DEVELOPMENT OF ENVIRONMENTALLY FRIENDLY FORMULATION FOR CORROSION RESISTANCE OF GALVANIZED STEEL SHEET

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ABSTRACT
This research studies corrosion resistance of galvanized steel sheets coated by environmentally friendly coating formulations. Each coating formulation contains a silane coupling agent, i.e.: 3-glycidoxypropyl trimethoxy silane or GPTMS, a resin and a metal additive. Two types of metal additives, namely compound A containing Zirconium and compound B containing Vanadium were used at different concentrations of 1%, 3% and 5%nv. Galvanized steel sheets were coated by the prepared coating formulations using the barcoat technique. Subsequently, the coating was cured in an oven. The obtained coating films were characterized by the Scanning Electron Microscopy (SEM) and potentiostatic technique. The corrosion resistance of coated galvanized steel sheets was evaluated by the Salt Spray Test (SST) in 5%(w/w) NaCl. The results indicate that the formulation containing GPTMS with metal additive compound A at 5%nv concentration improved anti-corrosion performance significantly.

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INTRODUCTION

Corrosion is the most concern problem with the material and equipment fail, waste of resources, loss of energy and material that usually expensive to repair. This cost includes the application of protective coatings. A generic way to protect metals from corrosion is to apply protective films or coatings, which also permit the desired properties of the substrate to be coated through the chemical modification of the coatings. Anticorrosion is commonly used to slow down the corrosion rate are protective coating. Surface coating is one of the most potential methods for anticorrosion of metal which conventionally isolate metal surface from the corrosive media. Chromate conversion coatings with hexavalent chromium or Cr (VI) are used to coat on material because of providing excellent anti-corrosion performance. Although Cr (VI) coating have high corrosion resistance, it is the hazardous chemical following EU directive 2000/53/EC which prohibit the use of Cr (VI) resulting from its carcinogenic nature. Recently, sol-gel which used silane coupling agent has become more attractive for coating that have high anticorrosion performance and alternate for chromate coating in order to environmentally coating. Alkoxy silane in type of 3-glycidoxypropyl trimethoxy silane (GPTMS) is widely used for coating formulation. Moreover, metal additives, namely compound A containing Zirconium and compound B...
containing Vanadium, resin and silica are widely used too because it can provide effective protection to metal substrate. In this research, the type of metal additives and concentration are studied and optimized. Therefore this research will be focused on the development of coating formulation for anticorrosion for galvanized steel

**EXPERIMENTAL**

**A. Sample preparation**

Galvanized steel sheet with the size of 22 cm × 35 cm × 0.05 cm was used as substrate to investigate surface coating properties. The galvanized steel sheets were cleaned with degreasing chemical and rinsed with deionized (DI) water and then remove water on galvanized steel sheet by removal machine. They were coated with coating formulation using a barcoat rod and cured at 230 °C in the oven. The process and conditions for treatment are described in Table 1. After coating process, test panel dried in natural air and stored in a desiccator for analyses. The coating film thickness was controlled in 0.4-0.5 g/m²

**B. Procedure for mixing coating formulation**

3-glycidoxypropyl trimethoxy silane(GPTMS) and water were mixed and stirred for 20 min at room temperature (30 ± 2°C). Then silica was dropped in to solution and stirred for 20 min. After that resin was dropped in to solution and stirred for 10 min. Finally, metal additive was added and solution was stirred for 20 min.

**C. Characterization and analysis**

**Corrosion test**

The edges of galvanized test panels were sealed with tape and then tested by salt spray test (SST) following standard JIS Z2371. The white rust area of test panels were evaluated as percentage every 24 hr until 240 hr. The appearance of test panel was photograph. The criterion of this test is % white rust of test panel must less than 5%.

**Electrochemical measurement**

The electrochemical studies on test panels that treated with coating formulation were conducted by using AUTOLAB PGSTAT 302N. The test was carried out in 0.5M NaCl solution (100±2ml) using three electrode cell equipped with test panel as working electrode (1cm²), platinum and Ag/AgCl as counter and reference electrodes, respectively. The corrosion current density (i_corr) and corrosion potential (E_corr) values were obtained by extrapolation of anodic and cathodic regions.

**Morphology of coating**

The morphology of bare and coated test panels was using Scanning Electron Microscope (SEM; Hitachi, model SU3500) at magnification 50x and 100x with voltage 10 kV.
Table 1
Coating process and conditions

<table>
<thead>
<tr>
<th>No.</th>
<th>Process</th>
<th>Detail</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cleaning</td>
<td>Degreasing machine by degreasing chemical</td>
<td>Spray at 50-60 °C</td>
</tr>
<tr>
<td>2</td>
<td>Water rinse</td>
<td>Tap water and DI water</td>
<td>Spray at R.T.</td>
</tr>
<tr>
<td>3</td>
<td>Drying</td>
<td>Blower by water removal machine</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Coating</td>
<td>Environmental coating formulation</td>
<td>Bar coat</td>
</tr>
<tr>
<td>5</td>
<td>Curing</td>
<td>Oven</td>
<td>230 °C</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

A. Corrosion study
Salt spray study

Fig 1 shows test panels of bare and coated galvanized steel sheet with GPTMS/resin/silica/Zirconium additive compound A at 1,3,5 nv% and GPTMS/resin/silica/Vanadium additive compound B at 1,3,5 nv% after salt spray testing until 240 hr. The bare condition cannot resist corrosion. It occurred 100% white rust rapidly at 72 hr. The film coating of GPTMS/resin/silica/Vanadium additive compound B at 1,3,5 nv% were occurred white rust of the test panel less than bare condition. These results informed that the corporation of vanadium additive compound B in GPTMS matrix (Fig.1 (B1-B3)) improved the anti-corrosion performance but did not significantly protect the galvanized steel after salt spray test in 240 hr. However, zirconium additive compound A in GPTMS matrix (Fig.1 (A1-A3)), the anti-corrosion performance increases significantly. Moreover, %nv of zirconium additive compound A effects to anti-corrosion performance. The more %nv of zirconium additive compound A, the more enhance the anti-corrosion performance.

![Fig.1. Bare and coated galvanized steel of GPTMS/resin/silica/metal additive after salt spray test for 0, 72, 120 and 240 hr; (A1) 1%nv compound A, (A2) 3%nv compound A, (A3)5%nv compound A, (B1) 1%nv compound B, (B2) 3%nv compound B, (B3) 5%nv compound B](image-url)
**Electrochemical study of coating**

The electrochemical behavior of coating formulation was investigated by potentiostat meter. A Pt counter electrode and Ag/AgCl reference electrode were used of this study. In this study, dry film coating was control in range 0.4-0.5 g/m². The result of this study was shown in Table2. It was found that bare condition have high corrosion current ($I_{corr}$). Adding metal additive (Zirconium compound A and Vanadium compound B) showed lower corrosion current ($I_{corr}$) and corrosion rate than bare condition. So, metal additive provides anti-corrosion performance. Moreover, an increase amount %nv up to 5%nv of zirconium compound A performed lowest corrosion current 0.211 µA/cm² with corrosion rate 0.002 mm/year. So, the best condition is A3: GPTMS/resin/silica/5%nv zirconium compound A for improve anti-corrosion performance on galvanized steel sheet.

**Table.2**
Corrosion potential ($E_{corr}$), corrosion current ($I_{corr}$) and corrosion rate ($R_{corr}$) calculated from Tafel plots for coating formulation on galvanized steel sheet in 0.5 M NaCl solution.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Condition detail</th>
<th>Electrochemical measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_{corr}$ (V)</td>
</tr>
<tr>
<td>Bare</td>
<td>Uncoated test panel</td>
<td>0.888</td>
</tr>
<tr>
<td>A1</td>
<td>GPTMS/resin/silica/1% compound A</td>
<td>-1.030</td>
</tr>
<tr>
<td>A2</td>
<td>GPTMS/resin/silica/3% compound A</td>
<td>-1.005</td>
</tr>
<tr>
<td>A3</td>
<td>GPTMS/resin/silica/5% compound A</td>
<td>-1.050</td>
</tr>
<tr>
<td>B1</td>
<td>GPTMS/resin/silica/1% compound B</td>
<td>0.931</td>
</tr>
<tr>
<td>B2</td>
<td>GPTMS/resin/silica/3%compound B</td>
<td>-0.914</td>
</tr>
<tr>
<td>B3</td>
<td>GPTMS/resin/silica/5% compound B</td>
<td>-0.923</td>
</tr>
</tbody>
</table>

**B. Coating surface morphology**

SEM image of coating surfaces are shown in Fig2. Surface of bare, A3 and B3 were observed at x50 and x100. Bare condition showed smooth surface of galvanized material. In conditions that add GPTMS, resin, silica and metal additive shown roughness and have grain on surface because of film coating formation. A significant condition was A3: GPTMS/resin/silica/5% compound A that shown many contiguous grains on surface when compare with bare and B3 condition.
CONCLUSIONS

Environmental coating formulation was successfully developed based on GPTMS/resin/silica/metal additive. It was found that both metal additives (Zirconium compound A or Vanadium compound B) enhance the anti-corrosion performance of film coating. The formulation with zirconium based additive provided more anti-corrosion performance than the formulation with vanadium based additive according to the results from salt spray test after 240 hr. The electrochemical measurements showed that the corporation of GPTMS with resin, silica and 5\%nv of zirconium compound A significantly improved the anti-corrosion performance and decreased corrosion rate of galvanized steel sheet. The best anti-corrosion performance with corrosion rate 0.002mm/year (I_{corr} of 0.211\mu A/cm^2) was achieved.

ACKNOWLEDGEMENTS

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REFERENCES
