Electrochemical Evaluation on Corrosion Resistance of Anti-corrosive Paints

Kyung-man Moon* · Myung-hoon Lee** · Yun-hae Kim†

(Received March 19, 2009 ; Revised May 13, 2009 ; Accepted May 29, 2009)

Abstract: It has been observed that coated steel structures are rapidly deteriorated than designed lifetime due to acid rain caused by air pollution etc.. Therefore improvement of corrosion resistance of anti-corrosive paint is very important in terms of safety and economic point of view. In this study corrosion resistance for five kinds of anti-corrosive paints including acryl, fluorine and epoxy resin series were investigated with electrochemical methods such as corrosion potential, polarization curves, impedance and cyclic voltammogram measurements etc..

There were somewhat good relationships between values measured by electrochemical methods such as corrosion current density obtained by cathodic and anodic polarization curves, value of impedance estimated with AC impedance, and polarization resistance on the cyclic voltammogram, for example, corrosion current density was decreased with increasing of values of impedance and polarization resistance on the cyclic voltammogram. However their relationships between corrosion current density and corrosion potential were not well coincided each other. Consequently it is considered that although a corrosion potential of F101 of fuoric resin series shifted to negative direction than other anti-corrosive paints, its corrosion resistance, indicating on the cathodic and anodic polarization curves, AC impedance curves and cyclic voltammogram, was the most superior to other paints, whereas A100 containing arcylic resin showed a relatively poor corrosion resistance compared to other paints.

Key words: Corrosion Resistance, Anti-corrosive Paint, Electrochemical Methods, Impedance, Cyclic Voltammogram

1. Introduction

In recent years, numerous steel structures widely used in both continental and marine area have been often exposed to severe corrosive environment due to increment of environmental contamination with a rapid development of industrial society. Therefore those structures should be controlled with the optimum protection methods such as coating, electrical and some other methods. For example, these
structures such as steel bridge established in continental or marine area or a warf crane etc. have been mainly protected by coating method and some steel piles of under sea water is generally protected by electric protection methods like impressed current or sacrificial anode method.\textsuperscript{[1-8]} And by a certain report of Japan, it is reported that cost of coating protection is of more than 63\% among total costs for numerous protection methods.\textsuperscript{[9]} It is supposed that in Korea, cost of coating protection would amount to be a higher percentage than that of Japan because Korea nearly have the same geographical and environmental condition like Japan. Furthermore increment of environmental contamination may be resulted in accelerating of corrosion of steel structures, as a result, it has been observed that coated steel structures would rapidly be deteriorated than designed life time due to acid rain caused by air pollution etc. Therefore corrosion resistance of anti-corrosive paint is considered to be very important in terms of safety and economic point of view. In previous papers some kinds of epoxy resin series by adding additives were investigated with electrochemical methods for corrosion resistance.\textsuperscript{[10,11]} In this study, corrosion resistance for five kinds of anti-corrosive paints having a different resin series were investigated with electrochemical methods such as corrosion potential, polarization curves, impedance and cyclic voltammogram measurements etc.

The purpose of this study is to see what kinds of resin and additives affect to corrosion resistance and whether there are some relationship each other between polarization curves, impedance and cyclic voltammogram. It is thought that these results will give some available data not only to improve a good anti-corrosive paint having the corrosion resistance of long lifetime but also to allow possibility of optimum evaluation for corrosion resistance by using of electrochemical methods.

2. Experiment

The test specimen used in this experiment is SS400 steel being widely used with general structure and its size of test specimen is 3cm x 20cm x 0.3cm. After the surface of test specimen was polished with sand paper (from No.200 to No.1000) and degreased with acetone, and then removed rust with blast cleaning method (Sa21/2) until white color appear to the surface of test specimen. And average of coarse intensity of the surface(Ra) is 12.5~20μm.

Coating is performed by an airless spray with injection pressure at 125kg/cm\textsuperscript{2} and condition of weather was temperature at 21°C, relative humidity at 65~70\%. Kinds of anti-corrosive paints for experimental coating are a acrylic resin series(A100, A101), fluoric resin series (F100, F101) and epoxy resin series (E100), and their dry film thickness are of 25μm.
Table 1 Chemical composition of various anti-corrosive paints (wt%)

<table>
<thead>
<tr>
<th>Comp. kind</th>
<th>Acrylic resin</th>
<th>Fluoric resin</th>
<th>Epoxy resin</th>
<th>Silica</th>
<th>Xylene</th>
<th>TiO2</th>
<th>Petroleum hydrocarbon</th>
<th>Butyl acetate</th>
<th>Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>A100</td>
<td>25~30</td>
<td>20~30</td>
<td>10~20</td>
<td>15~25</td>
<td>2~6</td>
<td></td>
<td></td>
<td></td>
<td>5~10</td>
</tr>
<tr>
<td>A101</td>
<td>35~40</td>
<td>5~15</td>
<td>10~20</td>
<td>15~25</td>
<td>2~6</td>
<td></td>
<td></td>
<td></td>
<td>5~10</td>
</tr>
<tr>
<td>F100</td>
<td>30~40</td>
<td>5~10</td>
<td>15~25</td>
<td>20~30</td>
<td>2~8</td>
<td></td>
<td></td>
<td></td>
<td>1~5</td>
</tr>
<tr>
<td>F101</td>
<td>40~45</td>
<td>1~5</td>
<td>10~20</td>
<td>20~30</td>
<td>2~8</td>
<td></td>
<td></td>
<td></td>
<td>1~5</td>
</tr>
<tr>
<td>E100</td>
<td>55~65</td>
<td>25~30</td>
<td>5~10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5~10</td>
</tr>
</tbody>
</table>

Table 1 shows their chemical composition. After test specimen with coating was cut with size of 3cm x 2cm, and connected copper wire to a hole of center of edge. And then its surface was insulated with an epoxy coating only except a 1cm² uncoated for the corrosion test. After all test specimens were immersed to the seawater solution, their polarization characteristics were examined respectively both soon after immersion and with 15 days after immersion.

Corrosion potential, polarization curves, AC impedance and cyclic voltammogram were calculated with electrochemical methods and surface morphology of corroded surface by polarization curves of test specimen with 15 days after immersion was observed with multi media microscope (Model: SV35, Sometech Com.Ltd.)

Experimental equipment for measurement is CMS-100 program imported by W.A. Tec. Co., Ltd. and reference electrode was SCE, and counter electrode was Pt. And scanning speed is 1mV/s but in case of drawing of cyclic voltammogram, its speed is 30mV/s.

3. Results and discussion

Fig. 1 shows the variation of corrosion potential of various anti-corrosive paints soon after immersion. Corrosion potential of F101 is the most negative potential and E100 showed the noblest potential with immersion time. Fig. 2 shows the variation of corrosion potential of 15 days after immersion. Corrosion potential of F101 is also the most negative potential, however the noblest potential was observed at the A101 of acrylic resin series. As shown in Fig.1 and Fig.2, we can see that their corrosion potentials didn’t show a regularly uniform pattern, however only corrosion potential of F101 indicated a constantly most negative potential regardless of immersion time.

Fig. 3 shows the variation of cathodic and anodic polarization curves. As shown in Fig. 3, most of the polarization curves
are nearly the same pattern regardless of kinds of resin in seawater solution 15 days after immersion, and it is known that corrosion resistance of F101 is seemed to be qualitatively the most superior to other paints and A100 showed a higher corrosion current density than those of other paints on the polarization curves. From Fig. 3, the data of corrosion current density and corrosion potential obtained by Tafel fit method of GMS-100 program summarized at Table 2.

Fig. 2 Variation of corrosion potential for various anti-corrosive paints with immersion time 15 days after immersion

Fig. 3 Variation of cathodic and anodic polarization curves in seawater solution 15 days after immersion

Fig. 4 Variation of corrosion current density for various coating specimens

Fig. 4 shows the variation of corrosion current density with kinds of test specimens. Corrosion current density of F101 was the smallest value among of those specimens and A100 showed the highest corrosion current density.

Table 2 The data of corrosion current density and corrosion potential obtained from Tafel fit method on polarization curves of Fig. 3

<table>
<thead>
<tr>
<th>Kinds of coating specimens</th>
<th>icor(A/cm²)</th>
<th>Ecor(V vs.SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A100</td>
<td>4.5 ×10⁻⁷</td>
<td>-1.009</td>
</tr>
<tr>
<td>A101</td>
<td>10.4 ×10⁻⁹</td>
<td>-0.303</td>
</tr>
<tr>
<td>F100</td>
<td>1.59 ×10⁻⁸</td>
<td>-0.883</td>
</tr>
<tr>
<td>F101</td>
<td>1.81 ×10⁻¹¹</td>
<td>-0.716</td>
</tr>
<tr>
<td>E100</td>
<td>7.68 ×10⁻¹¹</td>
<td>-0.63</td>
</tr>
</tbody>
</table>

Fig. 5 Variation of impedance for various coating specimens soon after immersion
Fig. 5 shows the variation of impedance value for various test specimens soon after immersion. Impedance of F101 at 10MHz showed the largest value compared to other specimens and its value of A100 was the smallest among of those specimens. Fig. 6 shows the variation of impedance of 15 days after immersion. F101 also showed the largest value of impedance and impedance of A100 was also the smallest value.

As a result, it is thought that there is a fairly good relationship between corrosion current density and impedance, for example, corrosion current density is decreased with increasing of impedance as shown in Fig. 4, Fig. 5 and Fig. 6.

Fig. 7 shows the variation of cyclic voltammogram of 1st curve for various anti-corrosive paints. As shown in Fig. 8 polarization resistance of A100 on both cathodic and anodic current density was significantly of the smallest value compared to other specimens, whereas other specimens such as A101, E100, F101 and F100 showed a relatively high polarization resistance. Variation of cyclic voltammogram of 15 days after immersion was shown in Fig. 8. Their pattern of cyclic voltammogram of 15 days after immersion was almost same as the pattern of soon after immersion of Fig. 7, for example, polarization resistance of A100 in both cathodic and anodic current density was also the smallest value than those of other coated specimens as shown in Fig. 7 and Fig. 8.

From these results, corrosion resistance of anti-corrosive paints is considered to be
depended on their polarization resistance and their resistance are generally being increased with decrement of permeation velocity of dissolved oxygen and chloride ion as well as increment of circuit resistance between cathode and anode of substrate metal,\(^{12,13}\) which is resulted from their unique intrinsic characteristics of coating film to control corrosion resistance. Therefore it expected that A100 of anti-corrosive paint may have a relatively poor corrosion resistance than those of other anti-corrosive paints. In particular fluoric resin is seemed to be a relatively good corrosion resistance compared to other resin series because it is extremely stable and inactivity due to molecular structure bonded strongly with carbon and fluorine.\(^{14}\)

Fig. 9 shows the variation of morphology of corroded surface by drawing polarization curves 15days after immersion. Corrosive products and oxide films were observed at the surface of A100 and the surface of other specimens indicated a little fine spots like pitting to the edge of surface and their morphologies of surface were nearly same as each other only except surface of A100.

4. Conclusions

Some kinds of resin series are to examine in terms of electrochemical point of view to see how those affect to corrosion resistance of anti-corrosive paint in seawater solution. F101 of fluoric resin series with adding additives showed a relatively good corrosion resistance compared to other resin. However A100 of acrylic resin series showed a higher corrosion current density than those of other anti-corrosive paints. Furthermore it is supposed that there are considerably somewhat good relationships each other between corrosion resistance, impedance and polarization resistance, for example, corrosion current density is decreased with increasing of impedance and polarization resistance of the cyclic voltammogram.

References

Electrochemical Evaluation on Corrosion Resistance of Anti-corrosive Paints


Author Profile

Kyung-Man Moon
He received his B.E and M.Eng. from Korea Maritime University and Dr.Eng from Nagoya University of Japan. He is currently a professor in Dept. of Mechanical and Material Engineering at Korea Maritime University in Busan.

Myung-Hoon Lee
He received his B.E and M.Eng. from Korea Maritime University and Dr.Eng from Nagoya University of Japan. He is currently a professor in Dept. of Marine System Engineering at Korea Maritime University in Busan.

Yun-Hae Kim
He received his B.E and M.Eng. from Korea Maritime University and Dr.Eng from Kyushu University of Japan. He is currently a professor in Dept. of Mechanical and Material Engineering at Korea Maritime University in Busan.