CHAPTER 5

CONCLUSIONS

The results of the present investigation may be summarized as follows:

1. Based on contact angle measurement and EIS studies, UA coatings on phosphated steel increased the contact angle from 3^o to $23\sim50^o$, and increased R_p from 21 kΩ to 69~95 kΩ. UA coatings exhibited lower hydrophobicity than silanes (VS and BTSE) but gave similar R_p values.
2. UA coatings alone did not improve corrosion resistance significantly as evaluated by salt spray test. However, when a resin topcoat was applied over UA coatings, the corrosion resistance increased significantly. UA plus resin coatings could withstand over 120 hours of salt spray (only about 72 hours without UA pretreatment). As a coupling agent between phosphated steel surface and resin topcoat, UA was comparable with, even better than silanes.
3. Fatty acids with various chain lengths were subsequently tested as an alternative of UA on consideration of the cost and availability. Palmitic acid, and stearic acid, all with intermediate chain length, showed a potential to replace UA when used together with resin.
4. Organosulfur compounds like *1*-octadecanethiol (ODT) can form a thin, close packed film on metal substrate. This close packed, strongly bound self-assembled monolayer formed on EG steel surface may resist corrosive attack of water, oxygen and other corrosive ions. ODT coatings on EG steel could resist 50 to 60 hours of salt spray without serious rust. The control sample usually started rusting only after 2~4 hours.
5. The optimal concentration of ODT was in the range of 0.02 *M* to 0.05 *M*. The method of drying the coatings, and whether heating the coatings did not make a significant difference. The solvents with a straight chain structure were identified as the suitable solvents of ODT for the formation of a robust film. The examples include ethanol, ethyl acetate and *1*-butanol.
6. The tests conducted at Virginia Tech had been repeated at POSCO, the sponsor of the present project. Based on the practical consideration for future industrial application, a series short dipping times of EG steel in ODT solution were tested at POSCO. It was

found that satisfactory corrosion resistance could also be achieved even though the dipping time was shortened to around 10 seconds.

7. It was found that surface oxidation of EG steel would deteriorate the corrosion resistance of ODT coatings, suggesting that ODT was inclined to react with fresh metallic zinc rather than zinc oxide. Surface oxidation of EG steel after exposure to air increased the water contact angle and reduced the surface tension.

8. The surface properties of EG steel changed significantly due to ODT coatings. The water contact angle increased from 72^o to 124^o. The surface tension of EG steel decreased from 45.25 mJ/m^2 to 34.63 mJ/m^2 accordingly. High hydrophobicity or low surface free energies are helpful for improving corrosion resistance but are detrimental to the adhesion of topcoats. Therefore, it is necessary to further study the thiols terminated with other functionalities (e.g., -OH, -COOH, and $-NH_3$) that may produce a higher-energy surface.

9. Tafel studies revealed that the corrosion current decreased from 49.07 $\mu A/cm^2$ to 8.78 $\mu A/cm^2$ due to ODT coatings on EG steel.

10. XPS analysis and FTIR studies confirmed the formation of ODT film on EG steel surface. AFM imaging revealed that the EG steel surface was extremely rough and edgy. The surface roughness was approximately 800 nm.

11. *11*-Mercapto-*1*-undecanol (MUO) and *16*-mercapto-1-hexadecenoic acid (MCA) were tested as the first layer prior to the application of resin topcoat. MCA plus resin coating successfully withstood over 120 hours of salt spray test. MCA was dissolved in ethanol at the concentration of 0.025 *M*. As the first step, the EG steel was immersed in MCA solution for 5 minutes or 5 second, and then rinsed with ethanol, and dried with nitrogen gas and heated at 120 ^oC for 5 minutes. As the second step, MCA-coated EG steel was subsequently applied with resin by using a No. 5 bar coater, and finally cured at 150 ^oC for 5 minutes. It was found that 5-seconds dipping could give the same corrosion resistance as 5-minutes dipping. MUO did not work well probably because its short chain was not as effective.

12. Another two-step process was tested with resin applied as the first layer and then rinsed with ODT solution. The resin was applied and cured in a conventional manner, and then immersed in a 0.05 M ODT solution for 5 minutes, and finally dried in air. This coating

system could give over 120 hours of corrosion resistance. ODT rinsing could improve the corrosion resistance of resin-coated EG steel because it increased the surface hydrophobicity significantly. The contact angle increased from 90^o to 128^o due to the ODT rinsing. The contact angle decreased at a much slower rate for ODT-rinsed surface (0.067 ^{o}/hour) than the resin-coated surface (0.2 ^{o}/hour) during the first 120 hours of salt spray test. It suggests that the ODT-rinsed surface is more corrosion resistant

13. Subsequently, a one-step process was tested with mixing resin solution and thiol solution together. MCA and ODT were added to resin solution separately in a certain ratio. The mix was then applied to EG steel by using a No. 5 bar coater and cured at 150 ^{o}C for 5 minutes. This treatment was supposed to produce an organic film of 1~2 μm on EG steel. Both treatments were able to give over 120 hours of corrosion resistance. The higher the thiol concentration in resin-thiol mix, the greater the corrosion resistance.

14. The process of resin-ODT mix coating was then optimized with salt spray test. *1*-Octadecenethiol (ODT) was dissolved in ethanol at the concentration of 0.1 *M*. This solution was mixed with resin solution under various mixing ratios. These mixtures were applied to EG steel for corrosion test and characterization. EG steel coated with resin-ODT mix could resist over 200 hours of salt spray under optimal conditions (7:3 or 6:4 by volume for resin to ODT solution). The water contact angles of resin-ODT coated surface increased by 6~11^o from 82^o of pure resin coating, and thereby the surface free energy decreased to less than 40 mJ/m^2 from 45.25 mJ/m^2.

15. Other solvents were also tested for preparing ODT solution. Butanol as a solvent of ODT was better than ethanol in term of the solution stability and the corrosion resistance of the resultant coating.

16. Film thickness measurement indicated that resin-ODT mix decreased the film thickness because of the dilution effect of solvents. Pure resin coating produced a 2.5 μm film but the thickness decreased to 1~1.8 μm for resin-ODT mix coating. Thinner film would help improve the electrical property of the organic coating.

17. Tafel studies confirmed the optimization tests. The corrosion current was the lowest under the optimal mixing ratios. XPS analysis revealed the existence of sulfur in the resin-ODT coating. The relatively high sulfur concentration was detected for the resin-ODT mix coating under the optimal mixing ratios.

18. The novel one-step process of resin-ODT mix coating had several advantages. It was very simple to apply such a coating continuously in the plant by just utilizing the existing facilities. Unlike pure resin, this new composition could constantly produce a uniform, gray-colored film on EG steel. The coating would be thinner due to the dilution of resin solution by the solvent and thereby had better electrical properties. Most importantly, the corrosion resistance of this novel coating composition was significantly improved.