# 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 $SiO_2$ 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.

K. W. Nam and K. H. Lee are with Pukyong National University, Busan, 48547 Korea (Corresponding author: K. H. Lee; e-mail: namkw@pknu.ac.kr, lkh09@dsme.co.kr).

H. R. Jeong is with Prepoll Co. Ltd., Busan, 46719 Korea (e-mail: prepoll5208@gmail.com).

S. H. Ahn is with Jungwon University, Chungbuk, 28024 Korea (e-mail: shahn@jwu.ac.kr).

K. Y. Seong is with DM, Gimhae, 50820 Korea (e-mail: mssky1@nate.com).

Seven types of organic/inorganic hybrid coating solutions were developed in this study and were coated onto two types of cold rolled SPFC780 steel sheets that are normally used for automobile manufacturing. The characteristics of the coating solutions were evaluated in terms of their corrosion resistance, adhesion, boiling water resistance, and rubbing and bending resistance.

## 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 taping to prevent corrosion from the edges when the salt spray test started.

TABLE I: Mechanical Properties

| Yield stress (MPa) | Tensile Strength (MPa) | Elongation (%) |
|---|---|---|
| 519 | 807 | 27 |

TABLE II: Chemical Compositions (%)

| C | Si | Mn | P | S |
|---|---|---|---|---|
| 0.1393 | 1.023 | 2.102 | 0.0118 | 0.003 |

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; 6.86μm). 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 ℃ 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

doi: 10.18178/ijcea.2016.7.6.614 

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 III: COMPOSITION OF COATING SOLUTION (WT.%)

| | Distilled water | EtOH | $SiO_2$ polysilicate | Urethane resin | Melamine |
|---|---|---|---|---|---|
| U | 53 | 58 | - | 21 | - |
| $US_7$ | 49.5 | 22.5 | 7 | 21 | - |
| $US_3M_3$ | 50 | 23 | 3 | 21 | 3 |
| $US_7M_3$ | 48 | 21 | 7 | 21 | 3 |
| $US_{11}M_3$ | 46 | 19 | 11 | 21 | 3 |
| $US_7M_1$ | 49 | 22 | 7 | 21 | 1 |
| $US_7M_5$ | 47 | 20 | 7 | 21 | 5 |

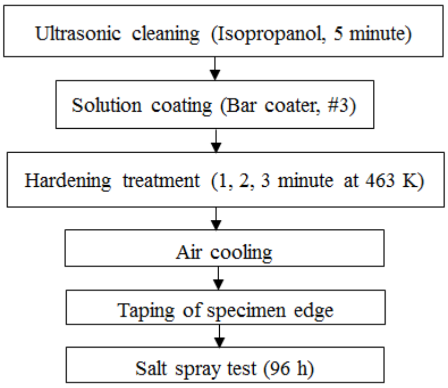


Fig. 1. Flow chart of salt spray test.

## 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, $US_7$, $US_3M_3$, $US_7M_3$, $US_{11}M_3$, $US_7M_1$, and $US_7M_5$ 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 $SiO_2$. 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.

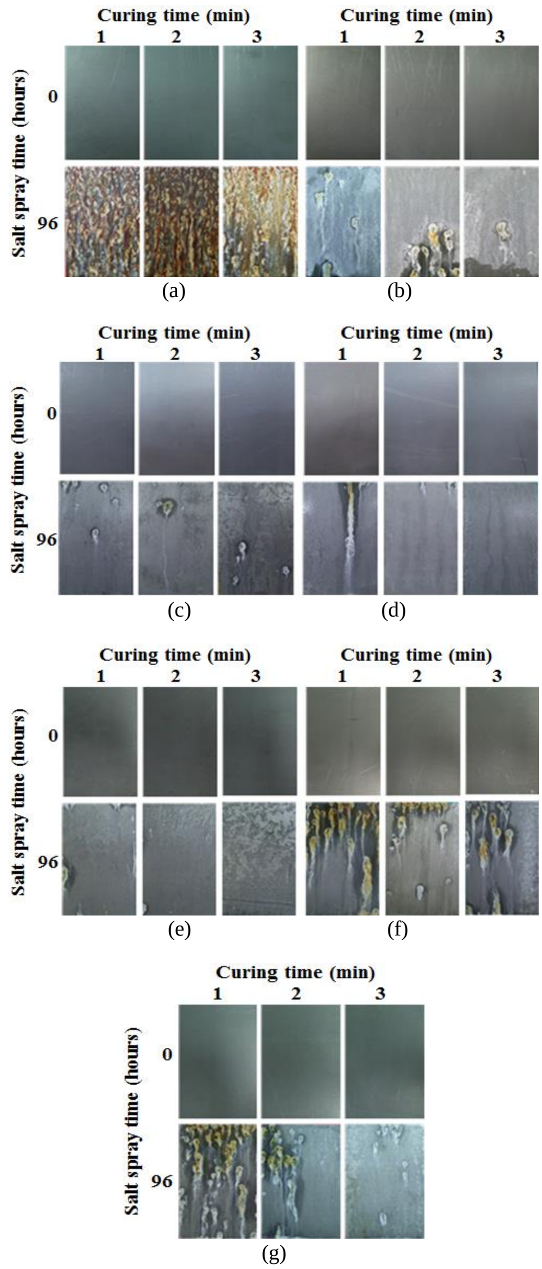


Fig. 2. Appearance after salt spray test in SPFC780 specimen. (a) U, (b) $US_7$, (c) $US_3M_3$, (d) $US_7M_3$, (e) $US_{11}M_3$, (f) $US_7M_1$, (g) $US_7M_5$.

The U solution without melamine (curing agent) and $SiO_2$ polysilicate exhibited a high corrosion rate. This indicates that the melamine resin became a bridge in the synthesis of the $SiO_2$ 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.

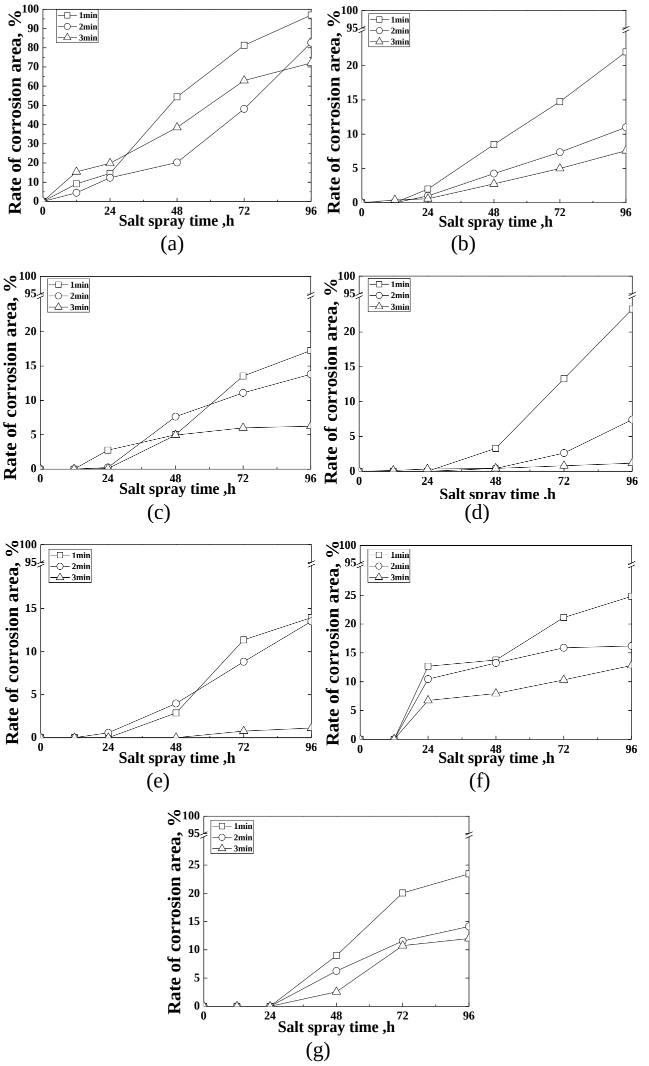



Fig. 3. Relationship between salt spray time and corrosion area rate in SPFC780 specimen. (a) U, (b) $US_7$, (c) $US_3M_3$, (d) $US_7M_3$, (e) $US_{11}M_3$, (f) $US_7M_1$, (g) $US_7M_5$.

TABLE IV: CORROSION AREA RATE (%) IN 96 HOURS OF SALT SPRAY TIME

| Solution \ Ct | 1 min | 2 min | 3 min |
|---|---|---|---|
| U | 97 | 82.63 | 72.08 |
| $US_7$ | 22 | 18.17 | 7.58 |
| $US_3M_3$ | 17.25 | 13.81 | 6.25 |
| $US_7M_3$ | 23.29 | 7.41 | 1.17 |
| $US_{11}M_3$ | 13.95 | 12.52 | 1.13 |
| $US_7M_1$ | 24.81 | 16.19 | 12.81 |
| $US_7M_5$ | 23.43 | 15.69 | 15.94 |

Ct : curing time

Fig. 4 shows the results that are enumerated in Table IV. The corrosion area ratio of the U solution decreased as the curing time increased, and it exhibited a high corrosion area of 72.08% for 3 minutes of curing. The corrosion area ratio of the $US_7$ solution showed about 20% for 1 and 2 minutes of curing, and it appeared a low ratio of 7.58% for 3 minutes of curing. The corrosion area of the $US_3M_3$ solution exhibited a 17.25% ratio with curing time of 1 minute, a 13.81% ratio with a curing time of 2 minutes, and a 6.25% ratio with a curing time of 3 minutes. The corrosion area ratio of the $US_7M_3$ solution decreased significantly as the curing time increased, and it was approximately 1.17% with a curing time of 3 minutes. The corrosion area ratio of $US_{11}M_3$ solution was 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 $US_7M_3$. The corrosion area of the $US_7M_1$ 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 $US_7M_5$ 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.

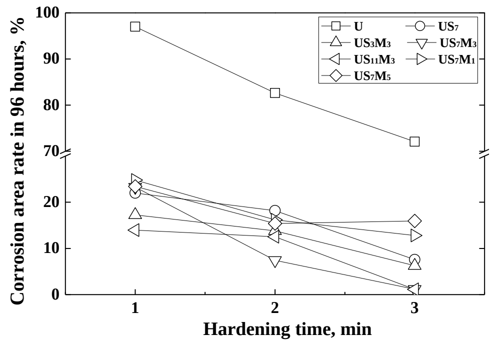



Fig. 4. Relationship between the corrosion area rate in 96 hours of salt spray time and the hardening time.

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, $US_7$, $US_3M_3$ solutions showed peeling of the coating layer, and the $US_7M_3$, $US_{11}M_3$, $US_7M_1$, $US_7M_5$ solutions did not show peeling or swelling of the coating layer at all.

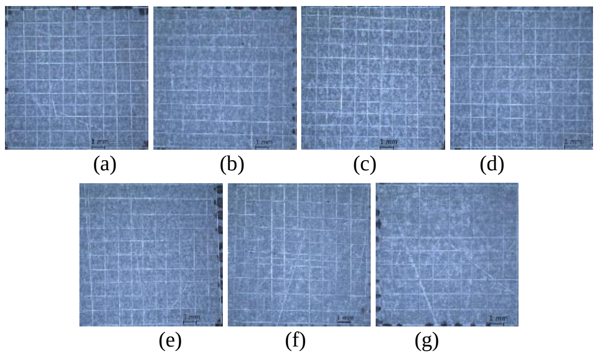



Fig. 5. Results of adhesion test in SPFC780 specimen. (a) U, (b) $US_7$, (c) $US_3M_3$, (d) $US_7M_3$, (e) $US_{11}M_3$, (f) $US_7M_1$, (g) $US_7M_5$.

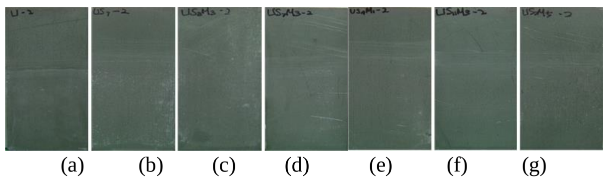



Fig. 6. Results of boiling water resistance test in SPFC780 specimen. (a) U, (b) $US_7$, (c) $US_3M_3$, (d) $US_7M_3$, (e) $US_{11}M_3$, (f) $US_7M_1$, (g) $US_7M_5$.

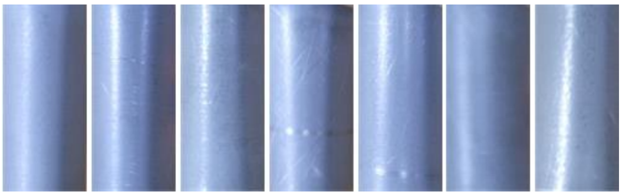
Fig. 7 shows the results of the rubbing test for all solutions. The surface color of the seven type solutions changed for all coating layers. The color changes in U and $US_7$ were the most severe, and $US_3M_3$ also showed a change in color. $US_7M_3$ and

$US_{11}M_3$ 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.

(a) (b) (c) (d) (e) (f) (g)

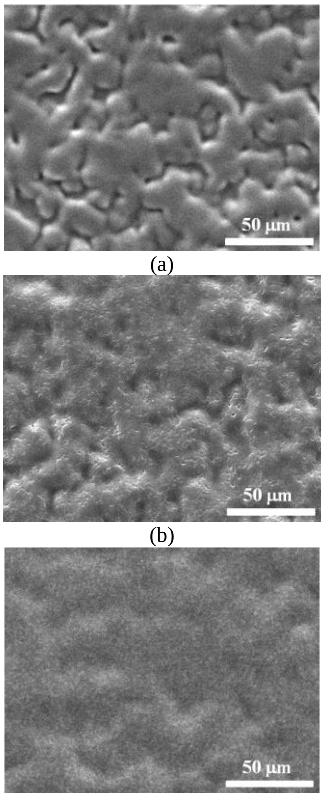
Fig. 7. Results of rubbing test in SPFC780 specimen. (a) U, (b) $US_7$, (c) $US_3M_3$, (d) $US_7M_3$, (e) $US_{11}M_3$, (f) $US_7M_1$, (g) $US_7M_5$.



(a) (b) (c) (d) (e) (f) (g)

Fig. 8. Results of bending resistance test in SPFC780 specimen. (a) U, (b) $US_7$, (c) $US_3M_3$, (d) $US_7M_3$, (e) $US_{11}M_3$, (f) $US_7M_1$, (g) $US_7M_5$.

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 $US_7$ solution, and Fig. 9(c) shows the $US_7M_3$ solution. Fig. 9(a) was made of a large crack by the shrinkage. Fig. 9(b) was formed a lot of fine crack by the addition of $SiO_2$ polysilicate. But in the Fig. 9(c), a melamine curing agent played a cross-linking role in the synthesis of $SiO_2$ polysilicate and urethane resin. So cracks did not occur at all. $US_7M_3$ is the optimal composition ratio in the range of solutions in this study.




(c)

Fig. 9. SEM photography of coating surface with curing time of 3 minutes. (a) U solution, (b) $US_7$ solution, (c) $US_7M_3$ solution.

## 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 $SiO_2$ polysilicate showed excellent corrosion resistance than the solution with only urethane. Melamine became a bridge for $SiO_2$ 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 $US_7M_3$ and $US_{11}M_3$, 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 $US_7M_3$, $US_7M_1$ and $US_7M_5$ solution. The surfaces of $US_7M_3$ and $US_{11}M_3$ showed the best conditions in the rubbing test.

## References

[1] S. W. Kim and C. T. Lee, "Invited review article: Environment-friendly trivalent chromate treatment for Zn electroplating," *Journal of Korean Industrial and Engineering Chemistry*, vol. 17, pp. 433-442, 2006.

[2] C. T. Lee, "Enlargement of anti-corrosion of Zinc plating by the trivalent chromium sulfate conversion coating," *Journal of Korean Industrial and Engineering Chemistry*, vol. 18, pp. 296-302, 2007.

[3] M. Kim, J. J. Lee, D. Y. Kim, S. U. Park, and S. C. Kwon, "The trend of study of echo-friendly hard trivalent chromium deposition," *Journal of the Korean Institute of Surface Engineering*, vol. 37, pp. 179-184, 2004.

[4] F. Deflorian, S. Rossi, L. Fedrizzi, and P. L. Bonora, "EIS study of organic coating on zinc surface pretreated with environmentally friendly products," *Progress in Organic Coatings*, vol. 52, pp. 271-279, 2005.

[5] E. N. Michael and P. B. Gordon, "Mg-rich coatings: A new paradigm for Cr-free corrosion protection of Al aerospace alloys," *Journal of Coatings Technology and Research*, vol. 1, pp. 69-80, 2004.

[6] G. B. Rudolph, G. Hong, M. Suhakar, and W. Fariaty, "Active corrosion protection and corrosion sensing in chromate-free organic coatings," *Progress in Organic Coatings*, vol. 47, pp. 174-182, 2003.

[7] R. Zandi-Zanda, A. Ershad-Langroudia, and A. Rahimia, "Silica based organic–inorganic hybrid nanocomposite coatings for corrosion protection," *Progress in Organic Coatings*, vol. 53, pp. 286-291, 2005.

[8] T. P. Chou, C. Chandrasekaran, S. J. Limmer, S. Seraji, Y. Wu, M. J. Forbess, C. Nguyen, and G. Z. Cao, "Organic–inorganic hybrid coatings for corrosion protection," *Journal of Non-Crystalline Solids*, vol. 290, pp. 153-162, 2001.

[9] H. J. Kim, "Development of anti-finger printed EGI steel sheet with high corrosion resistance," *Journal of the Korean Institute of Surface Engineering*, vol. 26, pp. 307-315, 1993.

[10] J. B. Bajat, V. B. Miskovic-Stankovic, N. Bibic, and D. M. Drazic, "The influence of zinc surface pretreatment on the adhesion of epoxy coating electrodeposited on hot-dip galvanized steel," *Progress in Organic Coating*, vol. 58, pp. 323-330, 2007.

[11] J. H. Steven, C. Lowe, T. M. James, and F. W. John, "Migration and segregation phenomena of a silicone additive in a multilayer organic coating," *Progress in Organic Coatings*, vol. 54, pp. 104-112, 2005.

[12] M. L. Zheludkevich, S. I. Miranda, and M. G. S. Ferreira, "Sol–gel coatings for corrosion protection of metals," *Journal of Materials Chemistry*, vol. 15, pp. 5099-5111, 2005.

[13] Y. J. Lee, "Effect of chromate treatment on corrosion resistance of galvannealed steel sheets," *The Corrosion Science Society of Korea*, vol. 24, pp. 250-257, 1995.

[14] K. W. Nam, D. W. Kim, N. S. Kim, and K. Y. Seong, "Characteristic of corrosion resistance under different heat treatment conditions of coated

Zinc coating steel with Cr-Free solution," *Lecture Notes in Electrical Engineering*, vol. 282, pp. 635-643, 2014.
[15] K. W. Nam, J. R. Kim, and C. M. Choi, "Corrosion resistance characteristics of cold rolled steel by Cr-free green organic/inorganic hybrid coating solution," *Journal of the Ocean Engineering and Technology*, vol. 27, pp. 33-38, 2013.
[16] K. W. Nam, J. R. Kim, and C. M. Choi, "Corrosion resistance of cold rolled steel coated organic/inorganic hybrid coating solution according to the heat treatment temperature," *Journal of The Ocean Engineering and Technology*, vol. 25, pp. 56-59, 2011.
[17] J. R. Kim, C. M. Choi, and K. W. Nam, "Corrosion resistance of cold rolled carbon steel by treating organic/inorganic hybrid coating solution," *Trans. Korean Soc. Mech. Eng. A*, vol. 36, pp. 405-412, 2012.
[18] H. S. Seo, H. J. Moon, J. R. Kim, J. S. Kim, S. H. Ahn, C. K. Moon, and K. W. Nam, "Corrosion resistance of galvanized iron by treating modified Si organic/inorganic hybrid coating solution," *Journal of Ocean Engineering and Technology*, vol. 25, pp. 32-38, 2010.
[19] H. S. Seo, H. J. Moon, J. S. Kim, S. H. Ahn, C. K. Moon, and K. W. Nam, "Corrosion resistance of Zinc coating steel coated Cr-free coating solution according to the heat treatment time," *Journal of Ocean Engineering and Technology*, vol. 24, pp. 67-74, 2010.
[20] H. S. Seo, H. J. Moon, J. S. Kim, S. H. Ahn, C. K. Moon, and K. W. Nam, "Corrosion resistance according to the heat treatment temperature of Cr-free coating solution on Zinc coated steel," *Journal of Ocean Engineering and Technology*, vol. 24, pp. 60-66, 2010.
[21] KS D 9502, "Acetic acid and copper-accelerated acetic acid salt spray," *Neutral*, 2009.
[22] *Standard Test Methods for Measuring Adhesion by Tape Test*, ASTM D3359-09.

**K. W. Nam** was born on November 11, 1958 in Changwon. He graduated from Yokohama National University in Japan. He is working with the Department of Materials Science and Engineering, Pukyong National University, Busan, Korea since 1990. He has an interest in strength of ceramics, development and evaluation of organic/inorganic hybrid coating solution.

**J. R. Jeong** was born on September 14, 1973 in Geochang. He graduated on February 2015 from Pukyong National University. He is now developing and producing products that are using filter for home appliances. Especially, He has been producing eco-friendly products. He is currently working as CEO of Prepoll Co. Ltd.

**S. H. Ahn** was born on February 10, 1966 in Busan. He graduated from Yokohama National University in Japan. He is working with the Department of Mechatronics Engineering, Jungwon University, Goesan-gun, Chungbuk, Korea. He has an interest in various materials and its characteristic evaluation.

**K. Y. Seong** was born on December 4, 1968 in Changyeong. He graduated on February 2006 from Pukyoung National University. He's thesis title is finite element analysis for wall thinned steam generator tubes. He is the DM CEO. He is now developing and producing products that are used in the dockyard. DM produces a product applied to the injection molding process. Such as blowers and air vest mainly produced. He has an interested in composite materials. He has an experience in the research for the production of products using lamination method or the winding process.

**K. H. Lee** was born on December 14, 1980 in Seoul. He graduated from the master's course at Hanyang University in Korea. He is currently enrolled in the PhD at Pukyong National University. He is working with Naval & Special Ship Production Team, Daewoo Shipbuilding & Marine Engineering Co. Ltd. (DSME), Geoje, Korea. He has an interest in organic/inorganic hybrid solution.