Chapter 3

SELF-ASSEMBLED MONOLAYER OF THIOLS COATED ON COLD-ROLLED STEEL SHEETS

3.1 INTRODUCTION

Self-assembled monolayer (SAM) has been widely studied in the past two decades for its potential applications in the area of wetting, lubrication, adhesion, corrosion, biocompatibility, catalysis, chemical sensing, and nano-scale lithography (Finklea, 2000). A majority of the papers published in this area deal with thiols adsorbed on gold, although the substrate may be extended to other metals such as silver, platinum, mercury and copper. The surfactants used for forming a SAM include thiols, disulfides, and sulfides, etc. Ulman has given a comprehensive review on this topic in his publications (1996 and 1998).

An organic SAM is a single-layer of molecules on a substrate in which the molecules exhibit a high degree of orientation, ordering, and packing as illustrated in Figure 3.1. It is generally believed that formation of the SAMs on metal substrate involves two steps, i.e., i) chemical interaction (chemisorptions) between the head group (-SH) and the metal substrate, and ii) aliphatic chain reorganization (Ulman, 1997).

It is well known that sulfur compounds have a strong affinity to transition metal surface. They can form a strongly bonded, well ordered, and dense self-assembled monolayer on metal surface. This self-assembled film may act as an excellent barrier for corrosion protection of

Figure 3.1 Illustration of self-assembly of ODT on an ideal metal substrate.
metal substrates. It can also provide a good adhesion to topcoats.

As introduced in Chapter 1, a few attempts have been made recently for the application of thiols in corrosion prevention of metals. Zamborini and Crooks (1998) studied the ability of n-alkanethiol SAMs to protect gold from corrosion in aqueous Br⁻ solutions by electrochemical measurement. Scherer, et al. (1997) reported their in-situ STM and electrochemical study on the corrosion behavior of alkanethiol (n=8 and 16) covered Cu (100) in 1 mM HCl solution. Azzaroni, et al. (2001) also found that the SAMs of alkanethiol (n=12) were able to hinder copper oxide formation and copper dissolution in electrolyte solution containing chloride anions.

Jennings, et al. (1996) studied the SAM of alkanethiols of long carbon chains (C_{18}H_{37}SH and C_{22}H_{45}SH) on copper to provide corrosion resistance in aqueous environments. They used evaporated copper films on silicon wafers as substrate and measured water contact angle. This SAM film could provide a barrier against water penetration. According to Nozawa (1997, 1999), a monolayer coating of 1-Octadecanethiol (ODT) on an iron electrode could give a protective efficiency of 76.3% (as calculated from impedance measurements) in a 0.5 M NaCl solution. When an iron surface was coated first with 11-mercapto-1-undecanol (MUO, HO(CH₂)_{11}SH) and then coated with octyltriethoxysilane, its protective efficiency increased to 88.0% due to crosslinking polymerization. Teneichi, et al. (2001) modified the MUO SAM with alkylisocynate (CₙH₂n+₁NCO) for the protection of copper in an aerated solution of 0.5 M Na₂SO₄. Protective efficiencies of 94.7% and 95.4% were obtained with octyl- and octadecyl- isocynate, respectively.

In U.S. patent No. 6,102,521, Halko, et al. (2000) disclosed a technique of treating a gold-plated orifice of ink-jet pen with thiol-type SAMs to control wettability of the surface in order to reduce the accumulation of residual ink, and to inhibit corrosion and contamination of the plate. In U.S. patent No. 6,183,815 B1, Enick and Beckman (2001) claimed a method of coating a metal surface with amide thiol solution. The preferable compounds had a general formula, F(CF₂)ₘCONH(CH₂)ₙSH, where n and m are each 2~20. In U.S. Patent No. 5,487,792, King, et al. (1996) claimed a specific SAM as a protective barrier and adhesion promoter. They used 12-thiol dodecanoic acid to form an organized molecular assembly that was impervious to water, alkali and other corrosive substances.

In spite of these attempts, there is still a need, therefore, for developing a state-of-art technique that can lead to industrial application. It is an objective of the present work to coat
cold-rolled steel sheets with thiol SAMs for corrosion protection. Another feature of this work is to evaluate corrosion performance of a coating with a standard salt spray test that is closer to corrosion condition in industrial applications.

A literature survey showed that no thiol (R-SH) had been tested for the corrosion protection of galvanized steel. Furthermore, most previous studies were focused on the basic studies such as surface characterization, electrochemical studies, contact angle measurements, and impedance measurements instead of state-of-art test for corrosion protection.

In the present work, 1-Octadecanethiol (ODT) was studied on both phosphated EG steel sheet and electrogalvanized (EG) steel in order to develop a practical application of thiol for corrosion prevention of CRS sheets. Of various surfactants containing different reactive groups, ODT showed a great potential to compete with silane as a conversion coating for steel sheets. Subsequently, surface characterization and electrochemical studies were conducted in order to explain the mechanism of corrosion resistance provided by thiols.

### 3.2 EXPERIMENTAL

#### 3.2.1 Reagents

1-Octadecanethiol (ODT, CH₃(CH₂)₁₇SH ) of technical grade (98%) was purchased from Sigma-Aldrich Chemical Co. and used without further purification. Its boiling point is between 204-210 °C and the melting point 31-35 °C. Ethyl alcohol of 200-proof grade made by AAPER Alcohol & Chemicals Co. was used as a solvent for the preparation of ODT solutions.

γ-Aminopropyl silane (APS), vinyl silane (VS), and 1,2-bis(triethoxysilyl) ethane (BTSE) were purchased from Gelest, Inc., Tullytown, PA. These reagents were research grade and used without further purification. Silane solutions were prepared in the same manner as described in Chapter 2. Resin solutions were provided by POSCO and prepared in the same way as described as in Chapter 2.

Sodium chloride of 99.5% purity was purchased from Fisher Scientific for salt spray test. DI water was used for the preparation of test solutions of surfactants, but the saltwater used for SST was prepared with purified water (2 megohms) obtained from a Corning Water Purifier (LD-5).
3.2.2 Steel Samples and Coating Method

In the present work, two types of CRS samples, phosphated EG steel (A3 treatment) and electrogalvanized (EG) steel were studied. Both samples were provided by POSCO and sent to VT by courier service when requested. Initially, the samples were stored in a dry desiccator. It was found, however, that the EG samples oxidized rapidly, which adversely affected the performance of ODT coatings. Therefore, later samples were stored in a vacuum desiccator. But oxidation cannot be avoided completely.

The CRS samples were coated by surfactant solution with a simple dipping method. The sample was coated as received without a further cleaning procedure. The samples were cut into appropriate sizes (12×7.5 cm) and immersed into a surfactant solution for a desired period of time. It was then removed, and dried by blowing a gentle stream of nitrogen gas or dried naturally in air. The coated sample was cured in an oven at a desired temperature, if necessary. The temperatures reported in the present report represent the oven temperature instead of the actual temperature on metal surface unless specified otherwise.

3.2.3 Contact Angle and Surface Free Energy

A Rame-Hart goniometer was used to measure the contact angles. A small drop of liquid was placed by means of a hypodermic needle on the surface of a CRS plate. The contact angles were measured through the aqueous phase. The measurements were made at 3~6 different spots of a CRS plate, and the measured values were averaged.

To determine the surface energy, contact angle measurements were conducted with three different liquids, namely water, formamide, and 1-bromonaphthalene. The contact angle values were used to determine the surface free energy and its components in the way as introduced in Chapter 1.

3.2.4 Tafel Studies

A standard three-electrode electrochemical cell was used. The working electrode consists of a CRS sheet coated with surfactant(s). One side of the phosphated sheet was scratched with a knife to obtain a conducting surface, which in turn was connected to a potentiostat by means of a copper cable, while the other side (coated) was in contact with the electrolyte in the cell. A platinum mesh was used as counter electrode, while a Luggin capillary connected to a standard calomel electrode (SCE) was used as reference electrode. The Luggin capillary was placed close to the working electrode to minimize potential drop.
The potential of the electrode was controlled by a potentiostat (Model 273A by EG&G), which in turn was controlled by a computer through GPIB interface. The Tafel studies were carried out with corrosion measurement software from EG&G (SoftCorr 352 III). The potentials were scanned in the range of ±250 mV from the open circuit potential (OCP) at a scan rate of 1~2 mV/sec.

The measurements were conducted in 5% NaCl solutions. The solution was aerated by compressed air during the test. With a given sample, the measurements were conducted at three parallel samples. The electrolyte solutions were replaced after testing three samples. By fitting the data with a computer program, corrosion potential ($E_{\text{corr}}$) and corrosion current ($i_{\text{corr}}$) were determined. $i_{\text{corr}}$ may be interpreted as corrosion rate of a material.

3.2.5 Salt Spray Tests

Salt spray test were carried out according to the standard procedure (ASTM B117, Test Method of Salt Spray (Fog) Testing). Dai Sung Engineering, Co., Korea, manufactured this salt spray tester used in the present work. A 5% salt solution was siphoned into the chamber in conjunction with hot compressed air saturated with moisture at a pressure of 1 kgf/cm². The flow rate of the salt water was controlled at approximately 2 l/h to ensure the fog amount in the range of 1 to 2 ml/(h.80cm²) over the test area. The temperature inside the fog chamber was maintained around 35 ºC.

The steel samples were cut into desired sizes (mostly 75×120 mm), and then coated with target chemicals. The edges of coated specimens were protected to minimize the galvanic corrosion by Magic™ tape (3M), or Super-Talc electrical tape (Bluefield Manufacturing, VA). The samples were taken out every 4 hours in most cases, and returned to the chamber after pictures were taken as quickly as possible to maintain the continuity of salt fog exposure. SSTs were conducted for periods in the range of 24-120 hours.

3.2.6 Fourier Transform Infrared Spectroscopy (FTIR)

For EG steel surface, RAIR spectra were collected on a BIO-RAD FTS 3000MX spectrometer equipped with a PIKE 80Spec reflectance attachment set at an incidence angle of 80°. Dry air was used for purging. The spectra were acquired using 4 cm⁻¹ resolutions and were averaged over 16 scans. Each spectrum was obtained by subtracting a background spectrum of a gold-coated mirror provided by PIKE. In order to collect IR spectra of powder sample of ODT, a
pellet of about 2 mm thick was made from 20 mg ODT and 200 mg KBr mixture by using a Specadie P/N 3550 (Graseby Specac). The IR beam went through this pellet and the spectra were collected at 4 cm$^{-1}$ resolutions and were averaged over 16 scans.

### 3.2.7 X-Ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed by Mr. Frank Cromer in the Department of Chemistry at VT, with a Perkin-Elmer Model 5400 photoelectron spectrometer. The XPS works on the photoelectric effect. A Mg X-ray is directed to the surface of a solid and electrons are emitted. The kinetic energy of the emitted electrons was measured with a hemispherical analyzer and Apollo Dn 3500 computer. Electrons have specific energies; though, the kinetic energy of the emitted electrons can be used to identify the elements from which electrons were emitted. The area scanned was approximately 1 mm × 3 mm. The maximum etch depth was 20 nm. Quantification was based on the peak area determined with a Shirley background, with sensitivity factors determined by the instrument manufacturer.

### 3.3 RESULTS AND DISCUSSIONS

#### 3.3.1 Salt Spray Tests

**3.3.1.1 Thiol Coatings on Phosphated Steel**

Figure 3.2 shows the photographs of the phosphated CRS samples with various treatments after 52 hours of salt spray test. The treatments include ODT and vinyl silane (VS) coatings. Another sample is phosphated steel treated with chrome rinsing.

A 0.02 $M$ ODT solution in ethanol was prepared; ODT coating was produced by immersing phosphated plates in 0.02 $M$ ODT solution for 5 minutes, drying it with nitrogen stream and then heating it for 5 minutes at 100–120 °C. For VS coating, the plate was dipped in 1 vol.% VS solution for 1 minute without heating after being coated.

After 12 hours of SST, the phosphated steel (control) was seriously corroded, while other samples were still in good condition. Note here that the ODT-coated sample was covered with a layer of small water droplets (“sweating”), indicating that the surface was non-wetting (or hydrophobic). The Cr-rinsed and VS-coated samples were not covered with water droplets, indicating more hydrophilic.
After 24 hours, the Cr-rinsed and VS-coated samples showed significant corrosion, while the ODT-coated plates were relatively intact. It seems that surfactants that can produce non-wetting surfaces may be desirable for corrosion protection. In addition, they may also give rise to fingerprint-free surfaces. After 36 hours, the ODT-coated sample was no longer sweating, and

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<tr>
<th>Phosphate (control)</th>
<th>Phosphate + ODT</th>
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<tr>
<th>Phosphate + Chromate</th>
<th>Phosphate + Vinyl Silane</th>
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Figure 3.2 Photographs of salt spray test for ODT and silane coatings on phosphated steel after 52 hours of test
began showing signs of corrosion. Nevertheless, its corrosion was significantly less than those of the Cr-rinsed and VS-coated plates. At the end of the test, red rusts appeared on the control sample, indicating serious corrosion. The samples with chromate rinsing and vinyl silane coating were also covered with white rusts. In comparison with these treatments, the ODT-coated sample was still in a relatively good condition.

3.3.1.2 Thiol Coatings on EG Steel

Figure 3.3 shows the results of the salt spray tests conducted on the EG steel plates coated with and without surfactants (ODT, VS, and BTSE). As expected, the zinc layer on the EG steel started to corrode very quickly. White rusts began to appear within 2 hours since the plate had been placed in the salt spray chamber. The red rust appeared after 24 hours when the zinc layer disappeared and the iron began to corrode. The EG plates coated with ODT and silanes, on the other hand, exhibited substantially increased corrosion resistance.

EG plate was immersed in 0.05 M ODT solution for 5 minutes and heated at 120 °C for 5 minutes after the plated were taken out of the solution and were dried by nitrogen gas or in air. It was found that drying the ODT-coated sample in air usually gave a better appearance than drying it with nitrogen stream, particularly in the case of higher ODT concentrations. It was assumed that the strong gas stream might disturb the reorganization of the absorbed molecules. The ODT concentration may be varied from 0.02 M to 0.05 M. The concentration of VS and BTSE was 2% by volume and the same coating procedure was taken except the heating temperature was 100 °C for silane coatings.

The photographs taken after 12 hours of SST showed that the ODT-coated EG plate was covered with tiny water droplets, more so than the BTSE- and VS-coated surfaces, indicating that the former was more hydrophobic. The untreated EG plate showed considerable white rust, while the surfactant-coated plates showed no corrosion.

After 36 hours of salt spray, BTSE-coated EG plates showed considerable amounts of white rusts. After 48 hours, the BTSE-coated plates showed increased amount of white rust, and the VS-coated plates began to show a small amount of white rust. After 60 hours, the white rust increased on the VS-coated surface, while the ODT-coated surface showed a small amount of white rust only near the edges. No white rusts appeared at the center. This test demonstrated that ODT was able to give a higher corrosion resistance than silanes for EG steel.
Other type of thiols such as 1-dodecanethiol, triphenyl methanethiol, and 1,10-decanedithiol were also studied with SST. But they did not perform as well as ODT. The poor results may be attributed to their short chains or the nonlinear structure; both are not favorable for the formation of self-assembled monolayer.

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<th>EG steel (control)</th>
<th>EG + ODT</th>
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<td><img src="image1.jpg" alt="Image" /></td>
<td><img src="image2.jpg" alt="Image" /></td>
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<tr>
<td>EG + BTSE</td>
<td>EG + VS</td>
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Figure 3.3 Photographs of ODT and silane coatings on EG steel after 60 hours of salt spray test
3.3.1.3 Effect of Solvents on the performance of ODT Coatings

Three ODT solutions of $0.05 \, M$ were prepared by using three different solvents, namely ethanol, ethyl acetate and benzene. EG specimens were immersed into each of these solutions for 60 hours of salt spray test.

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<th>EG + ODT (0.05(M) in ethanol)</th>
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<td>EG + ODT (0.05(M) in ethyl acetate)</td>
<td>EG + ODT (0.05(M) in benzene)</td>
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Figure 3.4   Photographs of ODT-coated EG steels when dissolved in different solvents were used (60 hours of salt spray test).
5 minutes, and then dried in air via vaporization. These ODT-coated samples and another EG steel sample without any treatment were subject to salt spray test.

Figure 3.4 shows the photographs of these test panels after 60 hours of salt spray test. The sample coated with benzene solution of ODT corroded almost in the same level as the control sample, while other two samples coated with ODT dissolved in ethanol and ethyl acetate still remained a good appearance. The water droplets still resided on the surface, indicating that the surfaces were still hydrophobic even after 60 hours of salt fog attack.

This test clearly demonstrated that benzene as a solvent of ODT had the lowest corrosion resistance when compared with the samples prepared with ethanol and ethyl acetate as solvents. It may be explained with the fact that the ring structure of benzene is detrimental to the formation of close-packed self-assembly of thiol molecules. Therefore, the preferred solvents of ODT for the formation of self-assembled monolayer on EG steel should be those with straight chain structure in order to achieve a satisfactory corrosion resistance. Methanol was tested but it could not dissolve ODT at the concentration of 0.01 M.

3.3.1.4 Summary

Salt spray tests were also conducted for both phosphated and EG steel plates after treating them with various surfactants. γ-aminopropyl triethoxyl silane (APS), oleic acid or sodium oleate (OA), 10-undecenoic hydroxamate (UH), n-octadecyl phosphonic acid (OP) and other reagents were tested. The results obtained with these reagents had been compared with those of VS, BTSE, and ODT reported in foregoing sections.

According to salt spray test results, the untreated EG steel could only last 2~4 hours without rusting, while phosphated EG steel could survive about 10 hours. The Cr-rinsed phosphated steel, on the other hand, could endure as long as 40 hours. This is the main reason that the steel industry has been using chrome as a conversion coating for so long.

The primary objective of this project is to develop organic coatings that can substitute for chrome, so that environmentally friendly CRS plates can be produced.

The UH-coated phosphated steel started corrosion after approximately 20 hours of SST, which was well below the performance of the Cr-rinsed phosphated CRS plate. When the phosphated steel was treated with ODT, OP, and VS, their performances were comparable to that of Cr-rinsed phosphated steel. In this regard, the original objective of developing Cr-free
coatings for CRS plates has been achieved. In fact, the performance of the ODT-coated plates was considerably better than that could be achieved by Cr-rinsing. When the project was first initiated, the silanes were considered to be the best available new technology. The results given in Figure 3.2 and 3.3 showed that ODT was actually better than silanes. Studies of Van Ooij’s group (Van Ooij, et al., 1991; Yuan, et al., 1997; Child, et al., 1999) suggested that a CRS plate coated with BTSE followed by $\gamma$-APS coating gave the best performance. In the present work, BTSE-APS coating was not as good as the single-step coating of VS. One should note that OP gave as good a result as silanes and Cr-rinsing. But it was an expensive reagent so that no further tests were conducted.

Figure 3.5 also includes the results obtained from both phosphated and EG steel. The results obtained with OA coating followed by $\gamma$-APS coating gave about 20 hours of corrosion resistance. The poor results may be attributed to the fact that silane coating requires hydroxyl (-OH) groups on the surface, whereas the OA-coated surface does not provide them. The EG steel coated with VS gave approximately 40 hours of corrosion resistance, which was equivalent to what could be achieved with the electrogalvanized, phosphated, Cr-rinsed surface. Thus, the
electrogalvanized and VS-coated surfaces involved one fewer step (i.e., no phosphating), yet it provided a Cr-free coating with equivalent corrosion resistance. When the EG steel was treated with BTSE instead of VS, the corrosion resistance increased up to 60 hours. When the EG steel was coated with ODT, the results were as good as those obtained with BTSE. Although Figure 3.3 showed that ODT-coated surfaces withstood 60 hours of SST, the actual photograph showed that the ODT-coated EG plate gave no signs of white rust in the middle of the plate. Thus, the EG-ODT combination may give substantially longer than 60 hours of corrosion resistance.

### 3.3.2 Confirmation Tests in POSCO

During the period of June 25 to August 2, 2002, salt spray tests were conducted in POSCO Technical Research Laboratory. The objective is to reproduce the test results previously obtained at VT.

The confirmation tests were carried out with a full-size machine made by SUGA Test Instruments, Japan. 5% salt water was used for all tests. The air saturation temperature was set at 47 °C and water tank temperature at 52 °C. Air pressure was adjusted at 0.1 MPa (1 kgf/cm²). The same procedure was taken for solution preparation. Two coating methods, dipping and bar coating, were investigated to simulate the production line. However, a harsher test procedure was taken by following POSCO’s protocol, in which samples were taken out of the salt spray chamber every 24 hours, and then washed with running tap water, dried with compressed air, even heated sometimes in an oven with temperature between 50~60 °C. They were finally returned to the chamber for continuous SST after taking photographs. ODT was recently purchased from Sigma-Aldrich Co., while BTSE, VS and ethanol were from POSCO’s chemicals stock.

#### 3.3.2.1 Comparison of ODT and Silanes Coated on EG steel

Figure 3.6 displays the photographs of four different treatments, i.e., EG steel without any coating (control); EG steel coated with 0.05 M ODT; 2 vol.% VS and 2 vol.% BTSE, respectively. The EG steel sample used for this test was freshly prepared with a laboratory-scale galvanizing instrument because of the failure of previous tests with aged, probably oxidized samples. The sample dimension was 100×40 mm with a zinc layer measured in the range of 20~30 g/m².
After 24 hours, an ODT-coated sample still remained perfect in appearance but the control sample had corroded seriously with red rust appearing on nearly one third of the surface. Meanwhile, white rust occurred on VS-coated sample and approximately 10% of the BTSE-coated sample surface was covered with red rust. After 48 hours, ODT coating was still in good condition, and only tiny white rust spots were observed near the edge. The control sample and

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<th>EG (control)</th>
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<th>EG+VS (2%)</th>
<th>EG+BTSE (2%)</th>
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Figure 3.6   SST photographs of ODT and silane coatings on EG steel after 60 hours of salt spray test
BTSE-coated sample completely corroded with red rust occupying almost all the surface.

A lower concentration (0.02 M) of ODT solution was also tested, but it did not give as good result as the higher concentration (0.05 M). The freshly-made EG plate was immersed in 0.05 M ODT/ethanol solution for 5 minutes and then dried in air, put in an oven with pre-set temperature of 100 °C for 90 seconds for heating, supposed to attain a metal surface temperature between 80~88°C. For silane, coating conditions were the same except the heating time was shortened to 60 seconds.

It is concluded from the previous results obtained at VT that ODT is capable of giving a better corrosion protection than VS and a similar performance to BTSE. In present work, however, ODT coating had repeatedly given much better corrosion protection than both VS coating and BTSE coating, as shown in Figure 3.6. It is postulated that ODT makes stronger attachments to the fresh galvanized surface. Another possible explanation relies on the fact that silanes may work better on oxidized or hydroxylated surface than on fresh metallic surface because these metal surfaces are preferred for silane adsorption (Finklea, 2000). The EG plates used in this test are newly made in situ and have less extent of oxidation than those samples tested at VT.

3.3.2.2 Tests on Short Dip Time for ODT Coatings

A 5-minute dipping process is extremely impracticable because of the limitation of space allowed in a steel mill. Generally, a ten-second process is acceptable for any treatment of steel sheets in the production line. Therefore, a series of short dip times were tested from 3 seconds to 11 seconds. The results are shown in Figure 3.7.

The EG samples were prepared on June 14, 2002 in POSCO’s laboratory. The plate size was 125×75 mm. They had been stored in a desiccator until they were taken out on July 2. These samples were coated with 0.05 M ODT on July 10, and put into salt spray chamber on the same day. Consequently, these samples had oxides on the galvanized surface when treated with ODT. Thus, they were not in the optimal condition for a ODT coating.

All samples remained intact, except for the control, after 24 hours of salt spray. Small spots of white rust occurred on the edge of the plate after 48 hours. The sample with 11 second of dip time gave the best appearance, and was almost comparable to that of 300-seconds dipping time. The results demonstrated that thiolate reacted with zinc quickly, and a self-assembly monolayer
of ODT could form on a galvanized surface in a very short time. These results had removed a major obstacle to commercialization of ODT coating technology in the steel industry.

Two heating temperatures, 100°C and 120°C were tested in parallel for the same heating time (2 minutes), which created metal surface temperatures of 83 °C and 99 °C respectively. No pronounced difference had been observed for these two treatments.

Another coating method, bar coating, was tested. It did not give as a good result as the dip process. It was assumed that the squeezing of bar over the surface might have destroyed the

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<th>Dip 3 sec.</th>
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<tr>
<td>Dip 9 sec.</td>
<td>Dip 11 sec.</td>
<td>EG (control)</td>
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Figure 3.7  SST photographs of ODT-coated EG steel with extremely short dip time after 48 hours of salt spray test
order of ODT monolayer and, therefore, it could not produce a compact, robust organic layer on metal surface.

3.3.2.3 Summary

(i) Under optimal conditions, ODT coatings could give EG steel a corrosion resistance of over 50 hours (see Figure 3.6 and 3.7). ODT worked more effectively on fresh surface than on oxidized samples. In this aspect, chemical cleaning or pickling of galvanized surface was not helpful of attaining a fresh, un-oxidized, fresh metallic surface. These treatments probably caused chemical contamination on the surface.

(ii) Almost in all cases, ODT coating outperformed silanes (VS, BTSE) on EG samples (see Figure 3.6).

(iii) Bar coating never achieved a test result as good as dip coating. Nevertheless, the extremely short dipping time (3–11 seconds) gave good results (see Figure 3.7). This indicated a fast reaction between ODT and zinc.

(iv) As for EG-ODT coating system, ODT solution of higher concentrations (e.g., 0.05 M) constantly gave higher corrosion resistance than lower concentrations (e.g., 0.02 M). This result was consistent with the result obtained at VT.

(v) Another interesting test was to squeeze the surface with a bar coater immediately after removing the specimen from ODT solution. This process had given similar results to bar coating. Therefore, it was assumed that the bar coater had disrupted the orientation of ODT self-assembly monolayer.

3.3.3 Contact Angle and Surface Free Energy

Figures 3.8 and 3.9 show the contact angles of three different liquids on ODT-coated phosphated steel and EG steel, respectively. The information of the liquids was given in Table 1.6. It was clearly seen that ODT coatings significantly increased the water contact angle. For example, the water contact angle rose from 72° to 120–140° after EG plates were coated with ODT. For phosphated samples, the contact angle increased from almost zero to 140–145°.

The contact angle measurements were conducted as a function of concentration from 0.005 M to 0.07 M. As shown, the concentration of ODT solution did not affect the water contact angles significantly for both samples.
Figure 3.8  Effect of ODT concentration on the contact angle of EG samples (dipping time: 5 min.; heating 5 min. at 120 °C)

Figure 3.9  Effect of ODT concentration on the contact angle of phosphated samples (dipping time: 5 min.; heating 5 min. at 120 °C)
The contact angle data given in Figures 3.8 and 3.9 are used to calculate the surface free energies and their components according to Eq. 1.28. The calculated surface free energies are shown in Table 3.1 and Figure 3.10. For both phosphated and EG steel samples, the surface tension decreased substantially due to ODT coatings. The reduction of surface free energy was

Figure 3.10 Effect of ODT concentration on surface free energy of ODT-coated phosphated and EG steels (dipping time: 5 min.; heating 5 min. at 120 °C)

The contact angle data given in Figures 3.8 and 3.9 are used to calculate the surface free energies and their components according to Eq. 1.28. The calculated surface free energies are shown in Table 3.1 and Figure 3.10. For both phosphated and EG steel samples, the surface tension decreased substantially due to ODT coatings. The reduction of surface free energy was

Table 3.1  Changes in surface free energy of phosphated and EG steel due to (ODT) coatings

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Contact Angle</th>
<th>Surface Tension, mJ/m²</th>
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<tbody>
<tr>
<td></td>
<td>water</td>
<td>FA</td>
</tr>
<tr>
<td>Phosphate</td>
<td>control</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>w/ ODT</td>
<td>142</td>
</tr>
<tr>
<td>EG</td>
<td>control</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>w/ ODT</td>
<td>124</td>
</tr>
</tbody>
</table>

(i) 0.01 M ODT for phosphated steel and 0.05 M for EG steel
(ii) immersing 5 min. and heating 5 min. at 120 °C
(iii) FA--formamide; BN--bromonaphthalene
attributed to the formation of close packed monolayer of ODT molecules with their non-polar methyl groups (CH$_3$) pointing outward. Note that surface free energy was lowest at 0.005 M ODT, and increased with increasing concentrations.

Results in Table 3.1 demonstrated that ODT coatings could reduce the polar component ($\gamma^{AB}$) of the surface free energy to zero. The surface became very hydrophobic because of ODT coatings. A highly hydrophobic surface may help increase corrosion resistance and create a fingerprint-free surface. On the other hand, it may generate a problem with water-based paints because the highly hydrophobic surface may hinder the spreading of the topcoat. Hopefully, this problem can be easily addressed by adding another surfactant such as alkyl amine as a second coating. This treatment may increase the surface free energy and make the surface more compatible with the topcoats. Alternatively, the methyl group may be substituted with other functional groups such as amino-, hydroxyl- or carboxyl- group. The surface coated with such chemically modified thiols should have a high free energy for the adhesion of topcoat without sacrificing the corrosion resistance.

Figure 3.11  Effect of dipping time on surface free energy of ODT-coated phosphated and EG steels (ODT conc. 0.03 M; heating 5 min. at 120 °C)
Figure 3.11 shows the change in surface free energy of ODT-coated phosphated and EG steel as a function of immersing time. ODT coating apparently decreased the surface free energy of both galvanized and phosphated surfaces due to the formation of ODT monolayer. The nonpolar hydrocarbon chains of ODT molecules caused the low surface free energy. However, the dipping time did not affect the magnitude of surface free energy significantly. This is also true for the effect of curing temperature (Figure 3.12).

It should be pointed that the surface roughness also affects the value of the contact angle. Therefore, the data of surface free energy derived from the contact angle should be viewed as an approximate. In addition, it was found that the Van Oss-Goods-Chandrey equation [1.28] was not applicable to calculate the surface free energy of a highly hydrophobic surface.

3.3.4 Tafel Studies

Figure 3.13 shows the results of the Tafel studies conducted on EG plates coated with ODT. The ODT coating was applied by dipping the steel plate in a 0.05 M ODT solution. The corrosion current ($i_{corr}$) of the coated surface was substantially lower than that of the control sample. Without ODT treatment, the corrosion current density of EG steel was 49.04 µA/cm², and then reduced to 8.78 µA/cm² when the EG steel was coated with ODT. Such a decrease in
$i_{\text{corr}}$ represented an approximately 5.5-times reduction of corrosion rate. On the other hand, however, the corrosion potential ($E_{\text{corr}}$) did not change significantly due to ODT coatings.

Figure 3.13 Tafel plots of EG steel with and without ODT coating (0.05 $M$ ODT; dipping time: 5 min.; heating 5 min. at 120°C)

Figure 3.14 Effect of ODT concentration on $i_{\text{corr}}$ of EG and phosphated steel plates (dipping time: 5 min.; heating 5 min. at 120°C)
Figure 3.15 Effect of dipping time on corrosion current of both EG and phosphated steel plates (ODT concentration: 0.03 M; heating 5 min. at 120 °C)

Figure 3.14 shows the effect of ODT concentration on corrosion current ($i_{corr}$). The corrosion current was measured on both phosphated and EG steel. Corrosion current of EG steel coated with ODT was more sensitive to the changes of ODT concentration, because ODT coating was the only protective layer for EG steel while there was another phosphate layer on phosphated EG steel. As shown in Figure 3.14, the corrosion current decreased with increasing ODT concentration for EG steel. Nevertheless, it did not change very much when the concentration was greater than 0.02 M.

Shown in Figure 3.15 are the results of Tafel tests at different immersing time on two types of steel samples in ODT solution. No substantial change in corrosion current can be observed over the immersing time from 30 seconds to 1 hour.

Different curing temperatures were also tested for both types of steel samples after being coated with ODT. There were two purposes for heating the coated plates. Firstly, it was thought that heating the organic coating would help the reorganization of adsorbed molecules, thereby making the film stronger for resisting corrosive attack; secondly, this heating test would probably be used to determine the thermal stability of the coating.

Figure 3.16 exhibits the effect of curing temperature on corrosion current of both EG and phosphated plates. Similarly, there was no obvious change in corrosion current over the curing temperatures from –10 °C to 180 °C for phosphated sample. This indicated the phosphate layer,
much thicker than the ODT film, also played a role in resisting corrosion during the electrochemical test. The ODT-coated EG sample, however, after being heated for 5 minutes at 180 °C, showed a significant increase in corrosion current density (from 8.78 µA/cm² to 35.61 µA/cm²). On the other hand, the corrosion currents were all below 10 µA/cm² over the low temperatures range. This result suggests that ODT coating on EG steel was thermally stable in the temperatures below 150~160 °C.

Interestingly, the samples of Tafel test described above exhibited a notably different appearance after 10 days’ exposure to air in laboratory. Serious red rust appeared on the area where the plate had contacted with NaCl solution during Tafel test on two plates: (a) the control sample, and (b) the ODT-coated sample that was heated at 180 °C. It is believed that heating at the temperature as high as 180 °C may have destroyed the monolayer of ODT coatings. This phenomenon is completely consistent with the measurement of corrosion current as presented in Figure 3.16. The highest corrosion currents were obtained from these two samples.

The temperature stated above is referred to the temperature of the air inside the oven. The actual temperature on the surface of metal depends on the oven temperature and the heating time. When the oven temperature was set at 150 °C, the temperature of metal surface could reach 113 °C, 132 °C and 151 °C after the sample was put in the oven for 3, 4 and 5 minutes, respectively.
3.3.5 Surface Oxidation and Thiol Performance

Zinc is one of the typical unstable metals in nature. When galvanized steel leaves a bath, it is oxidized in air at a rate of approximately 40 nm/24h (Porter, 1994). The oxidation products are usually ZnCO$_3$ and ZnO when it contacts with oxygen and carbon dioxides in the air. The initial reaction takes place rather quickly and progresses at a slow rate over a period of years (Munger, 1984).

At the beginning of the present work, the salt spray tests were not constantly reproducible for ODT coatings on EG steel. In general, the corrosion resistance of ODT-coated EG steel decreased with the prolonged storage time of EG steel samples, as shown in Figure 3.17. The reason was attributed to the oxidation of EG steel in air, which caused the surface less reactive to ODT than the fresh zinc surface. This observation was consistent with other researcher’s comments (Finklea, 2000). It is widely accepted that ODT adsorbs on a fresh, unoxidized metal surface more readily than on a surface of metal oxides. Therefore, EG steel must be coated before it is oxidized. Fortunately, this should not be a problem in plant operation, where EG steel will be treated shortly after the galvanization treatment is completed.

The changes in surface free energy of an EG steel sample as a function of exposure time were obtained by measuring the contact angles. As shown in Table 3.2, the surface tension ($\gamma_s$) of EG steel decreased from 45.25 mJ/m$^2$ to 43.25 mJ/m$^2$ after 10 days of air exposure. This decrease

![Figure 3.17 Reduction of corrosion resistance of ODT coatings as a function of surface oxidation of EG steel](image1)

Figure 3.17 Reduction of corrosion resistance of ODT coatings as a function of surface oxidation of EG steel
was mainly due to the decrease in the non-polar component (\(\gamma_{LW}\)). On the other hand, the polar component (\(\gamma_{AB}\)) increased from 0.96 mJ/m\(^2\) to 1.75 mJ/m\(^2\). The increase of \(\gamma_{AB}\) was caused by a nearly 20-time increase in the acidic component (\(\gamma^+\)). The basic component (\(\gamma^-\)) decreased from 9.82 mJ/m\(^2\) to 1.89 mJ/m\(^2\). The change in surface free energy of EG steel was caused by surface oxidation.

XPS analysis data of EG steel surface are given in Table 3.3. The EG steel samples were prepared six months ago in POSCO and have been stored inside a vacuum desiccator. Surprisingly, the carbon and oxygen content was extremely high while the zinc concentration was very low on the topmost surface of EG steel. The samples must have been oxidized and/or contaminated during the storage and shipping. The oxygen content was even increased by 1.74% after 10 days of exposure in air since the sample had been taken out of the vacuum desiccator. However, the carbon and oxygen content decreased significantly, especially the carbon content, after the sample was etched by 10 nm for XPS analysis. Therefore, it was thought that the most carbon on the topmost surface must have originated from the contamination, probably from the tissues that had been used for wrapping the steel sheets during shipping and storage, although part of them may come from zinc carbonates, the oxidation product.

Table 3.2  Changes in surface free energies of EG steel after exposure to air for ten days

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Contact Angle (degrees)</th>
<th>Surface Tension, mJ/m(^2)</th>
<th></th>
<th></th>
<th>(\gamma_s)</th>
<th>(\gamma_{LW})</th>
<th>(\gamma_{AB})</th>
<th>(\gamma^+)</th>
<th>(\gamma^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>water</td>
<td>FA</td>
<td>BN</td>
<td>(\gamma_s)</td>
<td>(\gamma_{LW})</td>
<td>(\gamma_{AB})</td>
<td>(\gamma^+)</td>
</tr>
<tr>
<td>Fresh EG steel</td>
<td>72</td>
<td>51</td>
<td>4</td>
<td>45.25</td>
<td>44.29</td>
<td>0.96</td>
<td>0.02</td>
<td>9.82</td>
<td></td>
</tr>
<tr>
<td>Oxidized EG steel</td>
<td>84</td>
<td>75</td>
<td>21</td>
<td>43.25</td>
<td>41.50</td>
<td>1.75</td>
<td>0.40</td>
<td>1.89</td>
<td></td>
</tr>
</tbody>
</table>

* FA--formamide; BN--bromonaphthalene
The data in Table 3.4 show the change in surface properties and corrosion resistance due to ODT coating on EG steel. ODT coating could produce a highly hydrophobic, low energy surface. It is commonly believed that high hydrophobicity may help achieve good corrosion resistance by shielding water or other corrosive substances from attacking the metal surface, although it does not necessarily bring about high corrosion resistance. But it is also probably detrimental to the paintability of EG steel. For this reason, thiols terminated with other functionalities will be studied in future work.

Salt spray tests demonstrated that ODT coating, despite of its nanometer scale of thickness, could remarkably increase the corrosion resistance of EG steel. Electrochemical studies also illustrated that the corrosion current decreased by approximately 6 times due to ODT coatings. The unique performance of ODT coatings may be attributed to the formation of a well-ordered, close packed, SAM of ODT molecules on EG steel surface, which can resist the attack of corrosive media like water, oxygen and chloride ions, etc.

### Table 3.3 Elemental composition of EG steel surface obtained from XPS analysis

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Atomic concentration (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Etch</td>
<td>C</td>
</tr>
<tr>
<td>Exposure in air for 10 days</td>
<td>No</td>
<td>43.31</td>
</tr>
<tr>
<td>Newly opened from vacuum desiccators</td>
<td>No</td>
<td>47.88</td>
</tr>
<tr>
<td>Newly opened from vacuum desiccators 10 nm</td>
<td></td>
<td>4.32</td>
</tr>
</tbody>
</table>

### Table 3.4 Change in surface properties of EG Steel due to ODT coatings

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Water Contact Angle (degrees)</th>
<th>Surface Tension (mJ/m²)</th>
<th>Corrosion Current (µA/cm²)</th>
<th>White rust occurrence (SST hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG</td>
<td>72</td>
<td>45.25</td>
<td>49.04</td>
<td>2–4</td>
</tr>
<tr>
<td>EG + ODT</td>
<td>124</td>
<td>34.63</td>
<td>8.78</td>
<td>50–60</td>
</tr>
</tbody>
</table>

* * 0.05 M ODT, dip 300 sec., heat 5 min. @120 °C
3.3.6 Surface Characterization: XPS Analysis

X-ray photoelectron spectra of Zn, O, C and S of the EG surface and ODT-coated EG surface are shown in Figure 3.18 (before etch). In the presence of ODT film, the intensity of peaks Zn2p (1022.8 eV) and O1s (532.0 eV) decreased but the intensity of the peak C1s (285.0 eV) increased. The change in peak intensity usually represents the change of atomic concentration.

Figure 3.18 XPS spectra (wide scan) obtained on EG steel (a) and ODT-coated EG steel (b), without etch for both samples
More remarkably, a new peak of S2p at 162.8 eV appeared on the spectra of ODT-coated surface. The binding energy of this peak was similar to the binding energies of the S2p spectrum of the alkanethiol SAMs adsorbed on copper, silver, gold and iron as reported by other authors (Yamamoto, 1993; Volmer-Uebing, 1992; Laibinis, 1991; Nozawa, 1997).

XPS of the S2p spectra are shown in Figure 3.19. Curve (a) represents the S2p spectrum of the zinc surface coated with ODT by dipping the zinc plate in 0.5 M ODT ethanolic solution for 5 minutes, and then drying it in air. Curve (b) is the S2p spectrum of the bulk ODT reagent. It is clearly seen that the S2p spectrum has shifted to the lower binding energy, indicating that thiol group formed a chemical bond with zinc.

It is thus concluded that ODT has been adsorbed on the EG steel surface by the formation of zinc thiolates:

\[
[Zn] + C_{18}H_{37}SH \rightarrow [Zn]SC_{17}H_{37} + H^+ + e^- \quad [3.1]
\]

Table 3.5 lists the atomic concentration of EG steel surface with and without ODT coatings. The sulfur concentration on the topmost surface (before etch) increases from zero to 3.5% due to the adsorption of ODT molecules. Similarly, the increase of carbon should result from the
presence of hydrocarbon chains of ODT molecules in the film. The concentration of both oxygen and zinc decreased dramatically because of the coverage of ODT film on the EG steel that mainly consists of zinc, oxygen and carbon because of the oxidation prior to the treatment.

Table 3.5 and Figure 3.20 also present a depth profile of the elements contained in the surface of EG steel. The atomic concentration was analyzed in different etch depths. The concentration of zinc and oxygen increased as the etch depth went down from the topmost surface to 3 nm deep. It is well known that the ODT molecular chains can stretch to about 2.2 nm from the substrate. The decrease of carbon concentration may be explained by assuming that the majority of ODT molecules oriented outward from the substrate surface while its polar groups (-SH) reacted with the substrate. But the sulfur should concentrate on the metal/ODT interface, as illustrated in Figure 3.1. However, the EG steel used in this work was far from an ideal smooth surface. Also, it has to be pointed out that the atomic concentration reported here was an average value of the elemental contents detected over a surface area of 1×3 mm. These facts may help explain the reason that all the elements can be detected across the section of 0 to 3 nm on the ODT-coated EG steel surface, and that sulfur concentration has no significant difference over the cross section.

It is thus conclude that the orientation of ODT self-assembled monolayer is not as perfect as illustrated in Figure 3.1.

Table 3.5  Elemental composition of EG steel with and without ODT coatings

<table>
<thead>
<tr>
<th>Samples</th>
<th>Atomic concentration, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>EG steel, before etch</td>
<td>46.08</td>
</tr>
<tr>
<td>ODT-coated EG steel, before etch</td>
<td>87.50</td>
</tr>
<tr>
<td>ODT-coated EG steel, 1 nm etch</td>
<td>71.76</td>
</tr>
<tr>
<td>ODT-coated EG steel, 2 nm etch</td>
<td>63.60</td>
</tr>
<tr>
<td>ODT-coated EG steel, 3 nm etch</td>
<td>56.25</td>
</tr>
</tbody>
</table>
3.3.7 Surface Characterization: FTIR Studies

Figure 3.21 shows the RAIR spectra of EG steel surface, ODT-deposited EG steel surface and the bulk ODT reagent. The spectra obtained from ODT are the same as that provided by Sigma-Aldrich Chemicals Co. Both CH$_3$ and CH$_2$ groups give characteristic bands at 2934 cm$^{-1}$ and 2857 cm$^{-1}$ (CH$_2$ stretch) as well as a weak band at around 1466 cm$^{-1}$ (CH$_2$ bend). The bands at 723 cm$^{-1}$ may be assigned to the CH$_2$ rock mode. There should be a characteristic band around 2600–2550 cm$^{-1}$ that belongs to S-H bond, but it is too weak to be discerned over these wide spectra. The C-S adsorbance band should occur at around 630 cm$^{-1}$, but it is not strong enough to be detected in these spectra. Interestingly, different C-S bands have been reported under various circumstances by different authors. It may locate in the vicinity of 630 cm$^{-1}$ (Taneichi, 2001), or 672 cm$^{-1}$ (Zucchi, 1996), or 800–860 cm$^{-1}$ (Perrin, 1998) or 860 cm$^{-1}$ (Baba, 1999).

The distinctive feature of the FTIR spectra of EG steel is a band at approximately 2361 cm$^{-1}$. The possible origin of this band is the adsorption of carbon dioxide or the oxidation product zinc carbonate (Stroeve, 1990). This band cannot be assignable to zinc oxide because the ZnO band should locate at around 450 cm$^{-1}$ (Manov, 2000).
Figure 3.21 IR spectra of ODT-coated EG steel surface (a), EG steel surface (b), and pure ODT powder (c)
The spectra of ODT-coated EG steel are almost equal to the summation of two separate spectra of EG steel and pure ODT, indicating the adsorption of ODT on the surface of EG steel. According to Manov (2000), the Zn-S band should be in the vicinity of 437–479 cm\(^{-1}\). Therefore, it was not detected in this mid IR spectra. No hydroxyl band (~3350 cm\(^{-1}\)) was detected in the spectrum of the ODT coating, indicating that ethanol had completely vaporized from the coatings.

### 3.3.8 Surface Morphology: AFM

AFM is a useful tool to study the topography of the organic surface. A Nanoscope™ 3100 AFM (Digital Instruments) was used in the present work. Figure 3.22 (a) shows the AFM image of a blank EG steel plate without further treatment since the steel plate was electrogalvanized at POSCO. The surface consists of zinc crystals (partly oxidation products) and are very rough and edgy.

Figure 3.23 (a) shows the sectional profile of this surface. Apparently, the roughness of EG steel surface is about 800 nm from the peak to the valley.

After the EG steel was coated with ODT, the surface seemed less edgy, as shown in Figure 3.22 (b). Presumably, the ODT molecules did not adsorb on the surface in a strict manner of self-assembled monolayer. There might be some ODT molecules that deposited inside the valleys or cracks of the surface in the form of physisorption. However, the ODT coating did not change the roughness to a discernible extent. The roughness of the ODT-coated surface was still around 800 nm as demonstrated in Figure 3.23 (b). ODT molecules are unlikely to flatten the extremely rough surface of EG steel because the length of its molecular chains is only 2–3 nm [Ullman, 1996; Schreiber, 2000].

Due to the edge effect, the tips or edges of zinc crystals on EG steel surface may remain uncovered, or the ODT molecules cannot be closely packed over there. Therefore, these sites may become the weaknesses for corrosion initiation. It may give an explanation for the observation that rust always initiated from a small point and progressively extended to a larger area in the process of salt spray test.
Figure 3.22 AFM image of EG steel surface (a), and ODT-coated EG steel surface (b). Z: 600 nm. (ODT concentration: 0.05 M; dipping time: 5 minutes; dry in air)
3.4 CONCLUSIONS

For the purpose of reagent screening, various long-chain surfactants with different reactive groups were evaluated by salt spray test. These reagents included alkanethiol, carboxylic acid, hydroxamate, imidazole, amine, sulfate, pyridinium, phosphonic acid, and silane. Of these, 1-Octadecanethiol (ODT) gave the most promising results on both phosphated and EG steel sheets.
ODT can form a thin, close-packed film on EG steel. The mechanism is similar to the formation of SAMs of organosulfur compounds on metal substrate. This close-packed film possesses lots of unique properties that make the substrate resistant to the attack of corrosive substances such as water, oxygen and other corrosive ions.

ODT coatings can give comparable or better corrosion resistance than silanes such as BTSE, VS. It can resist 50 to 60 hours of salt spray without serious rust on EG steel. The control sample usually started rusting only after 2~4 hours of salt spray. The optimal concentration of ODT is in the range of $0.02 \text{ M}$ to $0.05 \text{ M}$. The method of post treatments (drying, heating) did not make a significant difference in the performance.

The solvents with a straight chain structure were identified as the suitable solvents of ODT for the formation of a satisfactory film. The examples include ethanol, ethyl acetate and butanol.

The tests conducted at VT had been repeated at POSCO, the sponsor of the present project. Based on the consideration of 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.

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 would make the surface more hydrophobic.

The surface properties of EG steel changed significantly due to ODT coatings. The water contact angle increased from $72^\circ$ to $124^\circ$, and the surface free energy of EG steel deceased from $45.25 \text{ mJ/m}^2$ to $34.63 \text{ mJ/m}^2$ accordingly. High hydrophobicity or low surface free energy was helpful for improving corrosion resistance, but it was detrimental to the adhesion of topcoats. Therefore, it is still necessary to further study the thiols terminated with other functionalities (e.g., -OH, -COOH, and –NH$_3$) that may be able to produce a higher-energy surface.

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

Finally, XPS analysis and FTIR studies revealed the abnormally high concentration of carbon and oxygen on the surface of EG steel, and also confirmed the formation of ODT film on the EG steel surface. AFM imaging revealed an extremely rough and edgy surface of EG steel. The surface roughness was close to 800 nm.
REFERENCES