HIGH PROTECTION PERFORMANCE OF COATING SYSTEMS BASED ON ZINC RICH PRIMER AND FLUOROPOLYMER COATING

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ABSTRACT

Coating systems based on zinc rich primer and fluoropolymer top coat were exposed for 8 years at different atmospheric stations in Vietnam: Ha Noi, Ha Long and Nha Trang. For comparison the coating system with zinc rich primer and polyurethane topcoat was also tested. The degradations of coating systems were evaluated by gloss measurement and electrochemical impedance spectroscopy. The obtained results show that coating systems with zinc rich primer and top coatings based on fluoropolymer and polyurethane topcoats show very high weather resistance and corrosion protection performance, but the systems with fluoropolymer are better than the system with polyurethane topcoat.

Keywords: fluoropolymer, tropical atmospheric exposure, weather resistance, corrosion protection.

1. INTRODUCTION

The main factors of environment which cause the degradation of coatings are sunlight (in particular UV radiation), temperature, oxygen, water and pollutants [1, 2]. Recently fluoropolymer top coatings are developed to extend the service life of coating systems because they are highly resistant to ultraviolet rays. Besides that fluoropolymers have many other desirable properties like excellent chemical resistance, good thermal stability, oil, and water resistance [3-10]. Due to high weather resistance the fluoropolymer topcoat system has been adopted as a guideline by a transportation authority in Japan for use on bridges [11-12]. Furthermore high-build fluoropolymer coatings are developed in order to decrease the VOC (volatile organic coating compounds) emission from coatings to environment. In this work, the degradation of coatings systems with zinc rich primer and topcoat based on fluoropolymer and high-build fluoropolymer were evaluated and compared with coating system with polyurethane topcoat. Coating systems were exposed at three atmospheric stations: Ha Noi, Ha Long and Nha Trang. The protection performance of coating systems during atmospheric test was evaluated by gloss measurement and electrochemical impedance spectroscopy.

2. MATERIALS AND METHODS

2.1. Preparation of coated steel

Carbon steel sheets (150 mm × 100 mm × 2 mm) were used as substrates. The sheets were cleaned with ethanol and sandblasted. Coating systems with zinc rich primer and topcoat based on fluoropolymer, high-build fluoropolymer and polyurethane were applied to sandblasted steel by spraying method with spraying pressure of 60-65 kPa. The dry coatings thickness measured with Minitest 600 Erichen digital meter are presented in Table 1.

Table 1. Coating systems used for exposure test.

Sample	Primer coating	Intermediate Coating	Top coating
EF	Inorganic Zinc (75 µm)	Epoxy (150 µm)	Fluoropolymer (25 µm)
EHF	Inorganic Zinc (75 µm)	Epoxy (120 µm)	High-build fluoropolymer (50 µm)
EPU	Inorganic Zinc (75 µm)	Epoxy (150 µm)	Polyurethane (25 µm)

2.2. Atmospheric test

The coatings systems were exposed at three different atmospheric stations (Ha Noi, Ha Long and Nha Trang) for 8 years (from 2009 to 2017). During exposure time, the gloss and electrochemical impedance of coatings were measured.

Corrosion and blistering degree of coated steel were evaluated according to ASTM D610-01 and ASTM D714-02. The gloss of coatings was measured during exposure time at 60^{o} with a Micro-TRI-gloss from BYK-Gardner.

Electrochemical impedance of coated steel was measured during exposure time, using a classical three-electrode cell: the working electrode is the steel coated, saturated calomel is reference electrode (SCE) and a platinum auxiliary electrode. The test solution was a 3 % NaCl solution and the working surface was 28 cm^2. The electrochemical impedance measurements were performed by using Autolab PGSTAT30 over a frequency range of 100 kHz to 10 mHz with six points per decade using 30 mV voltage.

3. RESULTS AND DISCUSSION

3.1. Meteorological data of stations

The coatings systems were exposed at Ha Noi, Ha Long, Nha Trang station. The meteorological data were collected from statistical yearbooks of Vietnam [13]. The variation of air temperatures, total sunshine time, annual rainfall and average air relative humidity of atmospheric stations from 2009 to 2016 are presented in Figure 1. We can see that the air temperatures and total sunshine time at Nha Trang station were much higher than the ones at Ha Noi and Ha Long stations. The air temperatures and total sunshine time at Ha Noi and Ha Long stations were close each other. The annual rainfall changes every year, but during the last two years, the annual rainfall at Nha Trang station increased very much. This can be caused by the climatic change. But overall the annual rainfall at Ha Long station was higher than the ones at and Ha Noi and Nha Trang stations. The average air relative humidity at Ha Long station was higher than the ones of two other stations. Besides that, Ha Noi station has urban industrial atmosphere, meanwhile Ha Long and Nha Trang stations have marine atmosphere.

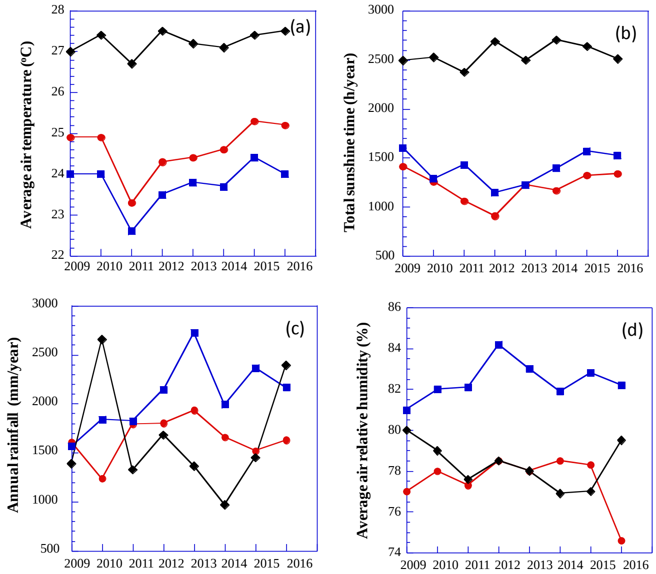

Figure 1. Meteorological dates of atmospheric sites: Ha Noi (●), Ha Long (■) and Nha Trang (♦).

3.2. Surface observation

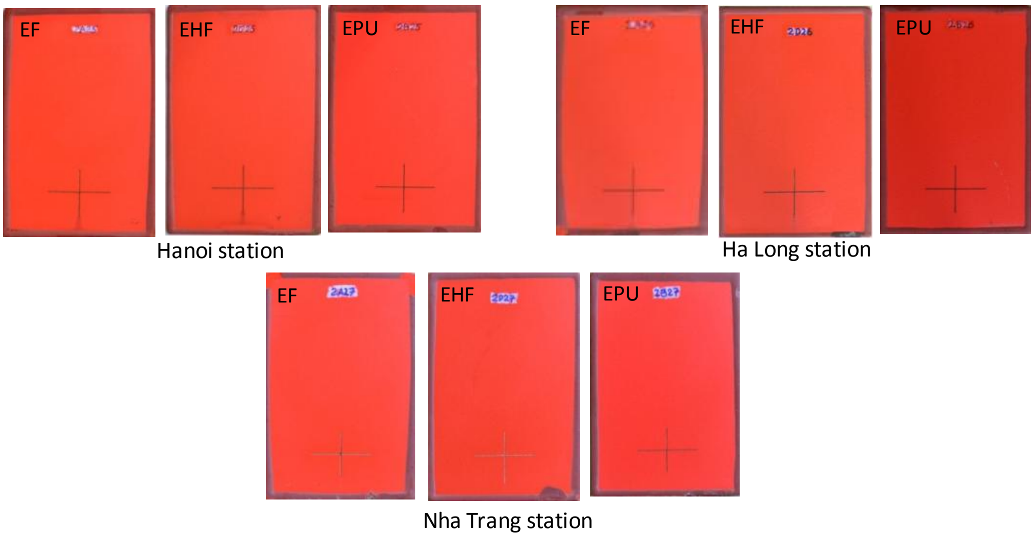

Figure 2. Images of coating systems after 8 years exposure at atmospheric stations.

The images of coatings after 8 years exposure are presented in Figure 2. The corrosion and blistering degree of coating systems was evaluated according to ASTM D610-01 and ASTM D714-02. It was found that there was neither observed corrosion nor blistering on the coating surfaces. This results indicate high protection performance of coating systems with zinc rich primer and topcoat based on fluoropolymer, high-build fluoropolymer and polyurethane.

3.3. Gloss measurement

The degradation of coatings was followed by gloss measurement. The variation of gloss retention of coating systems during exposure time at Ha Noi, Ha Long and Nha Trang stations are shown in Figure 3. It can be seen that for all systems the gloss of coatings decreased rapidly during first 4 years of exposure, but the gloss retention of systems with of fluoropolyemer and high-build fluoropolymer coating were higher in comparison with system with polyurethane coating. The loss of coating gloss is representative of the degradation of coatings due to effects of ultraviolet radiation [14]. The UV radiation of sunshine causes polymer chain breakdown and as a result a decrease of coating gloss. This result indicates that fluoropolymers have higher UV resistance than polyurethane. The gloss retention of high-build fluoropolymer coatings was higher than that of fluoropolymer coating. When the exposure time increased from 4 years to 8 years, the gloss of samples decreased progressively. After 8 years of exposure the gloss retention of all coating systems were close and about 20 %.

Comparing the gloss retention of coatings at 3 stations shows that the gloss retention was lowest at Ha Noi station. The gloss retention of fluoropolymer and high-build fluoropolymer coatings exposed at Nha Trang station was higher than the ones of coatings exposed at two others stations. This can be explained by lower rainfall at Nha Trang compared to the one at Ha Noi and Ha Long. The fluoropolymer and high-build fluoropolymer coatings show higher weather resistance than polyurethane coating, meanwhile high-build fluoropolymer coating shows higher weather resistance than fluoropolymer coating.

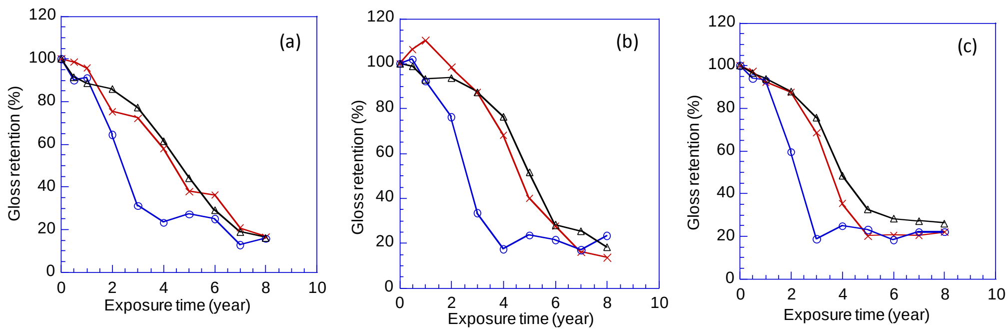

Figure 3. Gloss retention of coating systems versus exposure time at Ha Noi (a), Ha Long (b) and Nha Trang (c) station of samples: EF (x), EHF (Δ), EPU (o).

3.4. Electrochemical impedance measurement

Besides gloss measurement, the protective performance of coatings systems was evaluated by electrochemical impedance spectroscopy before and during exposure time at atmospheric stations. Figure 4 presents the bode impedance diagrams obtained of samples before and after 8 years of exposure at atmospheric stations. We can see that before testing the impedance diagrams of all coatings are characterized by a single time constant and the impedance modulus at low frequencies of samples are close and very high (>10^{10} $\Omega.cm^2$). After 8 years of exposure the impedance modulus of samples remained stable and very high. The obtained results show that systems with fluoropolymer, high-build fluoropolymer and polyurethane coating have very high protective performance.

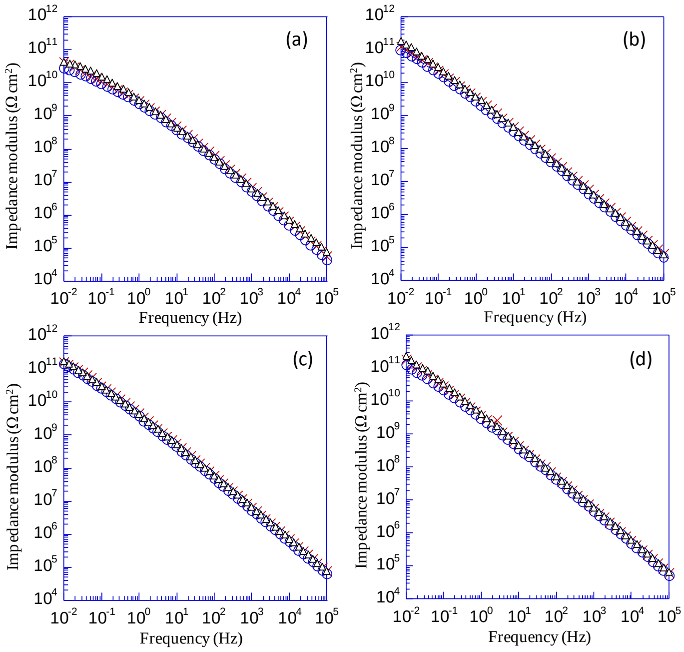

Figure 4. Impedance diagrams of samples: EF (x); EHF (Δ) and EPU (o) before exposure (a) and after 8 years of exposure at Ha Noi (b), Ha Long (c) and Nha Trang (d) stations.

From impedance diagrams the impedance modulus at low frequency 100 mHz (Z_{100mHz}) was determined to evaluate the degradation of coatings [15]. The Z_{100mHz} value gives the information about the corrosion resistance of coatings. Coatings with higher Z_{100mHz} value are more corrosion resistant. The variations of Z_{100mHz} values with exposure time are presented in the Fig. 5.

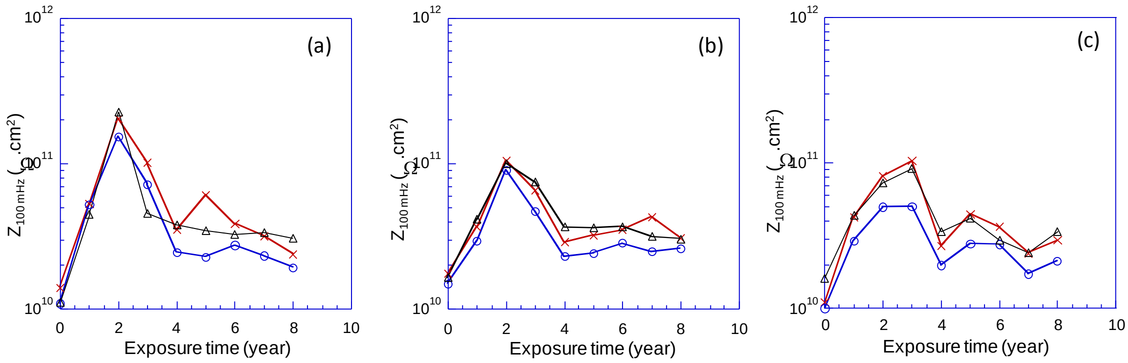

Figure 5. Variation of $Z_{100\ mHz}$ of coating systems during exposure time at Ha Noi (a), Ha Long (b) and Nha Trang (c) station of samples: EF (x), EHF (Δ), EPU (o).

The Z_{100mHz} values of samples before exposure were very high and very close to each others (>10^{10} $\Omega.cm^2$). The variation of Z_{100mHz} values of all three samples during exposure time is almost the same at three atmospheric stations. During first 2 years of exposure, the Z_{100mHz} value of all samples at all stations increased. The increase of Z_{100mHz} value of the coatings can be explained by the formation of zinc oxide, which filled the pores in the coatings [16]. When the exposure time increased from 2 years to 4 years, the Z_{100mHz} values of samples exposed at all stations decreased. The decrease of Z_{100mHz} values of coating systems indicates the degradation of coating systems and this corresponds to the decrease of coatings gloss presented in above part. When the exposure time increased from 4 years to 8 years, Z_{100mHz} values of samples did not change very much and still remained very high (> 10^{10} $\Omega.cm^2$). The Z_{100mHz} values of samples EF and EHF were higher than those of sample EPU. The results obtained by impedance measurements are in agreement with the surface observation and gloss measurements.

4. CONCLUSIONS

Coatings systems with primer coatings based on inorganic zinc coatings and topcoat based on fluoropolymer, high-build fluoropolymer and polyurethane were tested by exposure at Ha Noi, Ha Long and Nha Trang stations. Gloss retention and electrochemical measurement were used for evaluating the protection performance of exposed coated steel panels. All three coating systems showed high weather and corrosion resistance, but the systems with topcoat based one fluoropolymer, and high-build fluoropolymer coatings showed extremely excellent corrosion protection performance.

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