Results and discussion

Through the CRESCENDO MODEL 175 spraying gun suitable samples were air sprayed showing smooth surfaces and no physical observed defects (Fig.1). For each sample the coating thickness and mass were calculated through Vernier caliper (5-points average) and a 5-digit analytical weight (mass difference before and after the top coating) respectively. All samples were proper adhered according to ISO 2409 tests. After subjecting the samples to 40% H_2SO_4, 40% HNO_3, 40% HCl environments at RT and at 60°C, gravimetric mass loss per surface was recorded. Results are depicted in Fig.2 for 40% H_2SO_4, 40%HNO_3 and 40% HCl respectively.

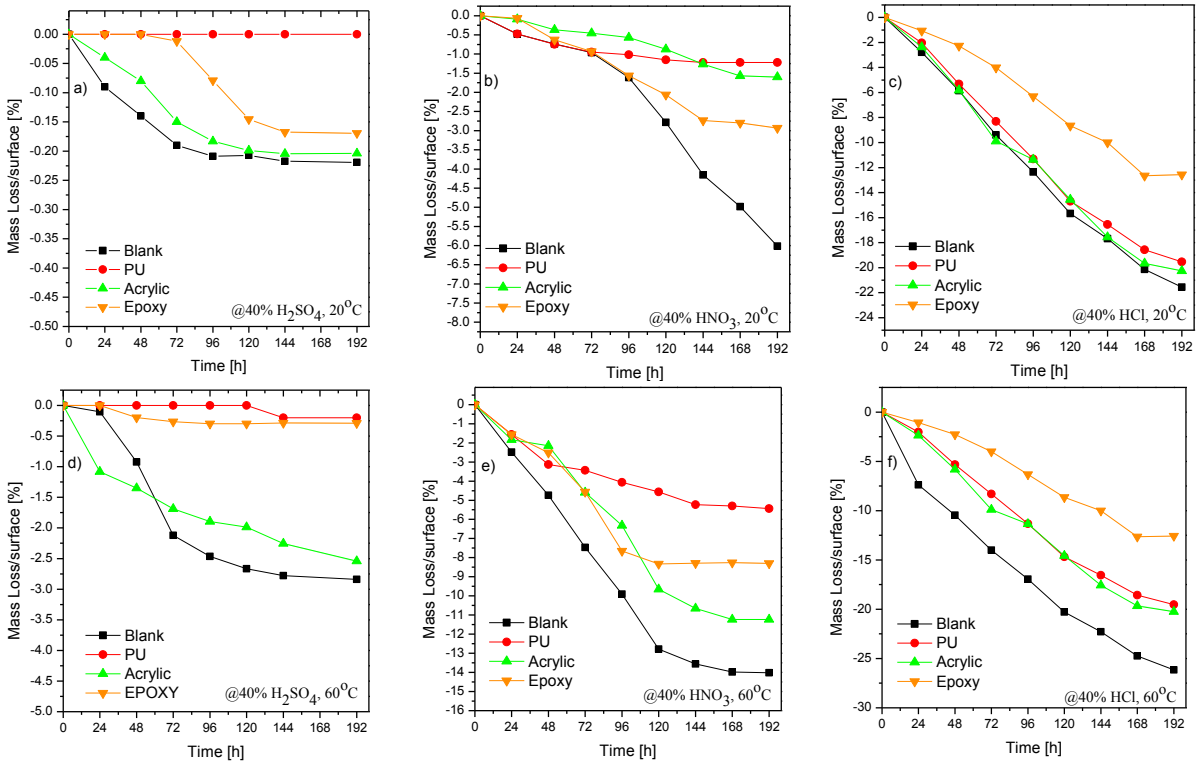

Fig. 2. Mass loss at 20 °C (top row) and 60 °C (lower row) in 40% H_2SO_4 (a), (d), 40% HNO_3 (b), (e) and 40% HCl (c), (f).

According to Fig.2, PU and Epoxy coatings are found to be significantly tolerant under 40% H_2SO_4 for both experimental temperatures. Slightly enhanced anticorrosive capabilities, in comparison with blank samples also was

observed for acrylic sample at 20 °C. At 60 °C acrylic paint is failing which is soon visible making acrylic paint not suitable for harsh H_2SO_4 environments. Under nitric acid rich environments PU paint is tolerant showing the least mass loss in comparison with all the other samples at both 20 and 60 °C. Despite the promising protection properties of acrylic paint at 20 °C no similar behavior was found at 60°C. In Figs.2(c,f)) the behavior of the same samples when tested in 40% HCl. Epoxy paint seemed to endure the corrosion caused by concentrated hydrochloric acid with reduced mass loss in comparison with other paints. At the temperature of 60 °C, paints presented a decreased anti-corrosive protection when compared to sulfuric acid.

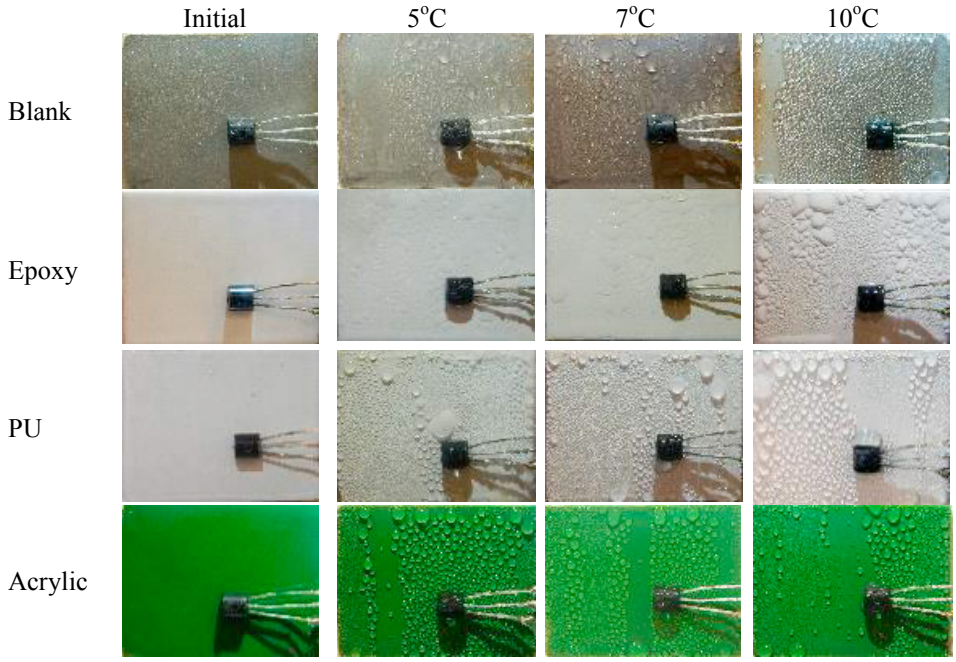

Fig. 3. Condensation effect at 20°C (%RH=100)

Considering a mixture of corrosive environments (with nitric, sulfuric and hydrochloric flue gases), the most promising results on anticorrosion properties may be attributed to PU paint when compared to the rest of the samples tested. Only for the case of hydrochloric acid environments, PU is found less corrosion protective than Epoxy paint. The latter is found much more effective than the rest of coatings tested both in 20 °C and 60 °C maintaining though out a better corrosion protective.

Condensation experiments on the coupons revealed significant information on the way that uncoated and coated surfaces may accumulate water droplets on their surfaces. Figs.(3, 4) show the physical state of water condensation on samples at 5, 7 and 10 °C after one hour in steady conditions (20 °C and 60 °C with %RH=100) (Figs.(3, 4), respectively).

According to this phenomenon, and the water collection data that are presented in Table 1 the following may be deducted: (i) At 20 °C with %RH=100 decreased values of water collection are observed only in Epoxy coatings. They exhibit a decrease in water collection values as sample temperature is increased. The maximum water collection is observed for PU paints in the sample temperature range. Also enhanced water collection values are observed in acrylic samples, always in relation to blank experiments. (ii) At 40 °C with %RH=100 the values of water collection are increased, in comparison with the values of the previous temperature. Acrylic and PU coatings present the maximum water collection values.

Open current potential verified the stability of PU and Epoxy samples over acrylic and blank samples. The relatively lower potential of PU and Epoxy based coatings indicated the enhanced resistance as indicated by potentiodynamic polarization curves. Based on the Tafel fitting parameters on E vs log(i) curves from Fig.5a and based on Eqs.(1, 2) results are shown in Table 2.

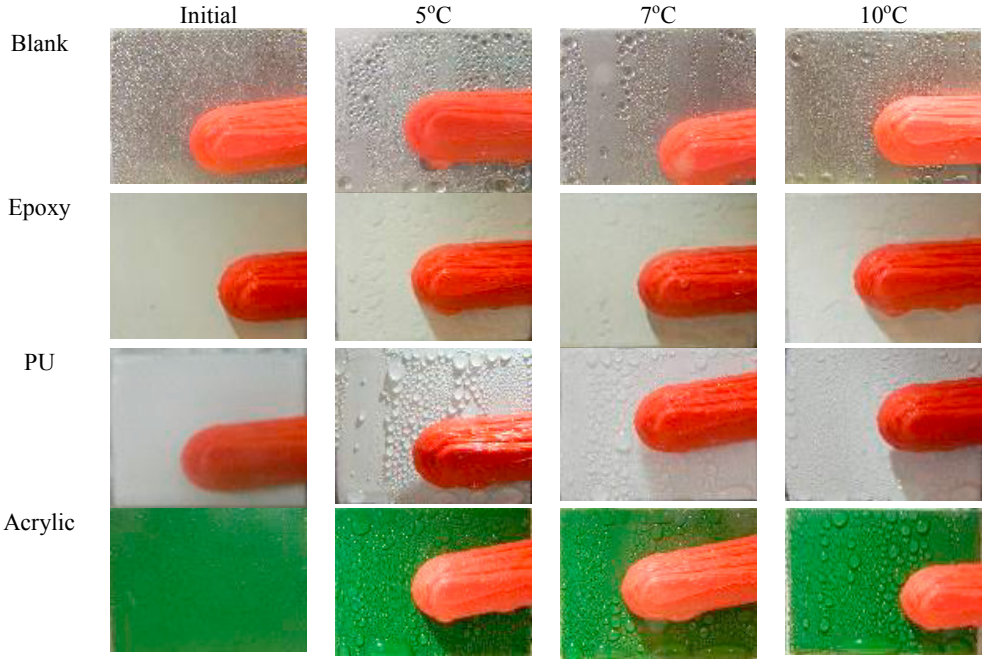

Fig. 4. Condensation effect at 40ºC (%RH=100), (Red PLA 3D printed protective cover for the thermocouple is visible).

Table 1. Coatings' features and water collection rates (ml· m^{-1}· h^{-1})

Sample	Primer Thickness	Topcoat thickness	Topcoat Mass	Experimental conditions					
				20ºC – 100% RH			40ºC – 100% RH		
	(μm)	(μm)	(mg)	5ºC *	7ºC *	10ºC *	5ºC *	7ºC *	10ºC *
Blank	n/a	n/a	n/a	0.262	0.250	0.281	1.010	1.093	1.059
PU	50	110	55	0.354	0.297	0.223	1.790	1.845	1.845
Epoxy	55	120	55	0.348	0.357	0.380	1.992	1.980	1.987
Acrylic	n/a	150	60	0.313	0.308	0.313	1.885	1.838	1.922

** Sample temperature*

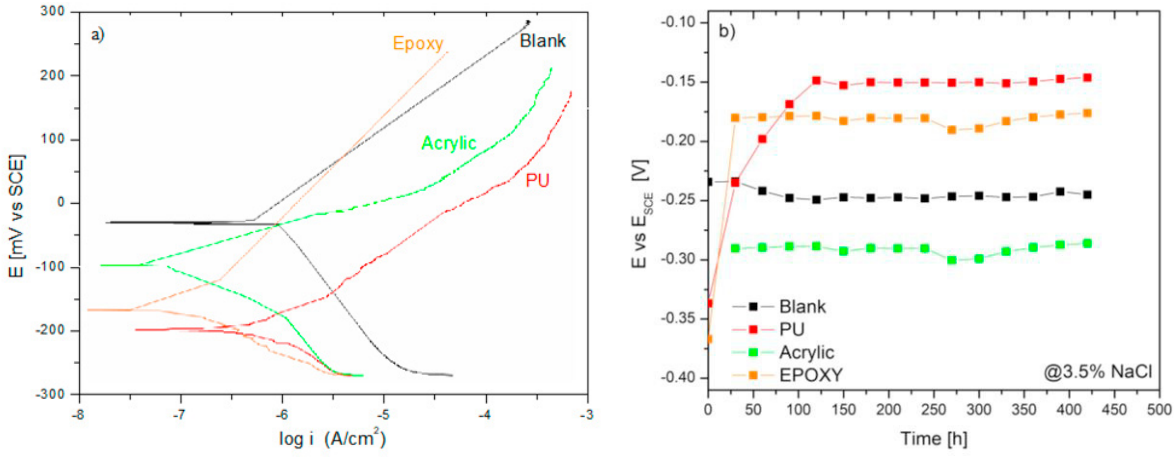

Fig. 5. (a) Potentiodynamic polarization curves of samples and (b) Open current potential (OCP) measurements in 3.5% wt NaCl.

Table 2. Current densities, OCP, corrosion protection efficiency and corrosion rate results of samples.

Sample	i_{CORR} (μA/cm^2)	OCP vs SCE (V)	%PE	mpy
Blank	83.7	-0.223	-	0.104
Epoxy	51.1	-0.179	39.0	0.065
PU	50.3	-0.149	40.0	0.067
Acrylic	60.2	-0.289	28.1	0.071

Results showed that Epoxy and PU coatings exhibited significantly lower corrosion current densities than the SS304 sample. This suggests that the coatings promote a more stable passive layer and protect the underlying metal against corrosion. Acrylic coatings provided less corrosion protection than the Epoxy and PU. OCP measurements at Acrylic samples indicated a lower potential value than the blank sample which indicates a fast diffusion of chloride ions through the coating.

4. Conclusions

The air spray method of developing protective organic coatings onto Stainless Steel surfaces was successfully applied on rectangle and cylindrical specimens. Smooth coatings over SS304 surfaces were fabricated with a mean value of 150 μm thickness. The commercial coatings were subjected as anticorrosive organic coatings in highly acidic conditions onto Stainless Steel (Grade304) with different surface chemistry (Polyurethane, Epoxy and Acrylic respectively). The PU organic coatings seemed to exhibit enhanced anticorrosive properties compared to the others. Epoxy coatings, clearly promoted the FwC effect on water droplet condensation. Acrylic coatings exhibited inferior resistance in comparison with the Epoxy and PU coatings. In conclusion, the results of this work may provide a suitable dataset for the designer of condensing economizers, in case of incorporating organic coatings in their design. The incorporation could be either as touch up or as protection of critical parts of the economizers.

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