Development of Organic/Inorganic Hybrid Coating Solution for High Strength Steel Sheet (SPFC780)

K. W. Nam, H. R. Jeong, S. H. Ahn, K. Y. Seong, and K. H. Lee

Abstract—Currently, a very popular method to reduce the corrosion on zinc is to use chemical conversion coating layers based on Cr+6. However, certain issues must be overcome to use chromium salts due to restrictions resulting from legislation targeting environmental protection. This study investigates the optimum conditions to form high-strength steel sheets (SPFC780) using an organic/inorganic solution containing Si. The curing duration for the coating solution was of 1, 2 and 3 minutes at a temperature of 463 K. Seven types of coating solution were used, and the corrosion resistance improved as the heat treatment time increased. The optimal coating solution was the urethane of 21 wt.%, the SiO2 polysilicate of 7 wt.% and the melamine of 3 wt.%. 

Index Terms—Organic/inorganic coating solution, cold rolled steel, salt spray test, corrosion resistance.

I. INTRODUCTION

Modern automobiles require a higher structural performance during high-speed impacts to improve passenger safety. In particular, the ensure the safety of the passengers under lightweight and side collisions, a high strength material should be applied to the upper part of the center pillar and an even higher impact rigidity should be achieved when compared to that of the lower part. Although car safety is extremely important, the visual appearance of the car is also important. Since cold-rolled steel sheets are use in car manufacturing, the center pillar is susceptible to corrosion, and needs to be painted with various materials to provide corrosion resistance. Currently, the use of chromate-treatment solutions containing Cr+6 to provide corrosion resistance has been prohibited due to the risks to human health. Due to such regulation, environmentally-friendly coating solutions are actively being developed by using inorganic or organic coating treatments [1]-[12]. Authors investigated the corrosion resistance of steel sheets coated with zinc and cold-rolled steel sheets coated with an organic/inorganic hybrid solution [13]-[19].

Manuscript received April 8, 2016; revised July 5, 2016. This work (Grants No. C0268714) was supported by Business for Academic-industrial Cooperative establishments funded Korea Small and Medium Business Administration in 2015.

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II. MATERIALS AND EXPERIMENTAL METHODS

The materials used in these experiments consist of cold-rolled SPFC780 steel sheets with a thickness of 1 mm, which are extensively used in automobile manufacturing. Tables I and II show the mechanical properties and the chemical compositions of the material that was used. The specimens were ultrasonic cleaned for 5 minutes in isopropyl alcohol in order to remove the oil that prevents corrosion during manufacture. The sizes of the salt spray test specimens were made according to KSD 9502, and the specimens were treated with tape to prevent corrosion from the edges when the salt spray test started.

An organic/inorganic hybrid coating solution was prepared using distilled water, ethanol, a urethane resin, SiO2 polysilicate, and melamine (curing agent). The compositions of the coating solution are shown in Table III. The compositions were obtained by the authors through analysis and testing. Coating was carried out using bar-coater No. 3 (wet film thickness; 6.86 μm). The coating solution was cured for 1, 2, and 3 minutes at 463 K.

The corrosion resistance properties of the coated cold-rolled steel sheet were determined by conducting a salt spray test using the ATS-SST900 equipment [20]. The specimens were tilted at about 45° in the chamber of the salt spray tester, and neutral salt water spray tests were conducted at 35±2 °C for 96 hours. The specimens were observed at 24 hours intervals, and the corrosion resistance of the specimens was evaluated according to the corrosion area. Fig. 1 shows a flow diagram of the salt spray test.

The other tests were evaluated using specimens with a curing time of 3 minutes at 463 K after coating. The coating

<table>
<thead>
<tr>
<th>TABLE I: MECHANICAL PROPERTIES</th>
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<tr>
<td>Yield stress (MPa)</td>
</tr>
<tr>
<td>519</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE II: CHEMICAL COMPOSITIONS (%)</th>
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<tr>
<td>C</td>
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<tr>
<td>0.1393</td>
</tr>
</tbody>
</table>

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adhesion [21], [22] was evaluated by placing 3M tape on the cross-cuts at 1 mm intervals on an area of 10 × 10 mm, and the boiling water resistance was observed on the surface after immersion for 1 hour in boiling water. The change in color at the surface was observed after rubbing the specimen 30 times using a cotton stick immersed in alcohol. Cracking and peeling was observed for the coating layer on the surface after bending until 180°.

<table>
<thead>
<tr>
<th>TABLE III: COMPOSITION OF COATING SOLUTION (WT.%)</th>
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<tbody>
<tr>
<td>Distilled water</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>U</td>
</tr>
<tr>
<td>US₃</td>
</tr>
<tr>
<td>US₃M₃</td>
</tr>
<tr>
<td>US₇M₃</td>
</tr>
<tr>
<td>US₇M₃</td>
</tr>
<tr>
<td>US₇M₃</td>
</tr>
<tr>
<td>US₇M₅</td>
</tr>
</tbody>
</table>

**Ultrasonic cleaning (Isopropanol, 5 minute)**

**Solution coating (Bar coater, #3)**

**Hardening treatment (1, 2, 3 minute at 463 K)**

**Air cooling**

**Taping of specimen edge**

**Salt spray test (96 h)**

Fig. 1. Flow chart of salt spray test.

### III. RESULTS AND DISCUSSION

The appearance of the SPFC780 specimens after a salt spray test of 96 hours is shown in Fig. 2. Fig. 2(a)–2(g) show the U, US₃, US₃M₃, US₇M₃, US₇M₃M₃, US₇M₃M₁, and US₇M₃ solutions, respectively. Corrosion was reduced with an increase in curing time, regardless of the type of solution that was used.

Fig. 3 shows the relationship between the corrosion area rate and the salt spray time. Fig. 3(a) shows white rust after a salt spray of 12 hours, regardless of the curing time. After 96 hours, corrosion occurred in the entire specimen. However, the specimens that had been cured for 3 minutes showed a corrosion area of about 20% lower than the specimens cured for 1 and 2 minutes.

Fig. 3(b) shows the specimen was fine until 24 hours, but white rust appears after 48 hours. After 96 hours, the specimens cured for 1 minute exhibit a corrosion area ratio that was as high as 20%, and the specimens cured for 3 minutes showed a corrosion area ratio of 7%. However, the specimen in Fig. 3(b) shows a lower corrosion area than those in Fig. 3(a). The specimen in Fig. 3(c) exhibited an increase in the corrosion resistance with an increase in the curing time, while the specimens cured for 3 minutes exhibited a corrosion area ratio of 6%. Fig. 3(d) shows that the specimens cured for 1 minute showed a corrosion area ratio of about 24%, and those cured for 3 minutes showed a very low corrosion area ratio of about 2%. Fig. 3(e) shows a coating solution with the highest content of SiO₂. The specimens cured for 1 minute and 2 minutes exhibited a similar corrosion area of 14%, but that cured for 3 minutes exhibited a low corrosion area ratio of about 2%. Fig. 3(f) did not show any corrosion until 12 hours, and corrosion occurred after 24 hours. The specimen cured for 3 minutes exhibited a corrosion area ratio of 10% or more. Fig. 3(g) did not show corrosion until 24 hours, but corrosion was observed from 96 hours on. The specimens cured for 1 minute showed a corrosion area ratio of 20%, and those cured for 2 minutes and 3 minutes exhibited a corrosion area ratio of 10% or more.

Fig. 2. Appearance after salt spray test in SPFC780 specimen. (a) U, (b) US₃, (c) US₃M₃, (d) US₇M₃, (e) US₇M₃M₃, (f) US₇M₃M₁, (g) US₇M₅.

The U solution without melamine (curing agent) and SiO₂ polysilicate exhibited a high corrosion rate. This indicates that the melamine resin became a bridge in the synthesis of the SiO₂ polysilicate and urethane resin.

Table IV shows the corrosion area rate in the salt spray after 96 hours according to the curing time for each solution. Here, Ct refers to the curing time.
about 13% for the curing time of 1 minute and 2 minutes, and the curing time of 3 minutes exhibited a ratio of 1.13%, similar to that of US₇M₇. The corrosion area of the US₇M₁ solution showed a 25% ratio for a curing time of 1 minute, and 16.19% for a curing time of 2 minutes. The curing time of 3 minutes exhibited a corrosion area ratio of 12.81%, which is similar to a half that for the curing time of 1 minute. The corrosion area ratio of the US₇M₁ solution was above 20% for a curing time of 1 minute, and it was similar to that at 15% for a curing time of 2 minutes and 3 minutes.

Fig. 5 shows the typical surface after the cross-cutting test of the specimens with a coating of the seven type solutions. The specimens showed no peeling and a superior adhesion for all solutions.

The stability of the coating layer is very important at boiling water temperatures. Fig. 6 shows the results of the boiling test for all solutions. The U, US₇, US₇M₃ solutions showed peeling of the coating layer, and the US₅M₅, US₅M₇, US₅M₉ solutions did not show peeling or swelling of the coating layer at all.

Fig. 7 shows the results of the rubbing test for all solutions. The surface color of the seven type solutions changed for all coating layers. The color changes in U and US₇ were the most severe, and US₅M₅ also showed a change in color. US₇M₃ and

Table IV: Corrosion area rate (%) in 96 hours of salt spray time

<table>
<thead>
<tr>
<th>Solution</th>
<th>Ct</th>
<th>1 min</th>
<th>2 min</th>
<th>3 min</th>
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</thead>
<tbody>
<tr>
<td>U</td>
<td>97</td>
<td>82.63</td>
<td>72.08</td>
<td></td>
</tr>
<tr>
<td>US₇</td>
<td>22</td>
<td>18.17</td>
<td>7.58</td>
<td></td>
</tr>
<tr>
<td>US₇M₃</td>
<td>17.25</td>
<td>13.81</td>
<td>6.25</td>
<td></td>
</tr>
<tr>
<td>US₇M₅</td>
<td>23.29</td>
<td>7.41</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>US₅M₇</td>
<td>13.95</td>
<td>12.52</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>US₅M₉</td>
<td>24.81</td>
<td>16.19</td>
<td>12.81</td>
<td></td>
</tr>
<tr>
<td>US₅M₁</td>
<td>23.43</td>
<td>15.69</td>
<td>15.94</td>
<td></td>
</tr>
</tbody>
</table>

Ct : curing time
US₃M₃ exhibited the best conditions.

The results of the bending test until 180 degrees are shown in Fig. 8. For the seven types of solution, the cracks and peels were not observed for the coating surfaces.

![Fig. 7. Results of rubbing test in SPFC780 specimen. (a) U, (b) US₃, (c) US₄, (d) US₅, (e) US₆, (f) US₇, (g) US₈.](image)

![Fig. 8. Results of bending resistance test in SPFC780 specimen. (a) U, (b) US₃, (c) US₄, (d) US₅, (e) US₆, (f) US₇, (g) US₈.](image)

Fig. 9 show typical SEM photography of coating surface. These are the results of a three minute hardening time. Fig. 9(a) shows the U solution, Fig. 9(b) shows the US₃ solution, and Fig. 9(c) shows the US₄ solution. Fig. 9(a) was made of a large crack by the shrinkage. Fig. 9(b) was formed a lot of fine cracks by the addition of SiO₂ polysilicate. But in the Fig. 9(c), a melamine curing agent played a cross-linking role in the synthesis of SiO₂ polysilicate and urethane resin. So cracks did not occur at all. US₃M₃ is the optimal composition ratio in the range of solutions in this study.

![Fig. 9. SEM photography of coating surface with curing time of 3 minutes. (a) U solution, (b) US₃ solution, (c) US₄-M₃ solution.](image)

IV. CONCLUSIONS

Seven types of organic/inorganic hybrid solutions were coated on cold-rolled SPFC780 steel used for automobile manufacturing. The characteristics of the corrosion resistance and the coating solution were thus evaluated.

1. The cold-rolled SPFC780 steel sheet was subjected to a salt spray and showed less corrosion as the curing time increased, regardless of the type of the solution. The solution with polyurethane, melamine and SiO₂ polysilicate showed excellent corrosion resistance than the solution with only urethane. Melamine became a bridge for SiO₂ polysilicate and urethane.

2. The corrosion area ratio was the lowest at about 1% for the salt spray test of 96 hours in the specimen cured for 3 minutes with US₃M₃ and US₄M₃, and very little corrosion occurred until 72 hours.

3. The adhesion and 180 degree bending did not produce peeling or cracks for all solutions. The boiling water resistance test did not show peeling or swelling of the coating layer for the US₃M₃, US₄M₃ and US₇M₃ solution. The surfaces of US₃M₃ and US₄M₃ showed the best conditions in the rubbing test.

REFERENCES


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