

## The effect of various cyclic Wet-Dry exposure cycles on the Failure Process of Organic Coatings

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The effect of various dry-wet cycles on the failure processes of the acrylic polyurethane heat-reflection topcoat and thick epoxy anti-rust primer was investigated, where simulated seawater constituted the wet condition and air constituted the dry environment. Electrochemical impedance spectroscopy (EIS), Fourier Transform infrared spectroscopy (FT IR) and Scanning electron microscopy (SEM) were used to characterize the coatings after exposure under the cyclic wet-dry conditions. The results herein indicate that the primary cause of coating degradations was the reaction of functional groups in coatings with the NaCl solution (the simulated seawater). Furthermore, alternate wetting and drying can promote the incidence of fillers falling off the coatings, and thus, increasing the micro-pores in the coatings. This pore-creating effect can multiply the number of defects in the coating and accelerate the degradation of the coatings. However, the degradation rate of the coatings is evidently influenced by the wet-dry cycle. Under conditions of the same total test times, increased length of the per-cycle wetting times accelerates the coating degradation even though the total wetting times may be equal. If the wetting time in one wet-dry cycle is shorter, the water absorption of the coating is lesser. During the following drying process, the absorbed water within the coating may be completely evaporated, and the hydrolysis of the coating can weaken. If the wetting time per cycle is long enough, the absorbing water does not fully evaporate from the coating during the following drying period. This can accelerate degradation of the coating. Moreover, oxygen accelerates the reaction on the cathode during the drying period in one cycle, leading to a relatively quick corrosion of metal matrix and a decrease of adhesive force of the coating.

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**Keywords:** acrylic polyurethane heat-reflection coating, thick epoxy antirust coating, wet-dry cycle, Failure, EIS.

## 1. INTRODUCTION

Using an organic coating is one of most effective and economical methods to protect steels against corrosion in marine environments. Various studies [1-7] have investigated the degradation process of the different organic coatings. Their results indicate that water absorption is a main factor causing the degradation of coatings and corrosion of undercoatings. In marine engineering, commonly used coatings, such as those for ship construction, the coating may have a different general environment associated with its location on the ship; due to the effect of differing wetting and drying environments, the failure process of coatings around the waterline may differ from those under a non-immersion or complete immersion environment. Park [8] studied the water uptake of epoxy and polyurethane double coatings by electrochemical impedance spectroscopy (EIS) and analysed the mechanism of undercoating corrosion under alternating wetting for 4-hours in chloride-containing solution and drying for 8-hours in an air environment. Lendvay-Gyorik [9] studied the degradation process of water-borne styrene-acrylate and alkyd-acrylate coatings under alternating conditions of 24-hours wetting and 24-hours drying. They proposed a model describing water uptake and release of the coatings in wet-dry cyclic environments. Allahar [10] studied the failure behaviour of an epoxy coating on an aluminium alloy of AA 2024-T3 under a cyclic condition of 24-hours of wetting in dilute NaCl solution and 24-hours of drying in an ionic liquid. They found that as the number of cycles increased the coating capacitance evolution was generally consistent with a Fickian-type evolution. In addition, the wetting time and/or drying time in each wet-dry cycle (circle feature) can also affect the failure behaviour of coatings under cyclic wet-dry conditions. Our previous works [11,12] investigated the failure process of an acrylic polyurethane coating and a high-build epoxy primer/polyurethane composite coating under alternate wetting and drying conditions. Although the studies on coating failure involve different wetting and drying conditions, the effect of the circle feature is not clear. In this work, the failure processes of an acrylic polyurethane heat-reflection coating and thick epoxy anti-rust coating under various cyclic wetting and drying conditions were studied, and the influence of cyclic wet-dry exposure conditions is discussed.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Materials and preparation of specimens

The tested substrate material was a 70×150×0.75 mm sample of Q235 carbon steel. The coatings employed were a SRF 2088 two-component polyurethane heat-reflection topcoat (A:B=10:1.3) and a H900 two-component high-build epoxy antirust primer (A:B=12:3.3), produced by Shanghai Haiyue Paint Co. Ltd, China. Component A of the H900 high-build epoxy anti-rust primer was composed of bisphenol A epoxy resin with alumina powder, iron oxide and silicon dioxide as pigments. The epoxy was 45-55% (mass fraction) and the pigment was 35-40% (mass fraction). Component B was primarily a tertiary amine curing agent. The SRF 2088 polyurethane heat-reflection coating was composed of urethane and hydroxy acrylic resins, titanium dioxide, colouring agent, auxiliaries and solvents. The urethane was used as a curing agent.

The metal surface was manually polished with 120# sand paper, and was degreased with ethanol and acetone in turn. The coating was manually applied to the substrate. Next, the samples were placed in air at room temperature for sufficient curing. The coating thickness was measured with a TT220 thickness tester (Time Instruments Co. Ltd., China). The average thickness value of the coatings was  $60 \pm 5 \mu\text{m}$ .

## 2.2. Testing conditions

The coating samples were tested at room temperature under different wetting and drying cycles. The cycles are listed as follows:

(i) Immersion in 3.5 wt% NaCl solution for 3 hours followed by drying in air for 3 hours, in turn. A cycle was 6 hours. We simplify this description, naming it a 3-3 cycle, signifying the immersion and drying hours.

(ii) Immersion in 3.5 wt% NaCl solution for 4 hours, followed by drying in air for 8 hours in turn. A cycle was 12 hours (a 4-8 cycle).

(iii) Immersion in 3.5 wt% NaCl solution for 6 hours, followed by drying in air for 6 hours in turn. A cycle was 12 hours (a 6-6 cycle).

(iv) Immersion in 3.5 wt% NaCl solution for 12 hours, followed by drying in air for 12 hours in turn. A cycle was 24 hours (a 12-12 cycle).

## 2.3. Experimental

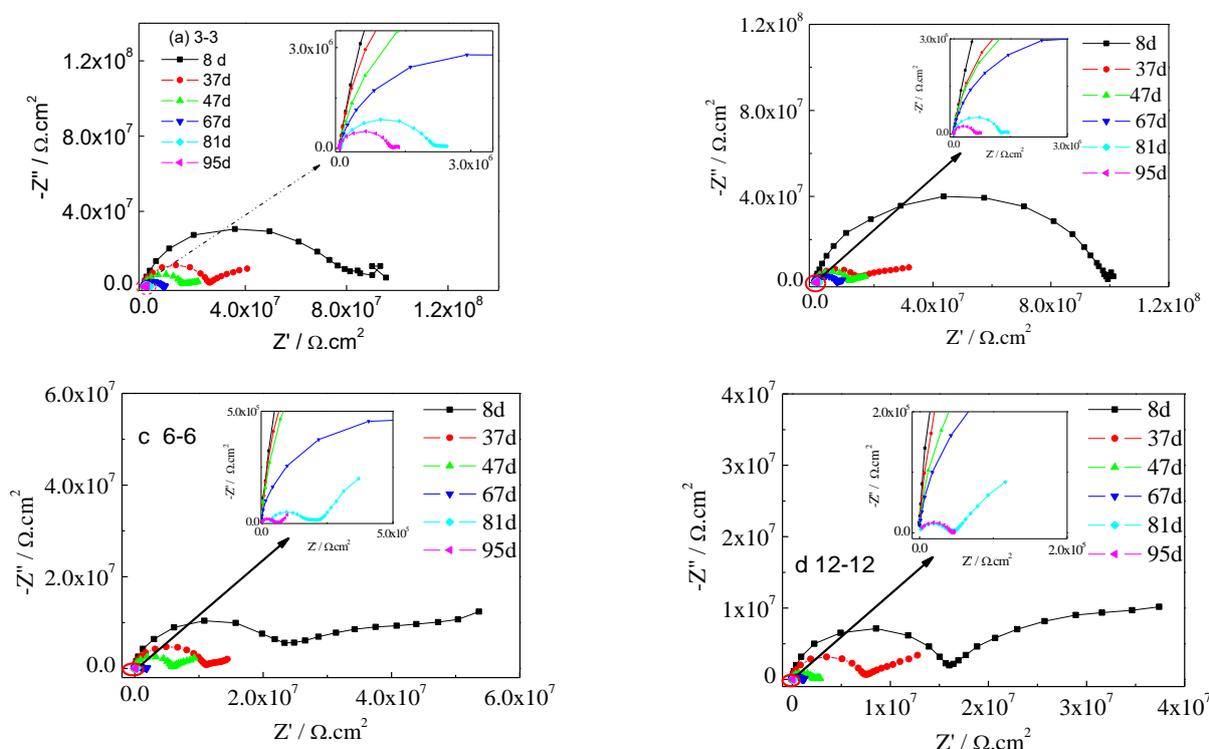
Electrochemical impedance measurements were conducted in 3.5 wt% NaCl solution at room temperature using a PARSTAT 2273 electrochemical system (AMETEK, Inc, USA) with a 10 mV sine perturbation at open circuit potential. The tested frequency range was from 100 kHz to 0.01 Hz. The reference electrode was a saturated calomel electrode (SCE), a Pt flat was used as the counter electrode. The working electrode was the coating sample with an exposed area of about  $10 \text{ cm}^2$ . The working electrode was removed after different exposure times based on the given alternating wet-dry environment cycle.

The coated samples were taken out of the wet-dry exposure cycle environment for final measurements. The surface morphologies of the coating samples were observed using a S4700 field emission scanning electronic microscope (SEM, Hitachi Co., Japan) to compare the effect of the different wet-dry exposure cycles. The coating samples were coated with gold to preclude charging during SEM measurement. Fourier transform infrared spectroscopy (FT-IR) analysis was carried out using a TENSOR 27 infrared spectrometer (Bruker Co., Germany) to analyze structural changes in the coatings; the window material was KBr. The coating powders, removed from the substrates, were pressed into thin pieces for FT-IR analysis. Differential scanning calorimetry (DSC) was used to study the changes of the glass transition temperature of the coatings after different exposure times in wet-dry alternate environments.

### 3. RESULTS AND DISCUSSION

#### 3.1. EIS results of acrylic polyurethane heat-reflection coating samples

Figure 1 shows Nyquist plots of the coating samples in 3.5% NaCl solution under different cyclic wet-dry conditions. It can be seen from Figure 1 that the capacitive loops in the high frequency region clearly decreased with exposure time as a function of the alternative wet-dry conditions. This is due to the electrolyte permeation into the coatings. For the coated samples exposed with the 6-6 and 12-12 cycles, after about 8 days, the second capacitive loop appears in the Nyquist plot (Figure 1c and 1d). This indicates that the corrosive medium has partly permeated through the coating, and that the corrosion happens on the surface of the metal substrate. For the samples undergoing the 3-3 and 4-8 cycles, the second capacitive loop appears much later, after about 37 days (Figure 1a and 1b). These results indicate that the effect of the varying wet-dry cyclic conditions has a notable influence on the degradation process of the coatings.



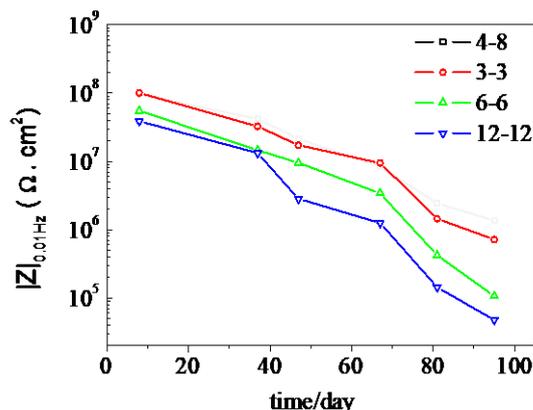
**Figure 1.** EIS curves of the acrylic polyurethane heat-reflection coating samples in 3.5 wt% NaCl solution after different exposure times in dry-wet alternate environments with different cycles. (a) 3-3, (b) 4-8, (c) 6-6, (d) 12-12

The impedance magnitudes of the coating samples at low frequencies (e.g., the impedance module value at 0.01 Hz, denoted as  $|Z|_{0.01\text{Hz}}$ ) can, to a certain extent, represent the shielding effect of the coatings. It is often used as a reference criterion to evaluate the protective performance of organic coatings [13]. In general, a  $|Z|_{0.01\text{Hz}}$  value above  $10^8 \Omega.\text{cm}^2$  indicates good protection of the coatings, while a  $|Z|_{0.01\text{Hz}}$  value below  $10^6 \Omega.\text{cm}^2$  implies poor protection of the coatings [14,15]. Figure 2 provides the measured  $|Z|_{0.01\text{Hz}}$  changes of the polyurethane heat-reflection coating under different cyclically

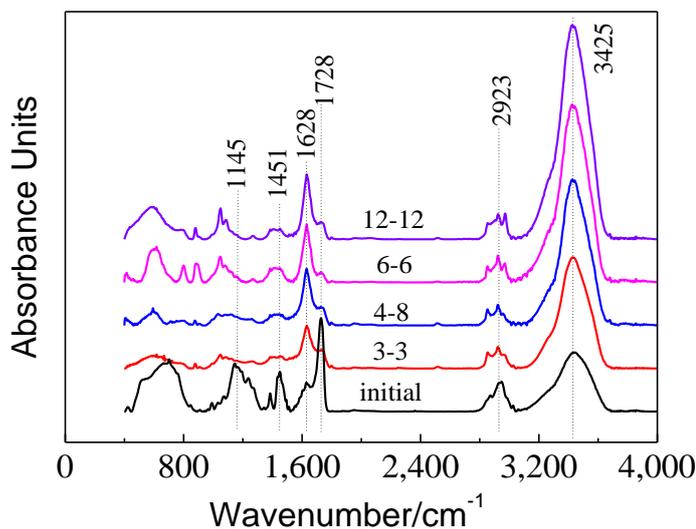
alternating wet-dry conditions. From figure 2 illustrates that the  $|Z|_{0.01\text{Hz}}$  values of coatings samples have a similar changing tendency with exposure time for each of the samples under different cyclic wet-dry conditions. As exposure time is prolonged, the  $|Z|_{0.01\text{Hz}}$  value decreased. This is due to electrolyte permeation into the coating by micro-pores. Comparing the 3-3, 6-6, and 12-12 cycles, for the same exposure time (e.g., 24 hours) the total wetting times are the same. From Figure 2, it can be seen that the 12-12 cycle sample yields  $|Z|_{0.01\text{Hz}}$  values that decrease more quickly compared to the 6-6 and 3-3 cycles. Thus, under different wet-dry conditions, for the same exposure time (e.g., 24 hours), the longer the wetting time in one cycle, the more serious the degradation of the coatings samples. In other words, lengthy wetting times cause more damage than repeated short wetting exposures. Comparing between the 4-8 cycle and 6-6 cycle, for the same exposure time (e.g., 24 hours), the number of cycles carried out is the same, but the total wetting time of the 6-6 cycle is greater than that of the 4-8 cycle. From Figure 2, it can be seen that the  $|Z|_{0.01\text{Hz}}$  values of coating samples under the 6-6 cycle decrease more quickly compared with that of the 4-8 cycle. If the wetting time in one wet-dry cycle is shorter, the water absorbed by the coating is less. During the following drying process, the water absorbed by the coatings may be completely evaporated, and thus, the hydrolysis of the coating can be weakened. If the wetting time in the cycle is long enough, the absorbed water within the coating cannot be completely evaporated during the drying period; this can cause the coating degradation to accelerate. Moreover, oxygen accelerates the reaction on the cathode during the drying period in one cycle, leading to a relatively quick corrosion of metal matrix, and a decrease of adhesive force of the coating [16].

### 3.2. FT-IR and DSC results of acrylic polyurethane heat-reflection coating samples

FT-IR was used to analyse the functional groups of the acrylic polyurethane heat-reflection coating samples after being exposed to alternating wet-dry conditions. Figure 3 shows the IR spectra of the coatings before and after 95 days of exposure under the different cyclic wet-dry conditions. All spectra peaks were normalized with respect to the stretching vibration peak of C-H in  $\text{CH}_2$  groups at  $2923\text{ cm}^{-1}$ . [12,17,18] The stretching vibration peak of the O-H bond is at  $3425\text{ cm}^{-1}$ . [12,18-20] The absorption peak at  $1728\text{ cm}^{-1}$  is attributed to the  $\text{-C=O}$  stretching vibration of the acrylate group. [12,18,20] The stretching vibration peak of N-H in the primary amine is at  $1628\text{ cm}^{-1}$ , the  $\text{-COO-}$  stretching vibration peak in the characteristic spectral band III of amide is at  $1451\text{ cm}^{-1}$ , and the  $\text{-C-O}$  stretching vibration peak in ester is at  $1145\text{ cm}^{-1}$  [12,17,18,21]. After 95 days of exposure, the functional groups in the coatings hydrolyzed with outer water. The  $\text{-O-H}$  absorption peak at  $3425\text{ cm}^{-1}$  increases clearly because of the hydrolytic degradation of polyurethane coating. The  $\text{-C=O}$  stretching vibration peak decreases because the  $\text{-C=O}$  bonds of the  $\text{-NHCOOR-}$  molecular chains were partly broken. The absorption peaks at  $1451\text{ cm}^{-1}$ ,  $1145\text{ cm}^{-1}$  and  $1728\text{ cm}^{-1}$  decline due to the partial reduction of the polyurethane components. Comparing between the different wet-dry cyclic conditions with the same total exposure time, longer wetting times correspond to stronger O-H absorption peaks at  $3425\text{ cm}^{-1}$ ; this implies an increase of the hydrolytic degree of the coatings.



**Figure 2.**  $|Z|_{0.01\text{Hz}}$  values of the acrylic polyurethane heat-reflection coating samples with exposure time under different cyclic wet-dry conditions



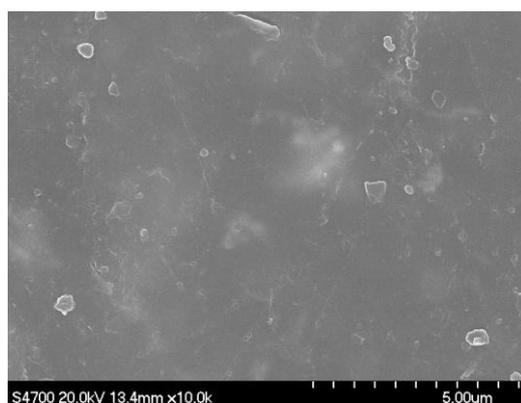
**Figure 3.** FT-IR spectra of the acrylic polyurethane heat-reflection coating samples before and after 95 days exposure under different cyclic wet-dry conditions

Table 1 shows the glass transition temperature ( $T_g$ ) of polyurethane heat-reflection coatings after 95 days exposure under the different alternating cyclic wet-dry conditions. In general, the  $T_g$  value is closely related to the cross-linking degree of resin in the coatings. For a given coating, the higher the cross-linking degree, the higher the  $T_g$  value corresponding to a stronger shielding effect of the coating. Therefore, the  $T_g$  value can be used to evaluate the protection of the coating [22]. The  $T_g$  values of the coating samples under different alternating cyclic wet-dry conditions are clearly different, as shown in Table 1. After 95 days of exposure, comparisons of the 3-3, 4-8, 6-6, and 12-12 cycles, show that as the wetting times in one cycle increase, the  $T_g$  values of the coating samples decrease. This indicates a more serious degradation of the coatings. This is consistent with the above EIS results.

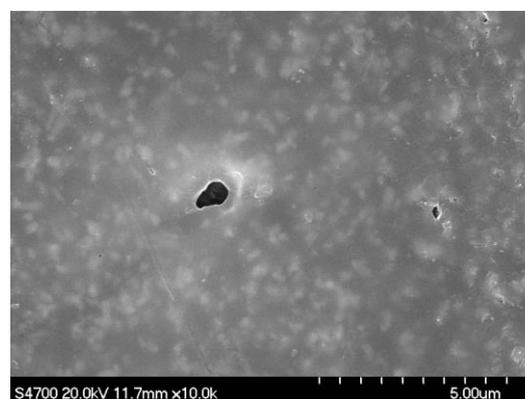
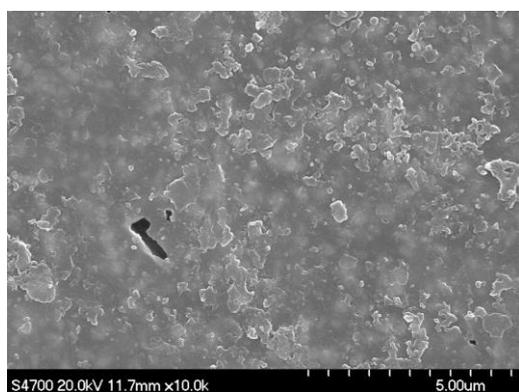
**Table 1.** Tg of acrylic polyurethane heat-reflection coating after 95 days exposure under different alternating cyclic wet-dry conditions

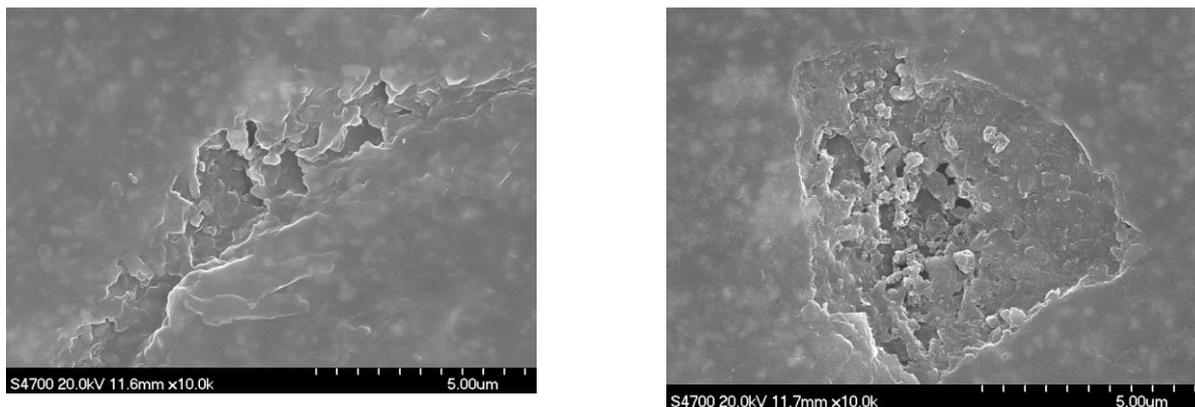
Cyclic feature	3-3	4-8	6-6	12-12
Tg / °C	52.3	50.0	44.8	41.7

Figure 4 and 5 show the surface SEM images of the acrylic polyurethane heat-reflection coating samples before and after 95 days of cyclic wet-dry exposure. In comparing Figures 4 and 5, it can be seen that after 95 days exposure, the defects on the coating surface clearly increase, and the coatings degrade. The main reason is due to the hydrolysis of functional groups such as -C=O, -COOR, and -C-N in the coatings with the electrolyte solution (confirmed by above infrared spectra analysis). In addition, due to the physical effect of wet-dry alternation, the fillers in the coating surface layer may fall off and result in micro-pores. This pore-effect can multiply the defects in the coating and accelerate the coating degradation. Comparing Figures 5a, b, c and d, we find that for the same exposure time under the cyclic wet-dry conditions, the longer the wetting time in one cycle, the higher the degradation degree of the acrylic polyurethane heat-reflection coatings.



**Figure 4.** The surface morphology of the acrylic polyurethane heat-reflection coating samples before exposure to cyclic wet-dry conditions





**Figure 5.** The surface morphologies of the acrylic polyurethane heat-reflection coating after 95 days exposure under different cyclic wet-dry conditions. a) 4-8 cycle; b) 3-3 cycle; c) 6-6cycle; d) 12-12 cycle

The above hypothesis is consistent with the above EIS and FI-IR results. A possible reason is that if the wetting time in one wet-dry cycle is shorter, the coating absorbs less water. During the following drying process, the absorbed water may completely evaporate, and the hydrolysis of the coating can weaken from this process. If the wetting time in one cycle is long enough, the water absorbed by the coating cannot be completely evaporated during the following drying period, and the coating degradation will accelerate. Moreover, oxygen accelerates the reaction on the cathode during the drying period in one cycle, leading to a relatively quick corrosion of metal matrix and a decrease of adhesive force of the coating. For thick epoxy anti-rust coatings exposed under the different cyclic wet-dry exposure conditions, a set of similar results were found, but are not detailed herein.

#### 4. CONCLUSIONS

The primary cause of coating failure is that the corrosive electrolytes of the NaCl solution (simulated seawater) chemically react with the functional groups of coatings. Furthermore, the physical effect of an alternating wet-dry environments can promote the detachment of fillers in the surface layer of the coating; this results in the formation of micro-pores, which could multiply the defects in the coating and accelerate the coating failure.

The degradation rate of the coatings is obviously influenced by the various exposure times of the dry-wet cycle. Under conditions of the same period of experiment, the coating degradation rate increases with the length of the per-cycle wetting time, even though the total wetting time may be equal.

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