

CHAPTER 2

CARBOXYLATE COATINGS ON PHOSPHATED STEEL SHEETS

2.1 INTRODUCTION

It is well known to produce a conversion coating on metal surfaces such as aluminum, iron and zinc surfaces by exposing metal substrates to an aqueous phosphate solution. The inorganic phosphate coatings may be any or the combination of those phosphates including zinc, iron, nickel, manganese, lead and cadmium phosphate. The iron phosphate coatings can be applied over iron, steel or alloys, and the zinc phosphate coatings generally are applied over iron steel, zinc, aluminum, or alloys thereof. The inorganic phosphate coatings can only provide the metal surface a limited corrosion protection and serves primarily as a base for the later application of siccative organic coatings such as paint, lacquer, varnish, primer, synthetic resin, enamel, and the like.

There have been substantial interests in the art for treating the phosphate surface prior to the application of an organic topcoat. The treatment of phosphate coatings has proven utility for fighting “undercutting” corrosion and the “loosening” of topcoats. It is well known that chromating treatment over phosphated surface can enhance the corrosion resistance and promote adherence of organic topcoat to metal surface. Recently, there is a need to find a replacement of chromate coating because of increasing environmental and healthy concerns.

As introduced in Chapter 1, silane coupling agents are capable of forming strong bonds to metal substrates and, at the same time, of possibly forming crosslinked polymers on the surface, both of which contribute to producing strong conversion coatings. Furthermore, proper choice of the terminal groups of silane coupling agents can improve the adhesion of organic topcoats. Recent publications claim that the conversion coatings formed by silane coupling agents are comparable to or better than the chrome conversion coatings and can provide excellent seats for paint adhesion (Child, et al., 1999; Van Ooij, et al., 1998; Tang, et al, 1997).

Silane coupling agents possess excellent coupling properties for most metal substrates and paints. However, the cost is an obstacle for a large-scale industrial application. Therefore, there still is a need to find a cheap, nontoxic, simple rinsing composition for treating phosphate surface prior to applying organic topcoats. U.S. Patent No. 3,975,214 describes a tannin-containing post-treatment composition for use over zinc phosphate conversion coatings on metallic surfaces to

provide an improved base for paint, lacquer, varnishes, etc. The tannin-containing solutions described in this patent are aqueous chromium-free solutions consisting essentially of a vegetable tannin in a concentration of 0.1 to 10g/L and having a pH of less than 6, preferably between 3 and 6.

U.S. Patent No. 4,110,129 describes the use of an aqueous solution containing a water-soluble titanium compound such as titanium fluoride, titanium sodium fluoride or potassium titanyl oxalate, and at least one adjuvant compound such as phosphoric acid, phytic acid, or tannin and hydrogen peroxide. U.S. Patent No. 4,182,637 describes a rinse containing the combination of citric acid and sodium nitrite to enhance corrosion protection. U.S. Patent No. 4,362,577 describes an aqueous acidic rinse containing hypophosphorous acid, salts of hypophosphorous acid or sodium hypophosphate. U.S. Patent No. 4,264,378 describes a rinse containing phosphate, a metal cation, and molybdate, vanadate, niobate or tantalate ions.

The inventions described in these four patents have a common shortcoming. They do not form insoluble complexes with phosphate and are therefore not suitable for use with electrodeposited paint. U.S. Patent No. 4,656,097 describes a method of treating phosphated metal surface to improve the corrosion-inhibiting properties and the adhesion of topcoats, comprising treating a phosphated surface with an aqueous solution of water-soluble organic titanium chelate that forms a water-insoluble film. U.S. Patent No. 4,650,526 discloses a method of treating a phosphated metal surface with an aqueous mixture of an aluminum zirconium complex.

Schulman and Bouman (1997) used long-chain carboxylic acids, preferably isostearic acid, as organic seals for anodized aluminum. Salt spray test showed that its corrosion resistance was superior to that obtained by chromates. Hefter, et al. (1997) used straight chain carboxylates as organic corrosion inhibitors for steel, copper and aluminum. When they used dicarboxylates, the longer carbon chain gave better the corrosion inhibition. For monocarboxylates, there was an optimum chain length for effective corrosion inhibition.

Park, et al. (1999) used *10*-undecenoic acid (UA) to synthesize a new class of polymer film on a platinum electrode by plasma polymerization technique. The cross-linking density of the polymer film can be modulated by step-wise varying the plasma power. The film thickness increases almost linearly with the increase in the plasma duration, and the deposition rate of the film is 13 nm/min.

Fousse, D. (1999) patented a surface treatment process for metal sheets such as bare steel, and zinc, chromate, tin-plated steel. An organic thin film was produced with a chemical containing an apolar alkyl chain at one end and a polar radical at another end, for instance, oleic acid, and palmitic acid. The sheet coated with a film of organic product is then heated to a suitable temperature for a suitable time to enhance its reaction with metal surface and to make it partly crosslink through physical entanglement.

Carboxylates have long been used as corrosion inhibitor of metals, specifically for aluminum. According to Kuznetsov (1996), an increase in the length of carbon chain in the anion (RCOO^-) has a beneficial effect on inhibition efficiency due to the increase of hydrophobicity. The presence of a double bond usually increases its polarizability and, thereby, its inhibiting effectiveness. Sodium 6-undecenate ($\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_4\text{COONa}$) is one of the most effective olefinic carboxylates, while sodium stearate is a weak inhibitor despite its activity as a surfactant. As for cyclic compounds, the effectiveness is to a large extent determined by their hydrophobicity.

10-Undecenoic acid (UA) was chosen in the present work because of the possibility that the terminal vinyl groups may form cross-linking polymers on the surface, and, thereby, provide an impermeable conversion coating for corrosion prevention. The mechanism of *in-situ* polymerization of UA was illustrated in Figure 2.1.

EIS studies and contact angle measurement of 10-undecenoic acid (UA) coatings and sodium oleate (OA) coating are presented in the first part of this Chapter. Both coatings can make the phosphate surface more hydrophobic and increase the polarization resistance (R_p) by 3 to 5 times.

Subsequently, additional resin coating over the top of UA coatings was evaluated by salt spray test. The phosphated steel coated with UA plus resin could remain clean without rust after 120 hours or longer in the salt-spray chamber. The double-coated UA was comparable to, if not superior to, silanes (BTSE and VS) as coupling agents between phosphated surface and resin. Based on the consideration of cost, other fatty acids with different chain length (C12 to C20) were tested. The results showed that fatty acids with relatively long chain, like myristic acid, palmitic acid and stearic acid exhibited a potential as an alternative to a UA layer beneath the topcoat of resin.

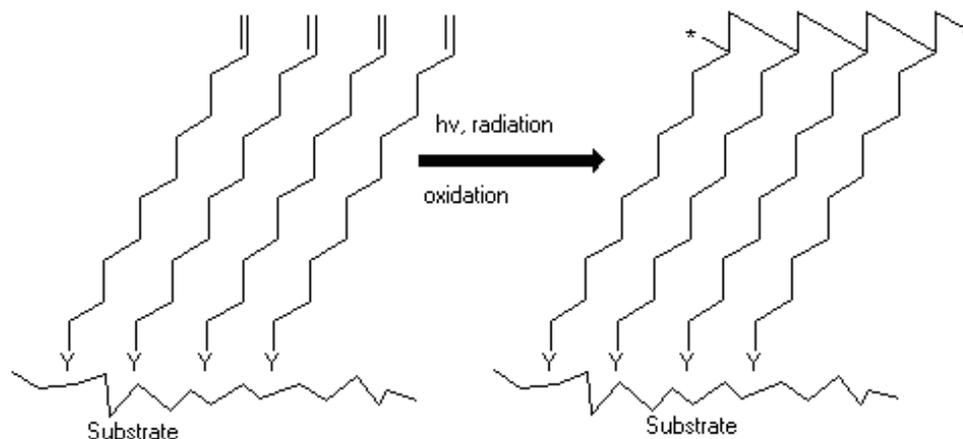


Figure 2.1 Proposed mechanism of cross-linking polymerization of the terminal vinyl groups of the undecenoic acid adsorbed on a CRS surface.

2.2 EXPERIMENTAL

2.2.1 Reagents

10-Undecenoic acid (UA, $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_8\text{COOH}$), also called undecylenic acid, was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. Its purity is 98% by weight. *10*-undecenoic acid is not readily soluble in water. However, it can be made water-soluble in an alkaline pH, where it dissociates to undecyanoate as follows when adding NaOH:



The following fatty acids were also purchased from Sigma-Aldrich Chemical Company:

Lauric acid (98%),	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
Myristic acid (99.5%),	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
Palmitic acid (99%),	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
Stearic acid (99%),	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Rachitic acid (98%),	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$
Oleic acid (90%),	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

Lauric acid, and oleic acid or sodium oleate were dissolved in DI water under the alkaline condition by adding NaOH to adjust pH to around 11.5. Other fatty acids were dissolved in ethanol to the desired concentration. The ethanol of 200-proof was made by AAPER Alcohol & Chemicals Co.

The resin used in the present work was provided by POSCO. It consists of solution A (base solution: modified acrylic polyethylene, white-colored) and Solution B (hardener: aziridin, brown-colored). Prior to coating, solution A and B were well mixed at the ratio of 99:1 by weight.

Vinyl silane (VS), 1,2-bis(triethoxysilyl) ethane (BTSE), and γ -aminopropyl silane (γ -APS) were purchased from Gelest, Inc., Tullytown, PA. These reagents were research grade and used without further purification. Silane solutions were prepared in the manner as described as follows:

One part of BTSE was thoroughly mixed with three parts of ethanol, one part of deionized (DI) water. After 4 hours of hydrolysis time under stirring, the solution was diluted with DI water to 1% by volume. The natural pH of the diluted solution was approximately 4.

One part VS was mixed with one part deionized water and three parts ethanol. After 4 hours of hydrolysis at room temperature under stirring, it was diluted to a working strength (1% by volume). Because the natural pH of the diluted solution was approximately 4.2, it was used without further pH adjustment.

One part of γ -APS was mixed with two parts of deionized water, and was then stirred for hydrolysis for 4 hours at room temperature. The hydrolyzed solution was diluted to 1% by volume with deionized water. The natural pH of the 1% γ -APS solution was approximately 10.4.

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).

2.2.2 Steel Samples and Coating Method

The phosphated-EG steel plates were prepared by applying A3 solution over electro-galvanized (EG) steel sheet at POSCO. A3 phosphate solution, containing zinc (1,900 ppm), nickel (300 ppm) and cobalt (50 ppm), was developed by POSCO as an optimized process.

For R_p and contact angle measurement, the CRS plate with the dimension of 14×7.5 cm was immersed in the surfactant solution prepared in the manner described above, and then dried in a stream of nitrogen gas at approximately 20 psi. Each plate was cut into 8 pieces of approximately 2.5×2.5 cm squares. Each small plate underwent EIS and contact angle measurement; finally, an average value of R_p and contact angle from these eight plates was reported. R_p and contact angle were measured immediately after UA coating except for the tests on aging.

The well-mixed resin solution was applied over the surface of surfactant-coated phosphated samples with a No.5 bar coater. Afterward, the plate was immediately put into an oven with pre-set temperature of 150 °C and cured for 5 minutes. The heating scheme is consistent with the procedure recommended by POSCO, which requires keeping the temperature on metal surface at 120 to 130 °C for 8 seconds. The actual metal surface temperature reached 122 °C in the present work. A uniform resin film with thickness of about 1~2 μm was expected after this treatment.

2.2.3 Contact Angle Measurement

A Rame-Hart goniometer was used to measure the contact angles of water droplets on the surface of CRS plates. A small drop of water was placed by means of a hypodermic needle on the surface of a CRS plate coated with a surfactant. The angles were measured through the aqueous phase. The measurements were made at 3 different spots of a CRS plate, and the measured values were averaged. The value of water contact angle represents the surface hydrophobicity. The greater the contact angle, the more hydrophobic and the lower surface energy the surface is.

2.2.4 Electrochemical Impedance Spectroscopy (EIS)

A conventional three-electrode cell (K0259 Flat Cell from EG&G) was used for EIS studies. It was connected to a potentiostat (EG&G Model 273A), which was connected with a lock-in analyzer (EG&G 5210). The potentiostat and the lock-in analyzer were controlled by a computer through the program PowerSuite V2.12.1 (EG&G PAR). All EIS measurements were carried out in de-aerated 3% NaCl solution.

Phosphated steel surface coated with surfactants behaves like a simple corroding metal/electrolyte interface as shown in Figure 1.11. The typical Nyquist plot can be represented by a single semicircle. The solution resistance was about 10 ohms and polarization resistance varied from tens of kiliohms to hundreds of kiliohms for different treatments.

2.2.5 Salt Spray Test (SST)

Salt spray tests were carried out according to the standard procedure (ASTM B117, Test Method of Salt Spray (Fog) Testing). Dai Sung Engineering Co., Korea, manufactured the 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 kg.f/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 °C.

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 by MagicTM tape (3M), or Super-Talc electrical tape (Bluefield Manufacturing Co., VA). The samples were taken out every 24 hours for taking picture, and returned to the chamber as quickly as possible.

2.3 RESULTS AND DISCUSSIONS

2.3.1 UA coatings: EIS Studies and Contact Angle Measurement

(1) UA Concentration

Figure 2.2 shows the results of R_p and water contact angle measurements conducted under different UA concentrations from 0.005 M to 0.05 M. The pH was controlled in the range of 11.62 to 11.68 by adding NaOH. Dipping time of phosphated steel plate in UA solution was 1 minute. There was no more post-treatment except being blown dry with nitrogen gas after coating.

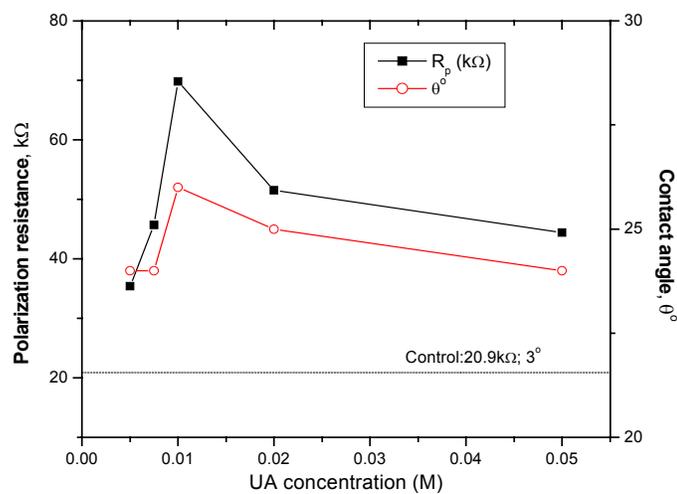


Figure 2.2 Effect of UA concentrations on polarization resistance and contact angle (pH11.62~11.68, immersion 1 min.)

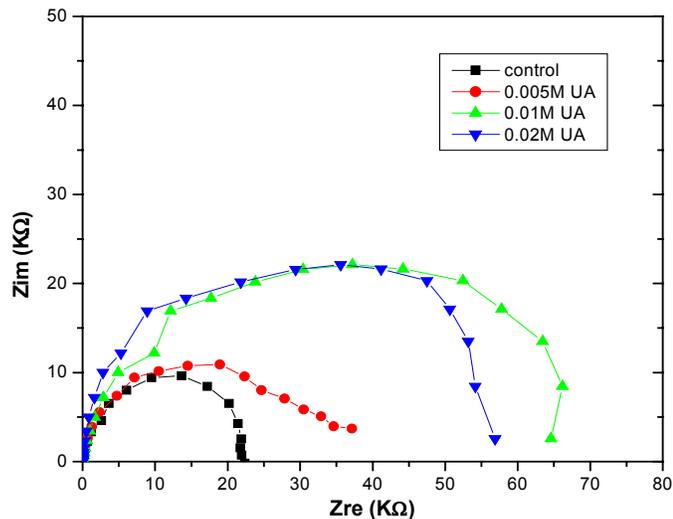


Figure 2.3 Nyquist plots of UA-coated phosphated samples at different concentration (immersion 1 min., pH11.64~11.67, single coating and no aging)

In general, contact angle increased with increasing compactness of the hydrocarbon chains of the surfactant molecules adsorbed on a surface. A peak occurred in both curves in the vicinity of 0.01 M, indicating an optimal adsorption and ordering of UA molecules on the surface of phosphated steel. For low concentrations, UA coating may be incomplete. For high concentrations, the inverse (or flip-flop) orientation of UA molecules may occur, or the formation of micelles in the solution has deteriorated the adsorption. Both assumptions help explain the decrease of R_p value and contact angle at high concentrations.

Rodriguez, et al. (1999) studied the critical micelle concentration (CMC) of 10-undecenoic acid and its sodium salt in aqueous solution. They found that pre-micellar aggregates started to form at 0.023 M, which grew to form micelles at 0.117 M for sodium undecenoate. Therefore, 0.01~0.02 M should be a reasonable concentration for having nonaggregated UA.

Figure 2.3 is the Nyquist plot of UA coatings on phosphated surface at different concentrations. In comparison with the control sample, UA coatings could achieve a nearly 3-fold increase of R_p value at the concentration of 0.01~0.02 M.

(2) Curing Temperature

It is widely accepted that UA is a polymerizable surfactant due to its active double bond at the end of hydrocarbon chains. Induced by UV, plasma radiation, chemical oxidation or heating, the terminal vinyl group is likely to form crosslinking polymerization on the surface and, thereby, provide an impermeable conversion coating. During the first year of this project, a lot of work had been conducted on the effect of UV radiation and permanganate oxidation on the polymerization of the adsorbed UA in order to enhance the barrier effect.

Only the effect of heating was studied in the present work. The results are shown in Figure 2.4. Heating could double the contact angle and significantly increased the hydrophobicity of the UA-coated surface. As far as R_p was concerned, however, there was an optimal heating scheme. Based on this test, heating 5 minutes at 50 °C gave the highest polarization resistance. Higher temperature or longer heating time was not beneficial to increasing R_p value. The boiling point of UA is 127 °C, and its melting point is unknown.

At this stage, it was unclear whether the breakup of the vinyl groups of UA molecules occurred due to the heating. But according to Fousse (1999), heating the organic film on metal substrate may help it react with metal and with itself, and enhance the cross-linking through

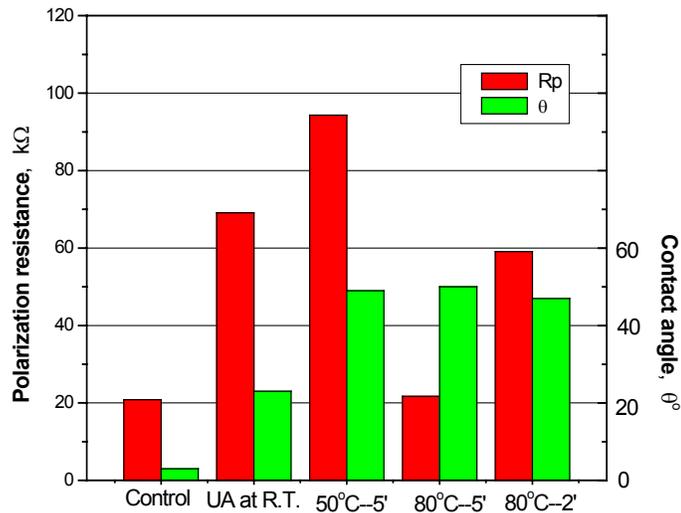


Figure 2.4 Effect of heating on polymerization of UA coating on phosphated samples (0.01 M UA, pH11.56, immersion 1 min.)

physical entanglement. Heating also helped the evaporation of the solvents. All these effects contributed to the compactness of the organic film and the improvement of its hydrophobicity.

(3) Alcohols as Co-surfactants

Figure 2.5 shows the results obtained with a solution containing 0.01 M UA and 0.001 M different alcohols at pH 11.52~11.58. Alcohol was added to the UA solution as a co-surfactant that was supposed to adsorb in between the adsorbed undecenoate ions on phosphated surface, and thereby form a more close packed monolayer.

As shown in Figure 2.5, UA coating alone increased the contact angle of phosphated steel from 3° to 23°. The contact angle further increased to nearly 40° with the addition of alcohols. R_p also increased with the use of alcohol as co-surfactants. Of the various alcohols tested, butanol co-adsorbed with UA gave the highest R_p value (about 100 k Ω). The results indicated that the use of alcohol as co-surfactant could increase the packing density of the hydrocarbon chain adsorbed on the surface of phosphated steel.

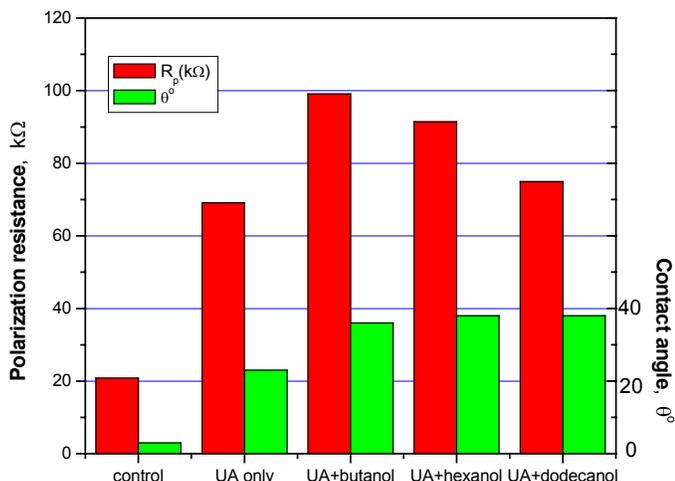


Figure 2.5 Alcohol of various chain lengths as co-surfactants of UA coating (0.01 M UA, 0.001 M alcohol, pH11.52-11.58, immersion 1 min.)

(4) Multilayer Coatings

The specimen was dipped in the UA solution for 1 minute and taken out, dried with nitrogen stream. This process was repeated; therefore, a double coating or a triple coating was obtained. A multilayer coating is supposed to make the organic film more complete in the ways: (a) UA

molecules would fill the pore of the first adsorbed layer; or (b) A second layer would form on the top of the first one through physisorption.

Figure 2.6 and Figure 2.7 display the results of these treatments. Obviously, both double coating and triple coating increased the contact angle by about 10° . The double coating also increased the value of R_p . However, the triple coating decreased the polarization resistance although it kept the contact angle at the same level as the double coating.

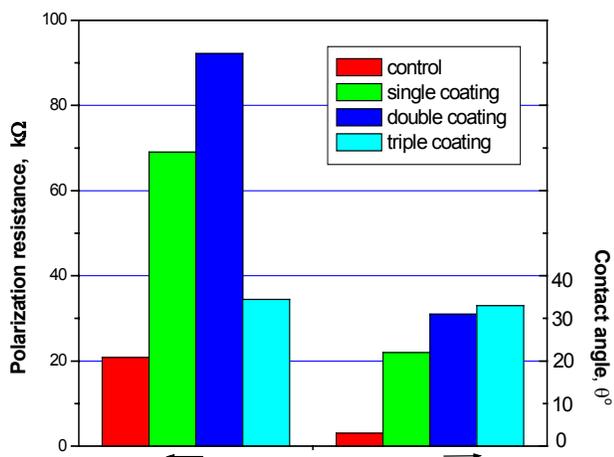


Figure 2.6 UA multilayer coatings on phosphated samples (0.01 M UA, pH11.70, immersion 1 min.)

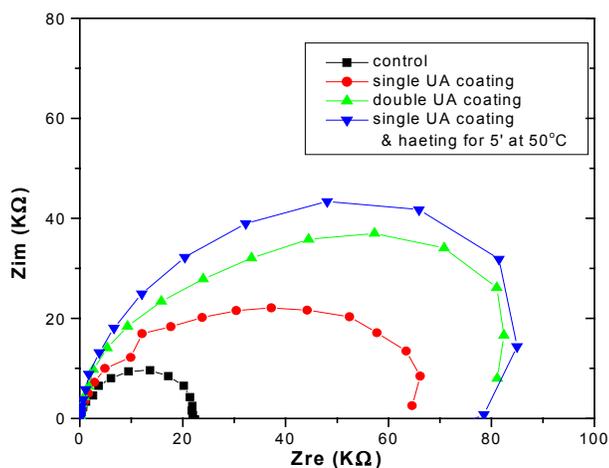


Figure 2.7 Nyquist plots of UA-coated phosphated samples with a single or multilayer coatings (immersion 1 min., 0.01 M UA, pH11.56)

(5) Aging

As shown in Figure 2.8, both contact angle and polarization resistance of UA coating increased with the time of aging. Here, aging means that the UA-coated specimen was placed inside a desiccator for a period of time prior to the test. During the first 5 hours, the properties of UA coating varied substantially in term of contact angle and R_p value, and then became stable. The change in coating properties during the process of aging may be attributed to the loss of water from the film. Hydrocarbon chains of the UA molecules may have stretched out and reorganized with the evaporation of the solvent. Heating after coating may serve the same function as aging does. However, the former treatment can be completed in much shorter time, usually in minutes or even in seconds.

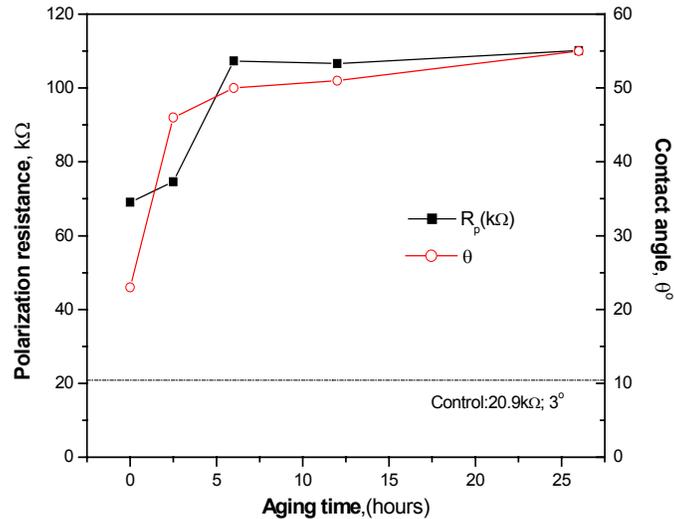


Figure 2.8 Effect of aging on UA coating applied on phosphated samples (0.01 M UA, pH11.67, immersion 1 min.)

(6) Activation of Ca^{2+}

As discussed above, undecenoate ions ($RCOO^-$) play a key role in the adsorption of UA molecules onto phosphated surface. The phosphate layer consists of phosphates of zinc, nickel, magnesium, etc. According to the data given in Table 3.1, the phosphated surface may be characterized as a basic surface. In order to enhance the adsorption of UA ions, the cation activation technique was tested that has been widely utilized in mineral engineering for the purpose of improving the adsorption.

Two types of solutions, both containing $1 \times 10^{-3} M Ca^{2+}$, were prepared by dissolving CaO and CaCl₂ in water. The natural pH of both solutions was 11.48 and 4.43, respectively. Activation process was completed by dipping the specimen in Ca²⁺-containing solution for 5 minutes, then taking it out and directly immersing it into UA solution for another 1 minute.

According to the results presented in Figure 2.9, Ca²⁺ activation did not improve the UA coating as expected. Contrarily, it deteriorated the adsorption and the integrity of UA coating. For both activators, the contact angle decreased from 23° to 8° due to the activation. The value of R_p remained unchanged for CaO activation but decreased by half for CaCl₂. The decrease of contact angle and R_p may be caused by the contamination of residual ions from the solution. Chloride ions, in particular, are extremely corrosive and have a detrimental effect on the performance of the UA coating. Also, this adsorption may be dominated by chemisorptions instead of basic-acid interactions.

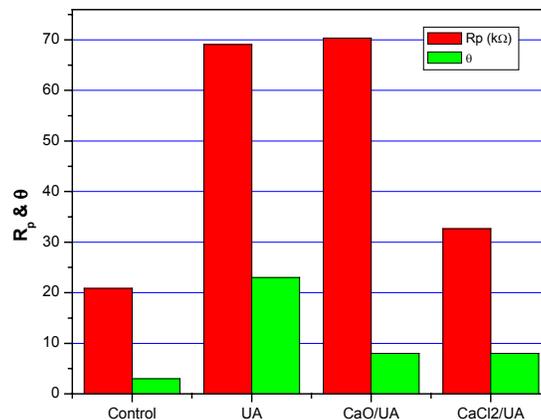


Figure 2.9 Activation of Ca²⁺ of phosphated plates prior to UA coating ($10^{-3} M Ca^{2+}$, pH 11.48 for CaO and pH 4.43 for CaCl₂, activation time: 5 min.)

(7) Comparison with Silane

Silane has been tested as a baseline. During the past two decades, various silanes have been studied and patented as coupling agents or conversion coating between metal substrate and the topcoat.

Van Ooij, et al. (Van Ooij, 1991 and 1998; Child, 1999) developed many methods of using vinyl trimethoxyl silane (VS), *1,2-bis*(triethoxysilyl) ethane (BTSE) and γ -aminopropyl silane (γ -

APS) for corrosion inhibition of steel and other metals. These silanes generally contain hydrolysable groups (e.g., CH_3O -, $\text{C}_2\text{H}_5\text{O}$ -) and, in water, may form the trihydroxyl silanes, which may be cross-linked via siloxane (Si-O-Si) bonds to become polymeric species that are able to adsorb on a substrate via H-bonding. Therefore, silane can form a robust coating on metal and give an excellent adhesion to the topcoat due to the functional group on the top.

The comparison of silanes and UA is presented in Figure 2.10. On phosphated steel, the coating of silanes in this test gave a much higher contact angle than the UA coating. In term of R_p value, however, UA single coating was almost equivalent to BTSE & APS coating, while the UA double coating was between BTSE & APS and VS coating. VS coating gave the highest value of R_p and contact angle.

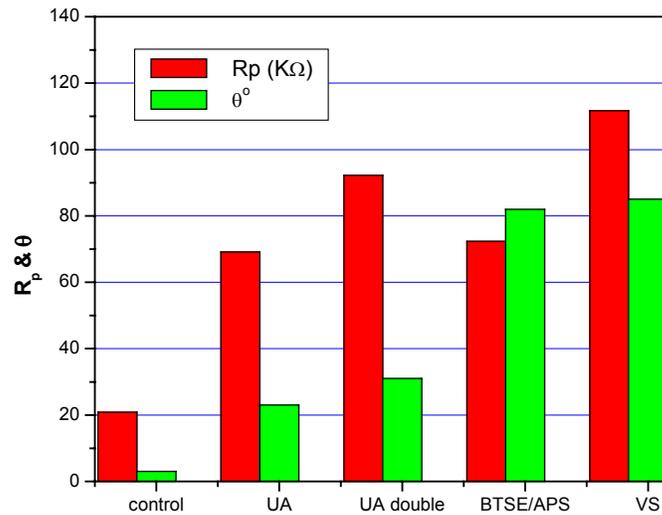


Figure 2.10 Comparison between UA and silane coating on phosphated samples (UA: 0.01 M, pH11.65; BTSE: 1%, pH4.15; APS: 1%, pH10.53; VS:1%, pH4.55)

(8) Summary

R_p and contact angle measurement of UA coatings were listed in Table 2.1. The data of silanes coatings were also included as a comparison. It was clearly seen that:

- (i) UA coating increased R_p by 3 to 5-fold for phosphated samples;
- (ii) Double coating and heating at a suitable temperature could help increase R_p value;
- (iii) UV or alcohol co-surfactant did not show pronounced improvement for R_p increase;
- (iv) UA was close to silane in increasing R_p although it gave lower contact angle.

Table 2.1 R_p and water contact angle of UA and silane coatings on phosphated steel

Treatment		θ°	R_p (k Ω)	Solution
Control		3	20.9	0.01 M; pH 11.50~11.70; heating for 5 min. at 50°C
UA	Single coating	23	69.1	
	Double coating	31	92.2	
	Single coating and heating	49	94.4	
Silane	VS	85	111.7	1%; pH=4.55(VS); 4.15 (BTSE); 10.53(APS)
	BTSE+APS	82	72.3	

2.3.2 OA Coatings: EIS Studies and Contact Angle Measurement

Sodium oleate ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COONa}$) or OA sodium salt is a long-chain fatty acid having an unsaturated bond in the middle of the hydrocarbon chain. Its polar carboxylic group is reactive to most metal substrates. Its melting point is 232~235 °C. It can be dissolved in water at alkaline condition, forming a clear, yellow solution. In the present work, it was tested for coating phosphated EG steel surface.

(1) OA concentration

A series of OA solutions having different concentrations were prepared by dissolving OA in DI water. The pH was adjusted to 11.0~11.5 with NaOH. A phosphated steel plate was immersed into the solution, taken out of the solution after 2 minutes, and was then dried with a nitrogen gas stream. The treated plate was stored inside a desiccator until the next day when R_p and water contact angle were measured. The results are given in Figure 2.11.

For the control sample without any treatment, the contact angle was 36° on average, and the R_p was close to 17.5 k Ω . θ increased to 60°~80° with OA coating applied onto the surface. It reached a peak value of 83° at 0.01 M concentration. However, R_p increased substantially only in the range of 0.01 M to 0.02 M, suggesting that the OA molecules were closely packed in this concentration range, therefore giving a high corrosion resistance. Its critical micelle concentration (CMC) at pH 8.1 is 1.5×10^{-1} M (Kuznetsov, 1996), but the CMC should be higher than 0.02 M for higher pH values.

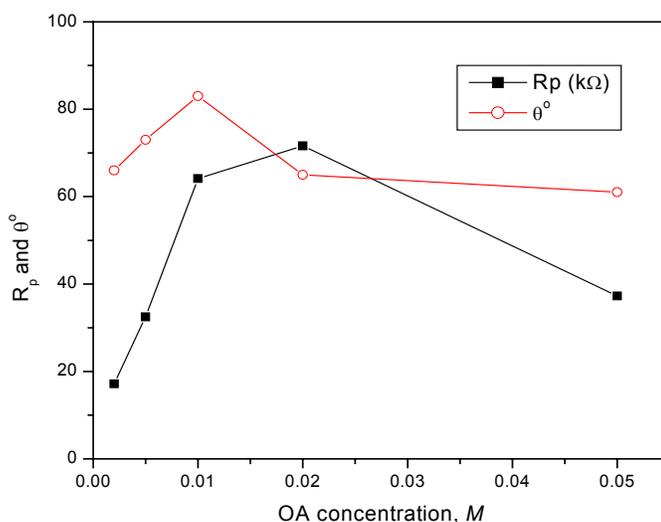


Figure 2.11 Effect of OA concentration on R_p and contact angle of OA-coated phosphated steel (pH11.37~11.48, immersion time: 2 min., aging 24 hours; Control: 17.5k Ω , 36 $^\circ$)

(2) pH of OA Solution

OA is sparingly soluble in water, but in alkaline solutions, it dissociates to become oleate ions, which are more soluble in water and reactive with the phosphate surface. In the present work, sodium oleate was used for coating phosphated EG steel for the purpose of corrosion prevention. Apparently, sodium oleate became more soluble in water at increasing pH when sodium hydroxide was used to adjust the pH. As shown in Figure 2.12, the contact angle of the coated surface increased as the pH value of the solution increased, but no longer changed after pH reached 9. R_p reached the maximum value in pH 7.5~9.5 range.

The main reason for the low contact angle and R_p at lower pH (<7.5) was most probably that the reagents were not completely dissolved and not in reactive form. But why did the polarization resistances decreased at higher pH (>9.5), even though sodium oleate was more completely dissolved in this pH range? It was probably attributed to the change of surface charge. The phosphate surface may become more negatively charged when pH exceeds 9.5, and therefore hinder the adsorption of oleate ions.

Figure 2.13 was the Nyquist plots obtained from EIS studies of OA coatings at different pHs. By extrapolating the semicircles, one can extract the R_p value from the interception at Z_{re} axis.

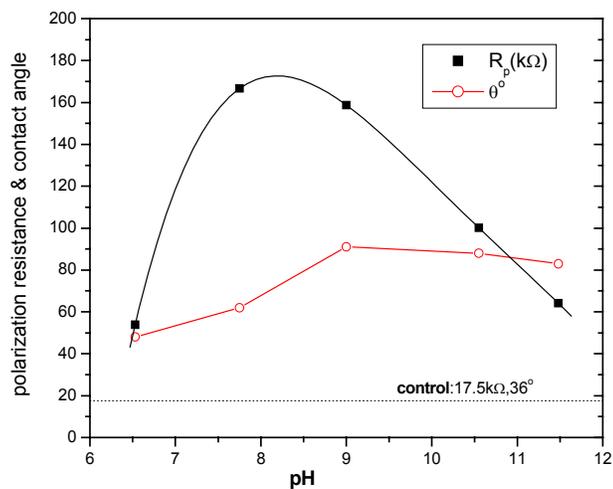


Figure 2.12 Effect of pH on OA coating on phosphated steel (0.01 M OA, immersion 2 min., aging 24 hours)

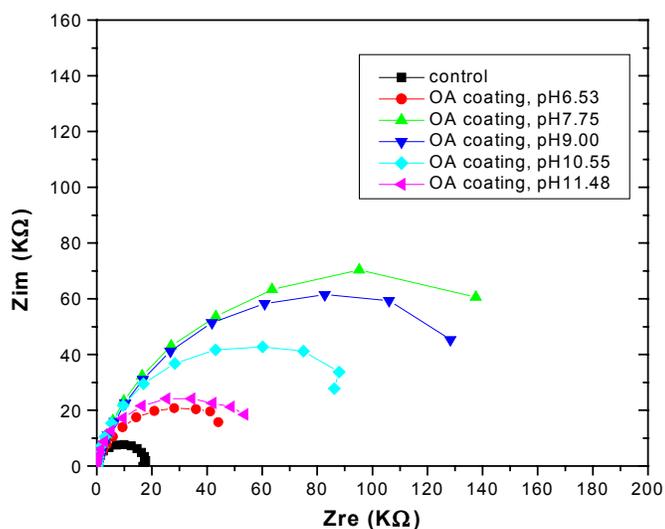


Figure 2.13 Nyquist plots of OA-coated phosphated plates at different pH (concentration: 0.01 M, immersion 2 min., aging 24 hrs)

(3) Multiple Coatings

As stated above, an organic film can form on the phosphated EG steel plate by dipping the plate in OA solution, drying it with nitrogen gas. This procedure was repeated in order to produce a multiple coating layer. The results shown in Figure 2.14 indicated that the double coating could increase the contact angle and R_p , but the triple coating did not improve the properties of the coating when compared with the single coating. It was assumed that a denser film of OA had formed on the surface after the plate was treated in OA solution twice. So there

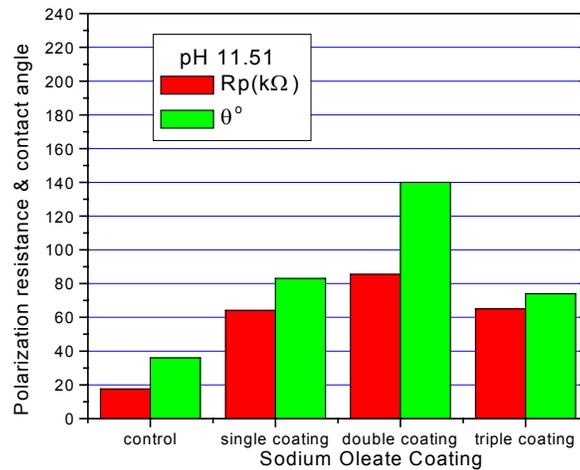


Figure 2.14 Multiplayer coating of 0.01 M OA on phosphated plates (immersion time: 2 minutes, aging 24 hours)

were no more active sites available for the adsorption of OA. Therefore, the third treatment did not make difference. According to Fousse (1999), a 10% or greater excess proportion of COOH radicals at the surface of the treatment film was regarded as a sign of satisfactory surface treatment than the stoichiometric proportion of the treatment reagent in the case of oleic acid.

Similarly, The Nyquist plots of these treatments are given in Figure 3.15 for the measurement of polarization resistance (R_p), an indicator of corrosion resistance.

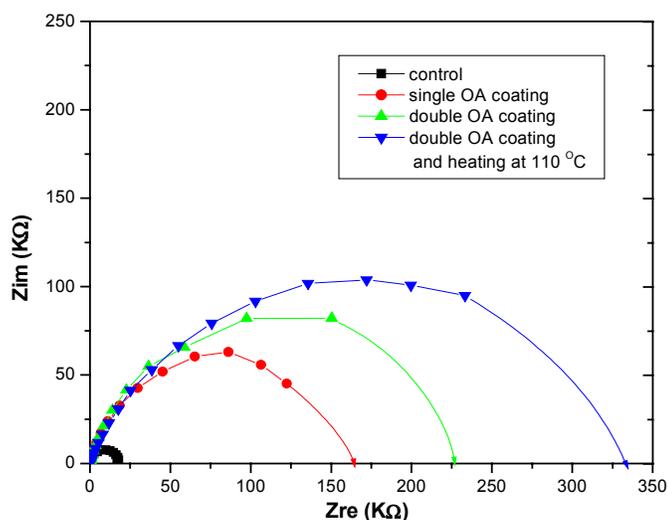


Figure 2.15 Nyquist plots of OA-coated phosphated plates (concentration: 0.01 M, immersion 2 min.)

(4) Heating Temperature

Figure 2.16 shows the results of contact angle and R_p measurement of OA double-coated phosphated steel surface. The coated plate was heated for 5 minutes inside an oven with different temperature between 25 to 180 °C. The results demonstrated that heating in this temperature

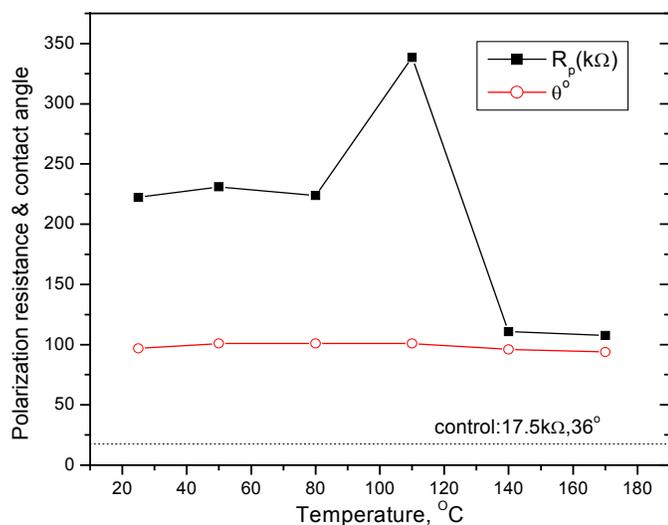


Figure 2.16 Effect of heating on OA coating of phosphated plates (0.01 M, immersion 2 min., pH 8.45, double coating, heating 5 min., aging 24 hours after heating)

range did not affect the contact angle significantly, which remained almost constant around 100°. Interestingly, the value of R_p did not change very much at the temperature below 80 °C, but it reached a peak value at 110 °C and then decreased rapidly at the temperature above 140 °C. It was believed that the organic film underwent crosslinking at the heating temperature about 110 °C, and thereby produced a more robust film for corrosion protection. R_p decreased as the temperature increased probably because the film fused and collapsed when it was heated at high temperatures. Generally, the preferred heating temperature should be lower than the boiling point or decomposition temperature of the organic product (Fousse, 1999). The heating temperature may be higher for a relatively short heating time, and vice versa.

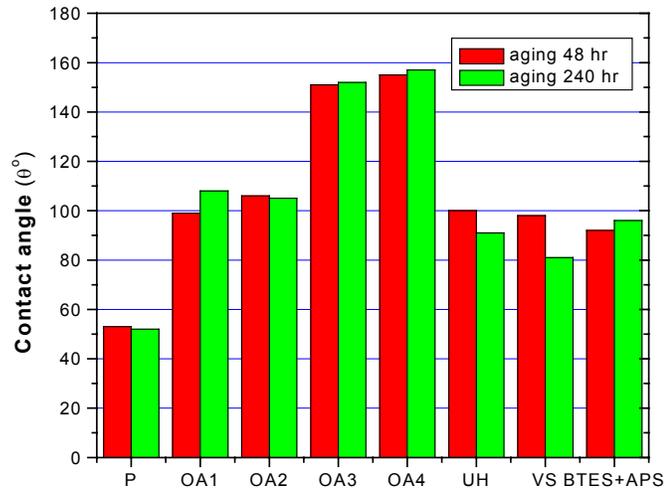


Figure 2.17 Comparison of water contact angle between OA, silane and UH under different post treatments

- P: phosphate EG steel (control)
- OA1: 0.01 M, pH 7.83, heating 15"@110 °C
- OA2: 0.01 M, pH 7.83, heating 5"@110 °C
- OA3: 0.01 M, pH 11.13, heating 15"@110 °C
- OA4: 0.01 M, pH 11.13, heating 5"@110 °C
- UH: 0.01 M, pH 10.47, heating 5"@80 °C
- VS: 1%, pH 4.26
- BTES+APS: 1%, pH 4.25 and 10.30

(5) Comparison with Silane

For the convenience of comparison, Figure 2.17 displays the data of contact angle of various coatings formed on phosphated EG steel. OA double coating could make the phosphate surface

more hydrophobic than other type of coatings such as that produced by vinyl silane (VS), *1,2-bis* (triethoxysilyl) ethane (BTSE) plus γ -aminopropyl silane (APS), and *10*-undecenyl hydroxamate potassium salt (UH, $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CONHOK}$), especially at high pH. After 10 days, the contact angle almost remained unchanged, indicating that these organic films were very stable in air. *10*-undecenyl hydroxamate potassium salt was synthesized by Dr. Yanyan Yang in the Department of Chemistry, Virginia Tech.

(6) Summary

OA coating was even better than UA coating for increasing polarization resistance (R_p) and surface hydrophobicity. Under the optimal conditions, OA coatings increased R_p by nearly 20 times while UA only by 3~5 times; the contact angle could reach as high as 150 degree. Double coatings or/and heating the coating increased the R_p value and contact angle substantially, especially for OA coating. It was expected that crosslinking had taken place after being heated. Neutral pH was good for increasing R_p while alkaline solution of OA was good for rising contact angle. An excellent hydrophobic surface may be achieved by double coating the substrate with OA at pH 11.5. However, a highly hydrophobic surface will be not compatible with the water-based topcoats.

2.3.3 UA and Resin Coatings: Salt Spray Test

Figure 2.18 was a series of photographs taken for various treatments of phosphated steel samples at the end of 120 hours of salt spray test, including:

- (i) phosphated steel (control);
- (ii) phosphated steel coated with resin coating (reference);
- (iii) phosphated steel coated with UA (single coating) plus resin;
- (iv) phosphated steel coated with UA (double coating) plus resin;
- (v) phosphated steel coated with VS plus resin;
- (vi) phosphated steel coated with BTSE plus resin.

Originally, pictures were taken every 12 hours, although only a part of them were shown herein. The UA concentration was 0.01 M and that of silane was 1% by volume. Immersing time was 5 minutes, and the coated plate was heated for 5 minutes inside an oven at temperature of 120 °C.

Phosphate	P + UA + Resin	P + UA(d)+ Resin
		
P + Resin	P + VS + Resin	P + BTSE +Resin
		

Figure 2.18 SST photographs of UA, silane plus resin coatings on phosphated steel after 120 hours of salt spray test (p—phosphated steel; d--double coatings).

The objective of this test is to explore the possibility of using UA as a coupling agent for the topcoat of resin. This novel coating system of UA plus resin was expected to have a corrosion resistance comparable to those of conventional chromate coated steels. For the chromate-treated

steels, the time to occurrence of white rust is usually between 72 to 150 hours as evaluated by SST (Kubota, et al, 2000).

In previous tests, the phosphated samples without any treatment usually began corrosion after 8 to 12 hours of salt spray in term of white rust occurrence. For this batch of samples, however, the initiation of corrosion occurred after 24~36 hours. From 72 hours on, red rusts appeared on the surface; this indicated that both the phosphate and zinc layers had been lost, and the base iron started to corrode.

If resin was applied directly on the phosphated surface without a coupling agent in between, the steel could last 84 hours without white rust. A UA single coating and BTSE coating beneath the resin could increase the corrosion resistance to 108 hours. VS did not perform as well as UA and BTSE when used together with resin.

The best result was obtained with UA double coating plus resin. Its surface still remained intact without discernible rusts; only a uniform film consisting of tiny water droplets remained on the surface, even after 120 hours of salt spray. The film of water droplets suggested that the organic coating still remained highly hydrophobic even under the attack of NaCl, oxygen and water, the corrosive substances involved in SST. This treatment may endure much longer than 120 hours if the test continues. Another SST for UA plus resin coating was conducted later and the results were almost the same (see Figure 2.19).

As discussed in the next Chapter, VS coating alone without resin on phosphated surface could last around 40 hours, which was a fairly good result for such a thin monolayer. In contrast, UA coating alone did not perform well in salt spray test. But it worked excellently when used in combination with resin. Also, the double coating was superior to the single coating. It was assumed that specific interactions between UA and the resin had taken place. The double bond at one end of UA molecule might have been broken during the curing process, which promoted the adhesion of resin on UA coated surface.

2.3.4 Other Fatty Acids and Resin Coatings: Salt Spray Test

Encouraged by the results obtained from UA plus resin coatings on phosphated steel, other fatty acids with different chain length from C12 to C20 were tested to replace UA. Fatty acids are much cheaper and more widely available than UA. Therefore, they would be more readily commercialized if the equivalent corrosion resistance could be achieved.

Figure 2.19 shows the results of salt spray test after 120 hours for phosphated steels with various treatments as below:

- (i) Myristic acid (double coating) + resin;
- (ii) Palmitic acid (double coating) + resin;
- (iii) Stearic acid (double coating) + resin;
- (iv) UA (single or double coating) + resin.

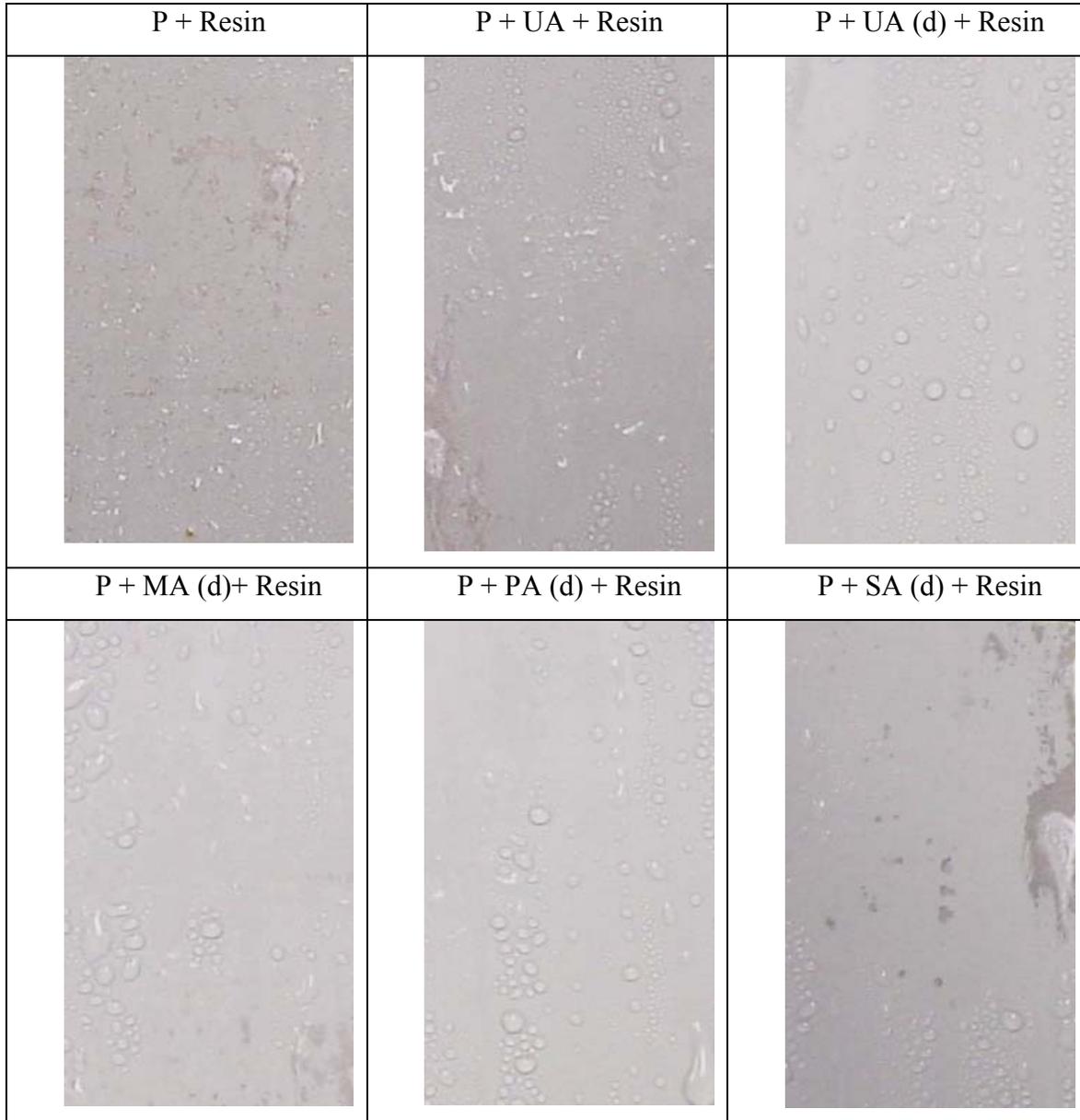


Figure 2.19 SST photographs of fatty acids, UA plus resin coatings on phosphated steel after 120 hours of salt spray test (p—phosphated steel; d--double coatings)

The solutions of carboxylic acids were prepared in the way as described in previous section. The phosphated plate was immersed in 0.02 M surfactant solution for 5 minutes. The double coatings were produced by immersing the plate twice. The plate was dried by nitrogen stream each time after immersing, and finally heated at 120 °C for 5 minutes. The surfactant-coated sample was eventually coated with resin by using a No.5 bar coater and cured for another 5 minutes at 150 °C.

After 84 hours of SST, all the treatments of surfactant plus resin did not exhibit any significant difference in appearance. This situation even continued to the end of the test after 120 hours of salt spray. With a close observation, UA double coating plus resin was still better than the single coating.

These results suggested that saturated fatty acids, with a appropriate chain length (C14 to C18), were likely to replace UA as a coupling agent in the application of resin coatings on phosphated steel.

Lauric acid, arachidic acid, and OA were also tested simultaneously, but the results were not as good as the others, So, the photographs were not included in Figure 2.19. The poor result of OA plus resin coating may be attributed to its unique structure with a double bond in the middle of the chain, which makes the close packing of OA molecules difficult. The adsorption and packing is also difficult for the surfactant molecules if the hydrocarbon chains are too short or too long.

2.3.5 Confirmation Tests in POSCO

Confirmation tests were conducted at POSCO's laboratory during June 25 to August 2, 2002. The preparation of surfactant solutions and coating methods were the same as described in the previous sections. The only difference was that a full size salt spray tester was used at POSCO, and rigorous test procedure was followed, in which the test panels were washed under running tap water and dried with blown air before the photographs were taken every 24 hours in the process of salt spray test.

Two types of phosphated steel samples, i.e., phosphated line-EG steel and phosphated lab-EG steel were tested. The phosphating process was the same except for the different sources of EG steel. The galvanizing steel of the former sample was taken from production line while the latter was made in laboratory. Surfactant coatings on phosphated line-EG sample always

outperformed the latter. Therefore, the samples reported in this section were referred to as phosphated line-EG steel if not specified otherwise.

UA, MA, PA and SA solutions were prepared at the concentration of 0.02 M while VS, BTSE at 1% by volume. The phosphated steel plate was immersed in surfactant solution for 5 minutes, dried with blowing air, and then cured at 100 °C for 90 seconds to attain metal surface temperature of 88 °C. Resin was applied on the top of the surfactant coating with a No. 5 bar coater and then heated in an oven with temperature of 150 °C for 100 seconds or 300 °C for 10

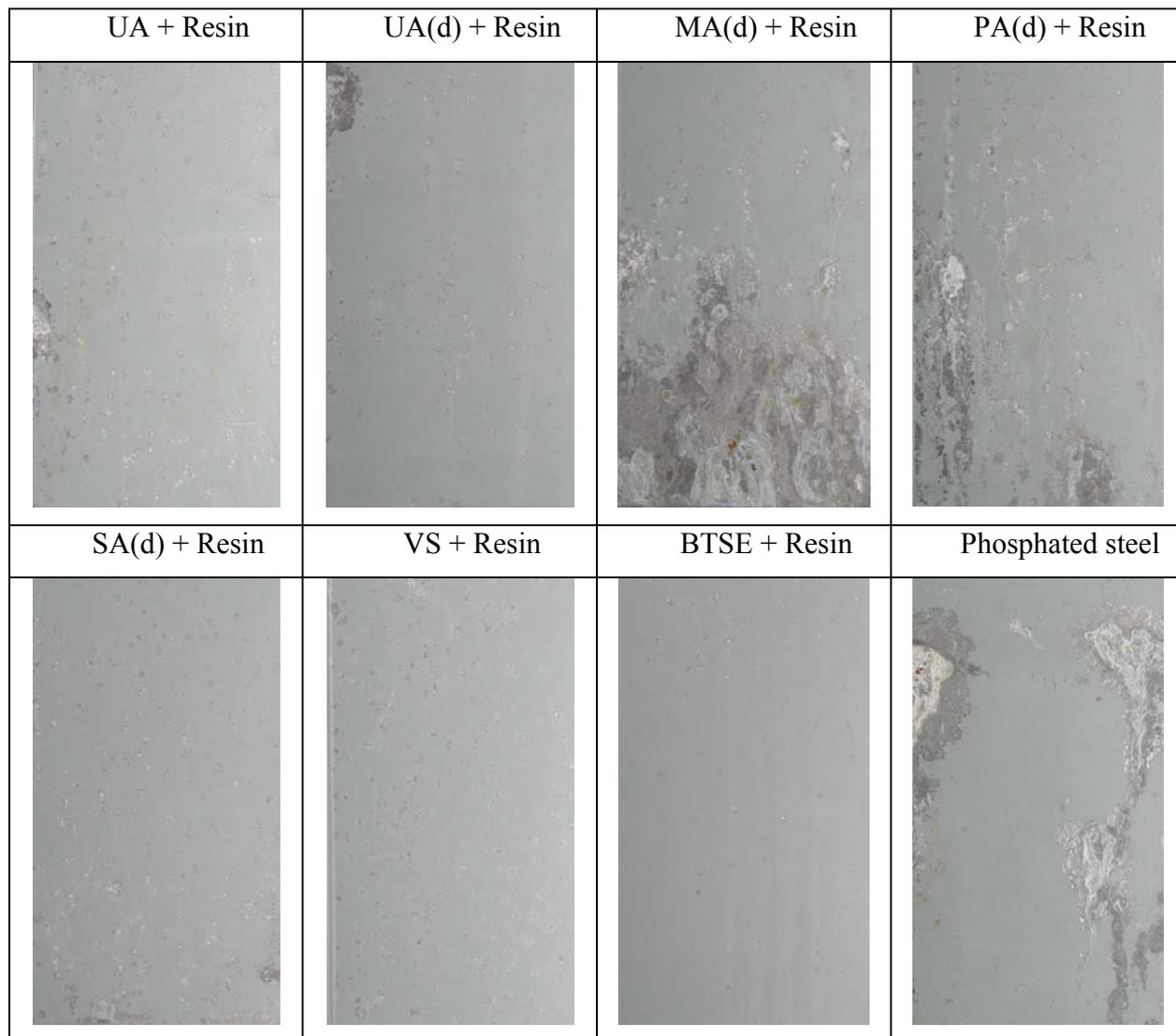


Figure 2.20 SST photograph of surfactant plus resin coatings on phosphated EG steel after 120 hours of salt spray test (p—phosphated steel; d--double coatings)

seconds. The temperature on metal surface reached 120 °C or 140 °C, respectively, after such treatments.

Figure 2.20 showed the photographs of various surfactants plus resin coating on phosphated line-EG steel after 120 hours of salt spray. UA, SA plus resin coatings could give as good results as VS, BTSE plus resin coatings. As discussed before, UA coating performed well probably because of its vinyl functionality. Among fatty acids, SA worked better than its short-chain equivalents.

Another test was conducted at higher concentration (0.04 M) for fatty acids. No improvement was observed for such a treatment. Contrarily, higher concentration of fatty acids caused trouble for adhesion of the top resin coating since it made the surface too hydrophobic, especially in the case of myristic acid. Bar coater was also used for applying the surfactant solutions but it failed to give a result as good as dipping.

Table 2.2 summarizes the hours of salt spray when white rusts started to appear on the surface of phosphated steel coated with surfactants plus resin.

In conclusion, UA, SA, VS and BTSE (all with resin) could withstand a salt spray test of 120 hours or more under optimal conditions (0.02 M for carboxylic acids and 1~2% for silanes, dipping 5 minutes for phosphated line-EG samples). Only 72 hours was obtained for the samples

Table 2.2 Corrosion resistance of surfactants and resin coatings on phosphated EG Steel

Treatment	SST hours	
	Line-sample	Lab-sample
Control (phosphated EG steel)	8~10	8~10
Resin coatings	72~96	48~72
UA + Resin coatings	144~168	48~72
UA (double)+ Resin coatings	120~144	96~120
MA (double)+ Resin coatings	72~96	72~96
PA (double)+ Resin coatings	96~120	96~120

- (i) 0.02 M for fatty acids; 1% for VS and BTSE; dipping time: 5 min., air dry, heating 90s at 120°C ($T_m=88$ °C); but for ODT, heating 80s at 120 °C ($T_m=95$ °C);
- (ii) Resin was coated by using a #5 bar coater, heating 100s at 150 °C ($T_m=120$ °C).

coated with resin alone. But MA and PA were not as effective.

This coating system worked much better on phosphated line-EG sample than on phosphated lab-EG sample. The phosphated line-EG steel was the sample that had been tested at VT. It was noticed that the phosphated lab-EG steel was a product still under development at POSCO.

2.4 CONCLUSIONS

The test results of UA coatings on phosphated steel were reported in this chapter. Based on contact angle measurement and EIS studies, it was concluded that UA coating could increase the contact angle from 3° to $23\sim 50^\circ$, and increased R_p from $21\text{ k}\Omega$ to $69\sim 95\text{ k}\Omega$. The improvement also depended on different post treatments such as heating, aging. Double coatings gave a better result than single coatings. UA coatings exhibited lower hydrophobicity than silane coating but gave equivalent R_p values.

UA coating alone did not show a significant improvement of corrosion resistance if evaluated by salt spray test. However, when a topcoat of resin was applied over the UA coating, particularly UA double coatings, it exhibited an excellent corrosion resistance. UA plus resin coating remained an intact appearance after 120 hours of salt spray test. In this case, UA coating was certainly comparable to, if not superior to, silane coatings such as VS and BTSE. Therefore, UA was a good coupling agent between phosphated surface and resin topcoat.

Fatty acids with various chain lengths were subsequently tested as an alternative of UA because of the cost effectiveness and wide availability. Myristic acid, palmitic acid, and stearic acid, all with intermediate chain length, showed a potential to substitute for UA when used in combination with resin.

REFERENCES

- Child, T. F. and van Ooij, W. J., *Trans. TMF*, 77(2), 64-70, **1999**.
- Claffey, W. J. and Reid, A. J., US Patent No. 4,650,526, May.17, **1987**.
- Claffey, W. J. and Reid, A. J., US Patent No. 4,656,097, Apr. 7, **1987**.
- Fousse, D., US Patent No. 5,925,417, **1999**.
- Hefter, G. T.; North, N. A. and Tan, S. H., *Corrosion*, 53, 8, 657-667, **1997**.
- Jones, J. P., US Patent No. 4,362,577, Dec.7 **1982**.

Kubota, T.; Yoshimi, N.; Ando, S.; Matsuzaki, A. and Yamashita, M., Proceedings of SEAIISI, Vol.1, Session 10, Tokyo, April **2000**.

Kulick, L. and Saad, K. I., US Patent No. 3,975,214, Aug.17, **1976**

Kuznetsov, Y., Organic Inhibitors of Corrosion of Metals, (Translator, Mercer, A. D.; Ed., Thomas, J. G. N.), Plenum Press, New York, **1996**.

Matsushima, Y.; Yashiro, K.; Kaneko, H. and Suzuki, M., US Patent No. 4,110,129, Aug.29, **1978**.

Oppen, D. and Lampatzer, K., US Patent No. 4,264,378, Apr.28, **1981**.

Otrhalek, J. V., Raymond, M. A. and Gomes, G. S., US Patent No. 4,182,637, Jan.8, **1980**.

Park, G. B.; Kagami, J. P.; Gong, D. C. and Osada, Y., *Thin Solid Films*, 350, 289-294, **1999**.

Rodriguez, J. F.; Schulz, P. C. and Puig, J. E., *Colloid. Polym. Sci.*, 277, 1072-10768, **1999**.

Shulman, G. P., and Bauman, A. J., Environmentally Acceptable Inhibitors and Coatings, Electrochemical Society Inc., 196-201, **1997**.

Tang, Nie and van Ooij, W. J., *Progress in Organic Coatings*, 30, 4, 255-263, **1997**.

Van Ooij, W. J. and Child, T. F., *Chemtech*, 26-35, Feb. **1998**.