DIFFERENT BEHAVIORS OF ZINC RICH PAINT AGAINST CORROSION IN ATMOSPHERIC ZONE AND TIDAL ZONE OF INDUSTRIAL PORT ENVIRONMENT

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ABSTRACT

A study on zinc rich paint (ZRP) and its behaviors of protecting JIS SS400 constructional steel against impacts of industrial port environment at Phu My port (Ba Ria - Vung Tau Province, Vietnam) was started in January 2014. After three years of investigation, thickness of ZRP decreased slowly and the reduction reached to 38 µm and 31 µm in atmospheric and tidal zone, respectively. Moreover, in accelerated environmental conditioning tests, separation and failures of ZRP from steel substrate were responsible for blistering. By comparison of field exposure test and accelerating test, growth of blistering on ZRP is caused by high temperature and time of wetness.

Keywords: zinc rich paint, JIS-SS400 steel, accelerated environmental tests, brackish environment, industrial port.

1. INTRODUCTION

Generally, the ability of coating materials to protect metallic structures against impacts of environments depends on their characteristics, as well as on properties of bonding interface between coating layers and metal substrate. For steel based structures and other steel type application exposed to either industrial or marine environment, zinc rich paint (ZRP) was commonly used for protection. ZRPs are those coatings that contain a suitably high amount of zinc dust or zinc powder mixed with organic or inorganic binder. Since the late 19\textsuperscript{th} century, zinc
Different behaviors of zinc rich paint against corrosion in atmospheric zone and tidal zone of...

Zinc rich paints were extensively applied as primer or topcoat on steel based structures or surfaces that operated in harsh environmental conditions and that had a continuous risk of corrosion. It is widely agreed that paint performance and life time are influenced effectively by corrosive agents of environment (such as humidity, time of wetness, dissolved oxygen…) and trapped soluble agents (such as oxygen, metal dust, moisture…) at interface of coating films and substrate. However, there is no standard precise of levels of corrosive agents for threshold value caused by many of characteristics of paints, steel substrate and exposed conditions [1-7].

Many studies exist in literatures and relate the protecting mechanism and degradation of such paints. Physicochemical properties and anti-corrosion efficiency of ZRP strongly depend on pigment volume concentration, shape and size of zinc particles. In ZRP based on organic binders, such as epoxy resin, zinc powder prevents the metal from becoming corroded by simply sacrificing itself when binder becomes a barrier to penetration by moisture that slows down the corrosion of either steel substrate or zinc powder. Commonly, that two fundamental protecting mechanism named the galvanic protection stage and the barrier effect stage [5, 7, 8 - 13].

For the purpose of predicting applications and life time ZRP, it is important to study the influence of environment on ZRP by a field exposure test. By installing a long term test of large samples at Phu My Port, the present article studied the degradation of ZRP exposed to either atmospheric zone and immersed in tidal zone of industrial port for 35 months. For the comparison, accelerating simulation of those two environments were operated to small samples. The behaviors of ZRP coating were studied by observation and statistical thickness measurement.

2. MATERIALS AND EXPERIMENT

2.1. Materials and test samples preparation

All reagents and solvents were used as received from commercial suppliers. Sodium chloride (95%) was purchased from Xilong Chemical (China). Epoxy resin and hardener were purchased from PACE Technology (USA). pH buffers were purchased from HANNA Instruments. DI water was obtained by Materials Technology Laboratory, HCMUT-VNUHCM.

![Figure 1](image)

*Figure 1. Preparation of ZRP coating on test samples: (a) processing, (b) drying, (c) inspection.*

Constructional steel substrate graded SS400 following JIS G3101. ZRP based on epoxy resin was used as topcoat (Figure 1). Those materials are products of J-Spiral Steel Pipe Corporation (JSP).
Figure 2. Design of flat sample (type I) with measuring positions.

Figure 3. Design and installation scheme of pile sample (type II) with measuring positions.

All test samples were prepared by process of JSP. Test samples were designed with two types:

- Type I - flat plate sample (Figure 2): Steel substrate was handed in rectangle shape with L (length) × W (width) × T (substrate thickness) = 150 × 75 × 5 mm. ZRP was coated on top side of steel substrate. Back side and edge of sample were covered by epoxy resin.

- Type II - pipe pile (Figure 3): Steel pipe piles were prepared with L (length) = 12 m, OD (outside diameter) = 165 mm, T (substrate thickness) = 9 mm. ZRP was coated outside along piles length (excepted 20 cm on top for experiment operation).
The initial thickness of ZRP of type I was measured by Elcometer A456 Separate Coating Thickness Gauge with 16 points/sample × 5 times/point (Figure 2). Initial thickness of ZRP onto type II was measured by same methods and with 4 points/level × 3 times/points (Figure 3). The initial thickness of ZRP is about 450 µm for both two types of samples.

### 2.2. Experiments

#### 2.2.1. Accelerated tests

Type I samples were used for two accelerated tests: salt spray test (simulated atmospheric zone); and immersion test (simulated tidal zone). Testing conditions are shown in Table 1. When finished testing periods, samples were removed from testers, cleaned by DI water and measured thickness of ZRP coating by same method as preparation.

| Test    | Used equipment                                                                 | Testing conditions                                                                 |
|---------|-------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| Salt spray | Salt Spray Tester TM-SST100 manufactured Test Mate Company, Korea (Figure 4a, b) | ● Test solution: 5% NaCl solution;  
● pH: maintained by pH 7.0 (± 0.2) buffer;  
● Temperature of spray chamber: 35 ± 2°C;  
● Quantity of spray chamber: 1.5 ± 0.5 mL/h (sprayed by air);  
● Angle of specimen: 20 ± 5°;  
● Testing time: 30, 60, 90, 120, 180 days. |
| Immersion | Immersion tester designed Materials Technology Laboratory, HCMUT-VNUHCM (Figure 4c, d) | ● Test solution: 3.5% NaCl solution;  
● Air flow: Neutral atmosphere was plunged deep into the tank from bottom with 2.5 L/min of flow velocity;  
● Temperature: 50 °C ± 3 °C;  
● Testing time: 30, 60, 90, 120, 180, 240, 360 days. |

*Figure 4. Accelerating testers: (a, b) salt spray tester, (c, d) immersion tester.*
2.2.2. Field exposure test

Field exposure test was started at January 2014 at Phu My port (Ba Ria - Vung Tau Province, Vietnam), which is an industrial port with complicated brackish environment. Type II samples were used for this test and planned for long term test up to 15 years. Thickness of ZRP coating was measured every 3 months in the same method as preparation. Figure 3 shows the scheme of installation and measuring positions at 1 m (atmospheric zone) and at 3 m (tidal zone) from top of piles.

3. RESULTS AND DISCUSSIONS

3.1. Accelerated tests

Observation of ZRP coating suffered two accelerated tests showed appearance of blistering, however, area density of blistering in salt spray test is lower than in immersion test (Figure 5). Different level of blistering area on paint caused by different level of test conditions. The immersion test was operated with higher temperature and concentration of dissolved oxygen, longer time of wetness than salt spray test. The literature on reporting ZRP and its failures [13, 14] refer that blisters are formed when water and corrosive agents permeated through coating layer during time of wetness.

Figure 5. Surface of ZRP coating: (a) original surface; (b) after 180 days of salt spray test; (c) after 180 and (d) 360 days of immersion test.

Coating process of ZRP on steel substrate in air must trap soluble agents (such as oxygen, moisture, metal dust...) at interface of paint and steel substrate. At start of tests, external surface of coating contacted with environment which are high wetness but containing either free of or lower active agent than the environment beneath coating. Furthermore, many research demonstrated ZRP is semipermeable membrane which is permeable to water but impermeable to dissolved solid [15]. Under such conditions, water was absorbed by film, then transferred to steel substrate to attempt equilibrium of pressure and solute concentration. The rate of osmotic blistering growth depends on rate of water migration which is controlled by hyper-equilibrium of
two side of film. The more different level of test conditions made the higher hyper-equilibrium which also explained rate of osmotic blistering on ZRP suffered the immersion test was higher than the salt spray test [15, 16].

Figure 6 shows thickness variation of ZRP coating after 180 days of salt spray test and after 360 days of immersion test. Thickness of ZRP coating suffered immersion test increased quickly and reached to maximum increase of 137 µm at 2 testing months when coating in salt spray test reached maximum increase of 80 µm at 4 testing months. In both two accelerated test, after thickness ZRP coating had reached maximum increase, it started decreasing in subsequent test periods. This phenomenon is reported in many literature [15 - 20]. Researches of Van der Meer-Lerk and Heertjes [17, 18] showed that blisters growth is fast at first, then slow later. While blisters were growing, concentration of trapped soluble agent within blisters decreased and, simultaneously, water concentration increased. Thus, driving force of migration decreased which slowed growing rate of blisters.

![Figure 6. Thickness of ZRP coating from accelerated test.](image)

Results of observation and thickness measurements revealed that behaviours of ZRP coatings during testing time have same tendency, but have different levels.

### 3.2. Results of field exposure test

Figure 7 shows thickness variation of ZRP coating in field exposure test from January 2014 to December 2016. After 35 testing months, thickness of ZRP reduced, generally, and reached to -38 µm in atmospheric zone and -31 µm in tidal zone. Decrease coating thickness demonstrated that the degradation of ZRP in either atmospheric zone or tidal zone of industrial port environment and atmospheric zone have stronger effect. Figure 8 shows external surface of ZRP with heavy encrustation of hard-shelled fouling organism and seaweed. These living communities changed environment by metabolism which generated oxygen, carbon dioxide directly to external surface of ZRP. Seasonal conditions, such as pH and salinity of water (Figure 9), replaced and developed the living community. Therefore, a high erosive environment was grown with development of living community. Along depth of testing zones, density of organism and seaweed is larger, such increase the attack to external surface of paint.
Subsequently, time of wetness and complicated components (dusty metal, powder from building materials, dusty cereals, waste water, etc.) of industrial port also contribute to degradation of ZRP [19 - 21].

Figure 7. Thickness of ZRP coating from field exposure test.

Figure 8. Observation of ZRP coated piles (a) with damaged positions in atmospheric zone (b) and tidal zone (c, d).
Different behaviors of zinc rich paint against corrosion in atmospheric zone and tidal zone of…

Blisters appeared rarely on ZRP surface in field exposure test, unlike accelerated test. Accelerated tests were operated with stronger conditions (longer time of wetness, higher temperature, increasing concentration of dissolved oxygen) than field exposure test. Hence, growth of blisters in accelerated tests are higher than in field exposure test.

4. CONCLUSIONS

Comparison between results of accelerated tests and field exposure tests indicated that growth of blisters on ZRP proportionate with time of wetness and temperature. Results of accelerated tests show that high temperature, concentration of dissolved oxygen, time of wetness increased blister growing rate. In field exposure test, the degradation of ZRP in atmospheric zone and tidal zone caused by complicated components of industrial port, especially by living organism and seaweed. Thickness reduction of ZRP in field exposure test is very smaller (with under 60 µm maximum) than initial thickness. Such result indicated that ZRP currently is an effective corrosion prevention method.

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