工學碩士 學位論文

表面處理 方法에 따른 에폭시 塗膜의 品質 評價 研究

指導敎授 朴 振 煥

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釜慶大學校 大學院

工業化學科

朴忠緖

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主 審 工學博士 徐 且 守

委 員 工學博士 李 根 大

委 員 工學博士 朴 振 換 (印)

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Evaluation of Epoxy Coatings' Performance Prepared by Power-Tooling Surface Treatments

Chung-Seo Park

Department of Industrial Chemistry, Graduate school
Pukyong National University

Abstract

Adequate pretreatment of steel surface is essential for performance of protective coating system. Among many surface pretreatment methods, Sa 2.5 grade of "Near White Grit Blast Cleaning" is the most widely used. The downside of the grit blast cleaning is the complexity of the process, which limits the accessibility. As an alternative, power tooling has been increasingly used for surface treatment of marine vessels and offshore structures. It has been known, however, that the conventional power tooling provides less favorable result than the grit blasting.

In this study, several power tooling methods were evaluated regarding their effectiveness with a purpose of finding the one capable of yielding the quality close to grit blast cleaning. Total of 4 different surface preparation processes (1 grit blast cleaning and 3 different power tooling) were selected and each was evaluated in terms of resultant surface profile, subsequent coatings qualities including long term corrosion resistance, and other pros and cons. The results indicated that it was plausible to come up with a certain power tooling, capable of providing an almost equivalent to grit blasting.

Keywords: Protective Coatings, Surface preparation, Blast & power tool cleaning, Surface profile

1. Introduction

Cleanliness of a substrate is essential to achieve proper adhesion. Any coating applied on the substrate contaminated with rust, dirt, or oil cannot be expected to have appropriate bonding strength. Early coating failure may occur unless these contaminants were properly controlled within a certain range.

Beside that, for better of adhesion of a coating, its substrate must have proper roughness as well, which produces an increased effective surface area for the mechanical bonding between a coating and its substrate. This roughness is also known as anchor pattern or surface profile, micro pattern of peaks and valleys on the surface. This anchor pattern can be obtained by a certain power-tooling method, which cleans and roughens the surface, although it can be done as well by an abrasive blast cleaning, which is known to provide excellent formation of surface profile [1].

The downside of abrasive blast cleaning is, however, the complexity and heavy weight of the process equipment, which limits the accessibility to the complicated and huge marine structures. Therefore, as an alternative, the power tooling has been increasingly applied for the surface treatment for some areas of marine vessels and offshore structures such as welding joint line. It has been known, however, that the conventional power tooling method provides less favorable coating quality than the abrasive blasting method. Recently, new and innovative methods of power-tooling methods of surface preparation have been increasingly employed in shipbuilding and offshore industries.

To evaluate the effectiveness of these new power tooling methods, in this study, total of 4 different surface preparation processes were selected and each was evaluated in terms of resultant surface profile, subsequent coatings qualities including long term corrosion resistance, and other pros and cons.

2. Theoretical Background

2.1 Surface Preparation

Various types of mechanical equipment are used to clean the surface and thus provide proper coating adhesion. Table 1 lists the surface preparation specifications by the SSPC, NACE, British, and ISO in a descending order of each method's effectiveness[2].

Abrasive Blast Cleaning (SSPC-SP10 or NACE 2 - Near-White Blast Cleaning)

Abrasive blast cleaning is known to the most productive method of surface preparation for coatings that require both an anchor pattern and a high degree surface cleanliness. A "Near-White Blast Cleaned" surface, when viewed without magnification, shall be free of all visible oil, grease, dirt, dust, mill scale, rust, paint, oxides, corrosion products and other foreign matter, except for staining. Staining shall be limited to no more than 5 percent of each square inch of surface area and may consist of light shadows, slight streaks or minor discoloration caused by stains of rust, stains of mill scale or stains of previously applied paint.

Power Tool Cleaning (SSPC SP3 & SSPC SP11)

Power tool cleaning is useful and sometimes necessary for surface preparation where abrasive blasting cannot be used. For spot maintenance works, it is effective in preparing small areas for painting, feathering edges into sound paint, and avoiding damage to the adjacent sound paint. Power tool cleaning (SSPC SP3) requires removal of all loosely adherent rust, paint, mil scale, etc. using pneumatic and/or electrically operated tools rather than hand tools. Power tools used for surface cleaning fall into three common categories:

- Reciprocating impact cleaning tools
- Rotary impact cleaning tools
- Grinders or sanders

Power tool cleaning to bare metal state (SSPC SP11) utilizes both newer fibrous disks and wheels to achieve a much cleaner surface than that prepared with SSPC-SP3 tools. It also requires a new surface profile of at least 1 mil (25 microns). The cleaned surface will resulted distinctly cleaner and better-profiled painting surfaces than those prepared by either SSPC SP2 Hand Tool Cleaning or SSPC SP3 Power Tool Cleaning [2]. Surfaces prepared by this method should be free of all visible oil, grease, dirt, dust, mill scale, rust, paint oxide, corrosion products, and other foreign matter. The tools used to prepare the surface to SSPC SP11 are similar to those used for SSPC SP 3. The availability of SSPC SP11 provides an opportunity to select a method of cleaning suitable for certain coatings in areas where abrasive blast cleaning is prohibited or not feasible, yet a greater degree of cleaning is necessary than can be produced by hand and power tool methods [1].

Table 1. Surface Preparation Standards

NACE	SSPC	Swedish	British	ISO 8501
#1 White metal	SP5 White metal	Sa3	First Quality	Sa3
#2 Near white	SP10 Near white	Sa2.5	Second Quality	Sa2.5
#3 Commercial	SP6 Commercial	Sa2	Third Quality	Sa2
-	SP8 Acid pickling	-	-	-
-	SP11 Power tool to bare metal	-	-	-
#4 Brush blast	SP7 Brush Blast	Sa1	-	Sa1
-	SP3 Power tool	St3	-	St3
-	SP2 Hand tool	St2	-	St2
-	SP1 Solvent wipe	-	-	-

2.2 Adhesion in Paint Systems

The objective of surface preparation is to create proper adhesion of a coating over the substrate. Adhesion is the key to coating effectiveness, and it determines whether the coating is merely a thin sheet of material lying on the substrate or whether it becomes an actual part of the substrate.

The type of adhesive bond depends on both the substrate and the coating. The three types of adhesive bonds are: (1) chemical; (2) polar; and (3) mechanical [2].

(1) The chemical bond, which is created by a chemical reaction between the coating and the substrate, is undoubtedly the most effective bond. One example of this type of bond is hot dip galvanizing, where the steel and the zinc metal amalgamate or dissolve within themselves. Inorganic zinc coatings are chemically bonded between the silicate molecule and the steel substrate. The vinyl wash primer reacts with the steel substrate to form an excellent adhesive bond. Such bonding is called primary valence bonding, where the chemical groups on the coating actually react across the interface with complimentary groups on the substrate, forming a chemical compound (Fig. 1). An example of this is the oxygen bonding of the silicate matrix in an inorganic coating to the metal. It is also possible that epoxy molecules are bonded to the metal surface by metal hydroxide groups through a condensation reaction (Fig. 2) [3].

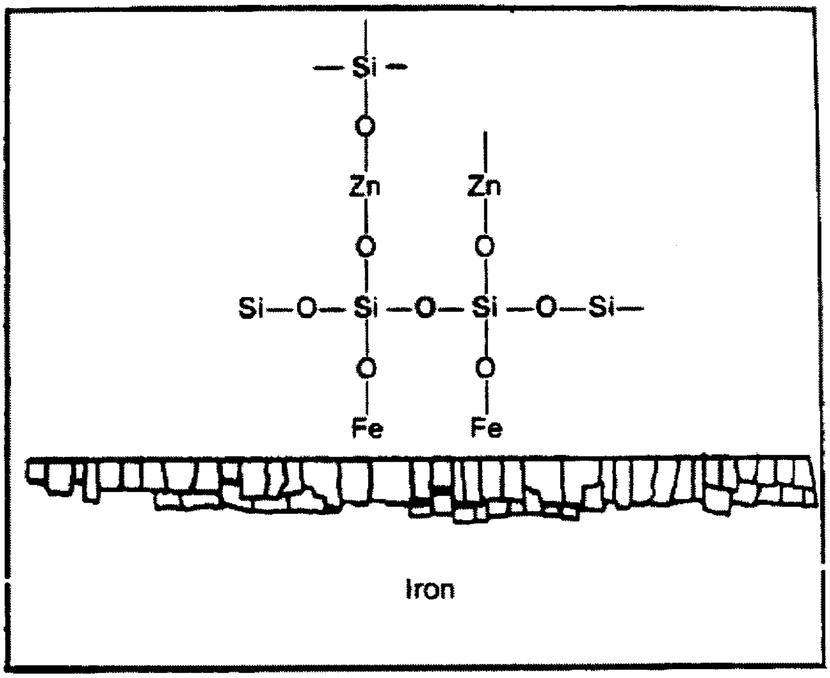


Fig. 1. Primary valence bonding [2].

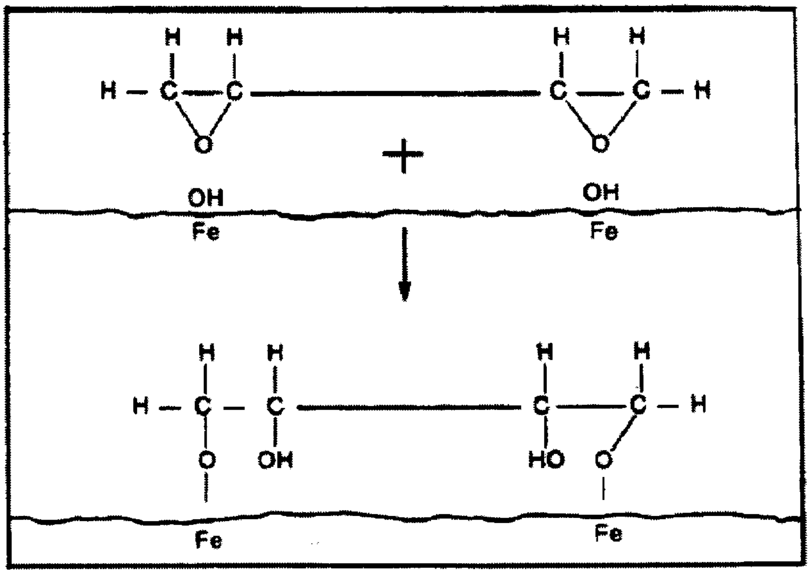


Fig. 2. Chemical Adhesion of and epoxy coating to a metal substrate [2].

(2) Polar adhesion is a more common type of adhesion than the previously described chemical adhesion, especially with organic coatings. Polar adhesion or bonding is the attraction of the resin molecule to the substrate. Actually, the polar groups are positively and negatively charged portions of the coating molecule that are attracted to oppositely charged areas on the metal or substrate.

Chemically, polar adhesion is considered secondary valence bonding where the adhesion occurs by way of physical physiochemical attractions between the resin molecules and the substrate surface molecular structure. Fig. 3 shows the secondary valence bonding of a hydroxylated coating, such as an epoxy, to the metal hydroxyl groups of a metallic surface by way of hydrogen bonds.

(3) Mechanical adhesion is the type of adhesion that is associated with surface roughness or anchor pattern. Anchor pattern is the surface roughness formed by peaks and valleys on the substrate. These can vary over a relatively wide range of depth; however, of most importance to coatings is the number of hills and valleys, which increase adhesion by the increase in surface area and by the actual roughness. Most high-performance coatings obtain adequate adhesion with an anchor pattern of from 1 to 2 mils in depth. Such a surface roughness substantially increases the surface area over which the coating has an opportunity to bond.

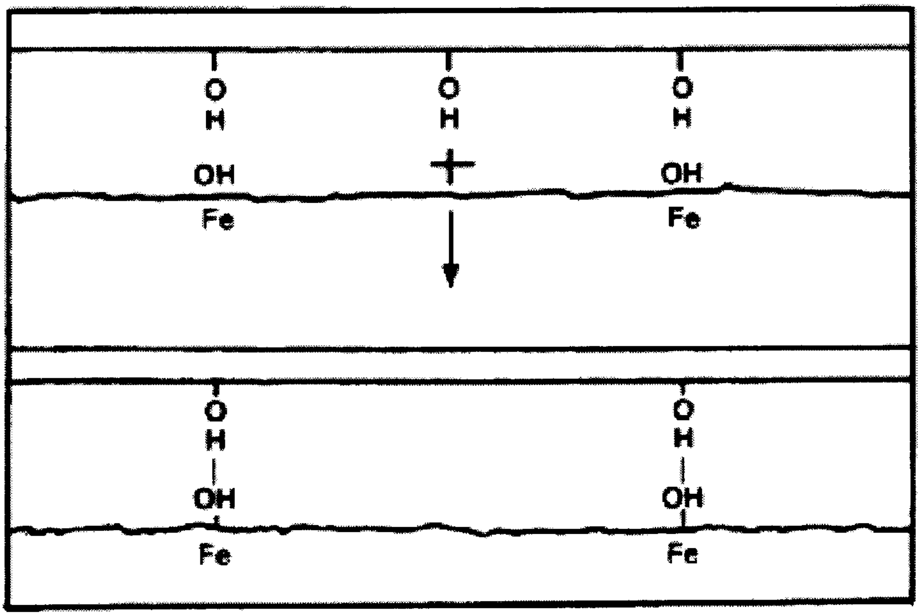


Fig. 3. Polar of secondary valence bonding of a hydroxylated coating to a metal substrate [2].

2.3 Cathodic Delamination

When cathodic protection is applied to a coated metal, loss of adhesion of the paint film adjacent to defects is often observed. This loss of adhesion is known as cathodic delamination, because the driving force is the cathodic reaction taking place at the interface. It may be the reduction of oxygen according to $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$, or the production of hydrogen according to $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. Because of the high pH values resulting from the cathodic reactions, delamination takes place. Under extreme cathodic polarization (over protection) blistering due to the evolution of hydrogen gas can take place. Cathodic delamination may also occur in the absence of an applied potential. Separation of the anodic and cathodic reaction sites under the coating results in the same local driving force as during extrernal cathodic polarization. In that case the major driving force is the reaction $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ [3].

Lateral blister growth due to cathodic delamination may take place if the cathodic reaction takes place at the edge of the blister. Depending on the actual coating system, the high pH may cause loss adhesion as a result of dissolution of the metal (oxide) at the interface or chemical disintegration of the coating polymer at the interface. For both mechanisms experimental evidence has been reported [4,5].

The propagation of a blister due to cathodic delamination under an undamaged organic coating on a steel substrate is schematically illustrated in Fig. 4. Under an intact coating corrosion may be initiated locally at sites of poor adhesion. After local corrosion initiation a complex iron oxide-hydroxide will be formed, by reaction $Fe2^+$ and OH^- with penetration oxygen. This compound can precipitate on the polymer as illustrated in Fig. 4. This oxide acts as a semipermeable membrane: it allows permeation of water but is virtually impermeable to oxygen. As a result of this, cathodic and anodic sites are separated. Under the precipitate we find the anodic site, while the cathodic reaction is forced to move to the edge of the blister, where oxygen may still permeate the coating. In this initial situation a large anodic area is coupled to a small cathodic area because of the high ionic resistance of the coating and the limited lateral progress of delamination. This meansthat the pH will eventually reach very high values at the edge of the blister, which will cause delamination and further growth of the blister, as illustrated in Fig. 4 [3].

A similar mechanism of blister formation was observed for corrosion under a defective coating, Fig. 5 [3]. Oxygen and water reach the exposed metal through the defect in the coating, corrosion takes place and corrosion products accumulate. Corrosion propagation and blister growth occur in the same manner as in the case of an undamaged coating [6].

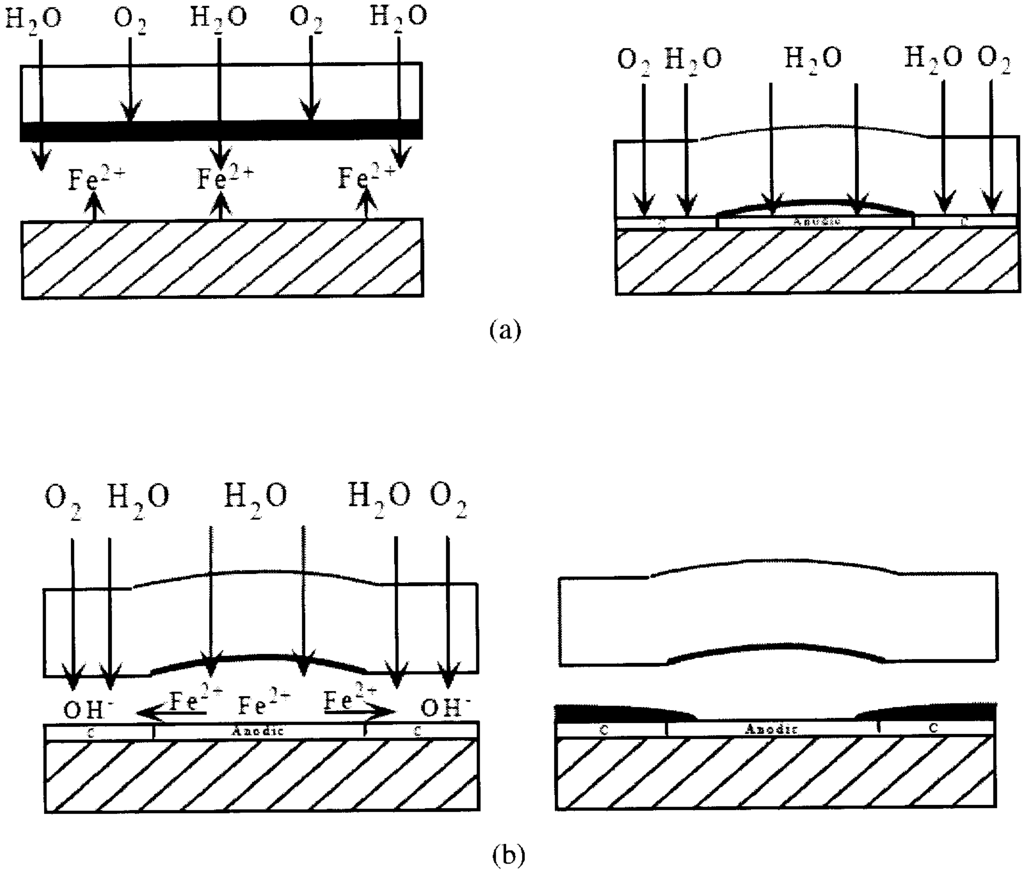
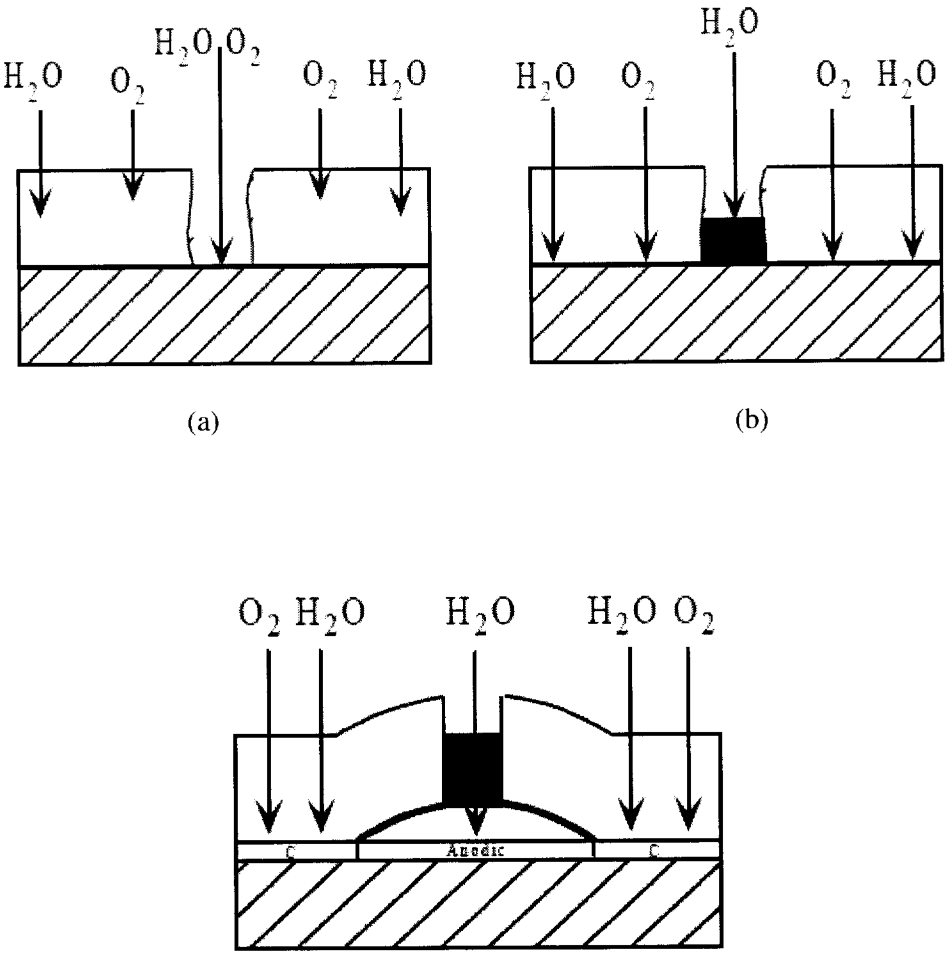


Fig. 4. Blister Initiation and Propagation Due to Cathodic Delamination under an Undamaged Organic Coating [3]:

(a) Separation of Anode and Cathode, (b) Cathodic Delamination.



(a)

(b)

(c)

Fig. 5. Blister Initiation and Propagation due to Cathodic Delamination under a Defective Organic Coating [3]:

(a) Corrosion Initiation, (b) Blocking of a Coating Pore,

(c) Cathodic Delamination.

2.4 Electrochemical Impedance Spectroscopy [7]

Electrochemical impedance spectroscopy (EIS) is a convenient and effective method of assessing the properties and performance of organic-coated metal systems. The AC impedance of an electrochemical cell can be determined by applying a sine wave of potential (V) of a certain frequency (ω) and measuring the corresponding current (I) flowing across the cell. The ratio of potential and current is the impedance of the cell (Z) at the chosen frequency, according to Ohm's law:

$$Z = V / I = Vo \cdot \sin \omega t \; / \; Io \sin(\omega t - \varphi) \tag{1}$$

The phase angle φ accounts for the shift of the current with respect to the potential, whereas Vo and Io are the moduli of potential and current, respectively.

The impedance is given by a complex number, with a real (Z') and an imaginary component (Z''):

$$Z = Z' - jZ'' \tag{2}$$

where $j = \sqrt{-1}$. A spectrum can be obtained by varying the frequency of the applied signal, in which case the technique is called EIS [7].

2.4.1 Basic Analysis

The easiest way of using impedance data is to make visual examination of the shape of the spectrum and or its evolution with time. In a coated system of high protection, the Nyquist plot comes as an arc of very large diameter that cannot be totally defined because of experimental limitations.

If water penetrates into the coating, the impedance of the system decreases. In this phase, the resistance of the coating decreases, whereas its capacitance increases with time. Upon prolonged immersion, the initial arc tends to close, approaching the real axis, and a second semicircle develops, corresponding to a corrosion reaction underneath the coating. The smaller the semicircles, the lower the resistance of the corresponding component, revealing a higher permeability of the coating, a higher corrosion rate, or the combination of both. An example of this evolution is presented in Fig. 6 [7].

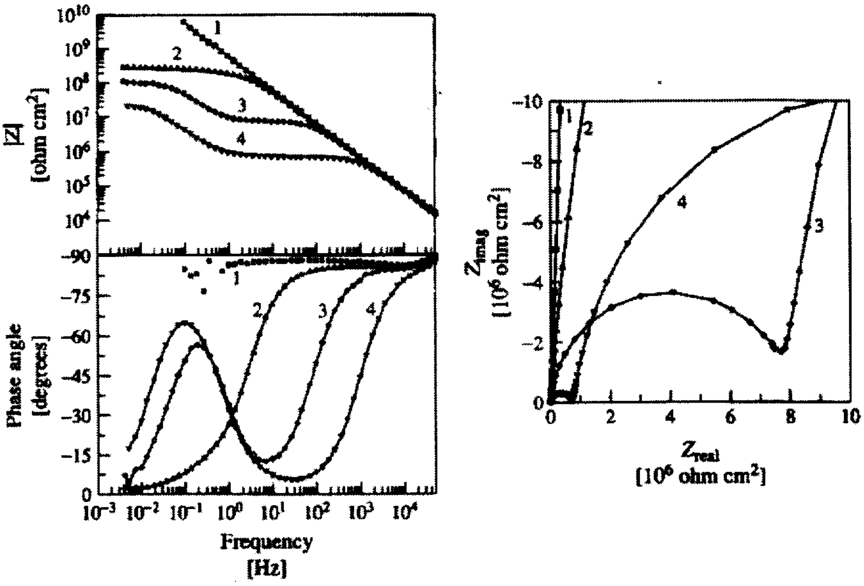
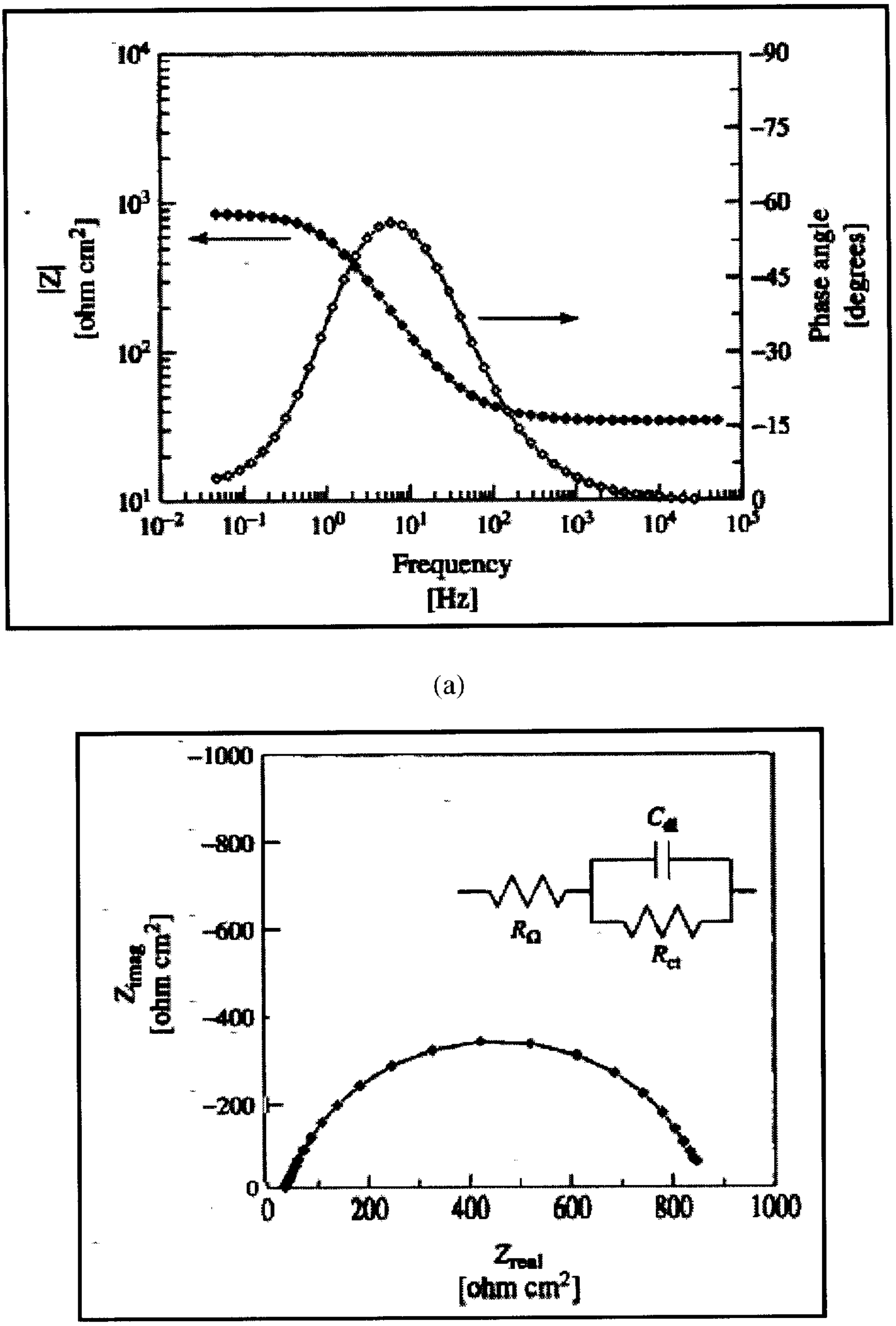


Fig. 6. Evolution of the impedance spectrum.



(a)

(b)

Fig. 7. Impedance spectrum and equivalent circuit for a metallic electrode undergoing a corrosion process: (a) Bode plot, (b) Nyquist plot.

2.4.2 Equivalent Circuits

A simple electrochemical cell with a bare metal, in which the corrosion process is controlled by charge transfer, is described in Fig. 7. In this circuit, R_Ω is the ohmic resistance, corresponding to the solution in the cell plus the cables and connections. R_{ct} is the charge transfer resistance and C_{dl} the capacitance of the double layer at the solution-metal interface. The Nyquist and Bode plots for this circuit are also presented.

For an electrode with a highly protective film of organic coating, the circuit in Fig.8 is usually applied. In this circuit, *Cc* is the capacitance of the coating and *Rc* the resistance of the film to ionic condition. If the coating is considered as a dielectric, then its capacitance is given by:

$$\mathrm{Cc} = \varepsilon \cdot \varepsilon_o \cdot A / d \qquad (3)$$

Where ε_o is the permittivity of free space (ε_o = 8.85 × 10^{-14} F cm^{-1}), ε is the dielectric constant of the polymer, *d* is the coating thickness, and *A* is the exposed area of the electrode under test. The coating resistance, *Rc*, accounts for the ionic conduction along preferential paths across the coating. In new coating, this resistance often exceeds the capabilities of the measuring equipment. The solution resistance R_Ω cannot usually be measured, since it becomes masked by the coating capacitance in the working range of frequencies.

In the case of corrosion underneath the coating, at disbanded or blistered areas, both the coating and the corrosion processed underneath can be detected. The circuit usually applied and the corresponding spectra are presented in Fig. 9. It is interesting to note that the resistance R_Ω is usually not detected in the range of frequencies tested, since it is masked by the coating capacitance. The coating capacitance has very low values, usually in the range $10^{-10} - 10^{-9}$ Fcm^{-2}, whereas a double layer capacitance can be taken as 20 - 60 μFcm^{-2} [7].

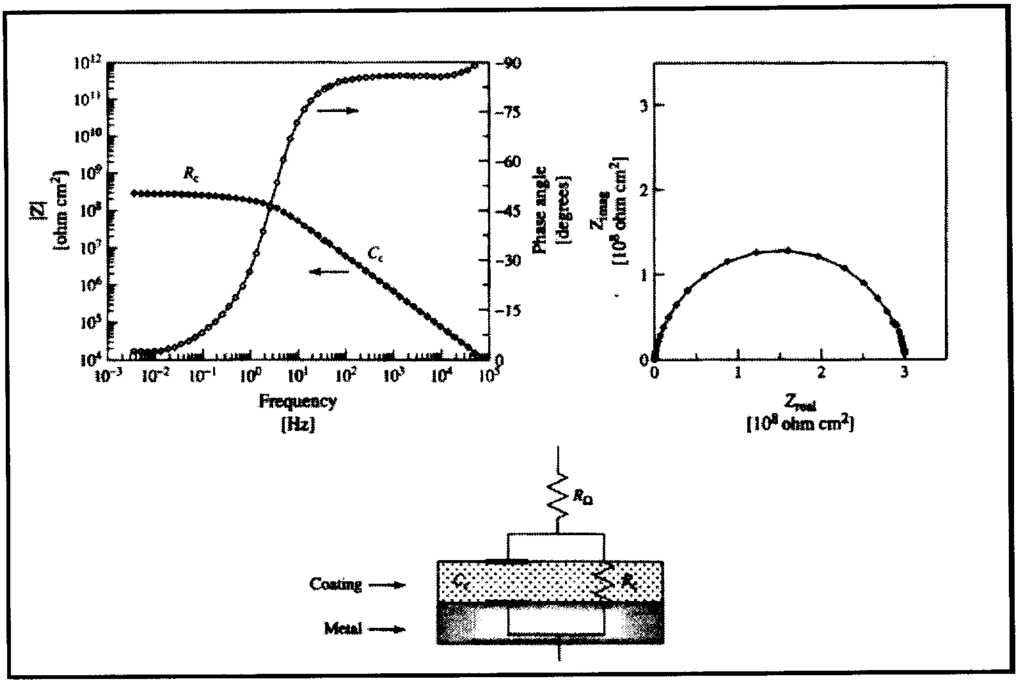


Fig. 8. Impedance spectrum and equivalent circuit for organic-coated metal without apparent degradation [7].

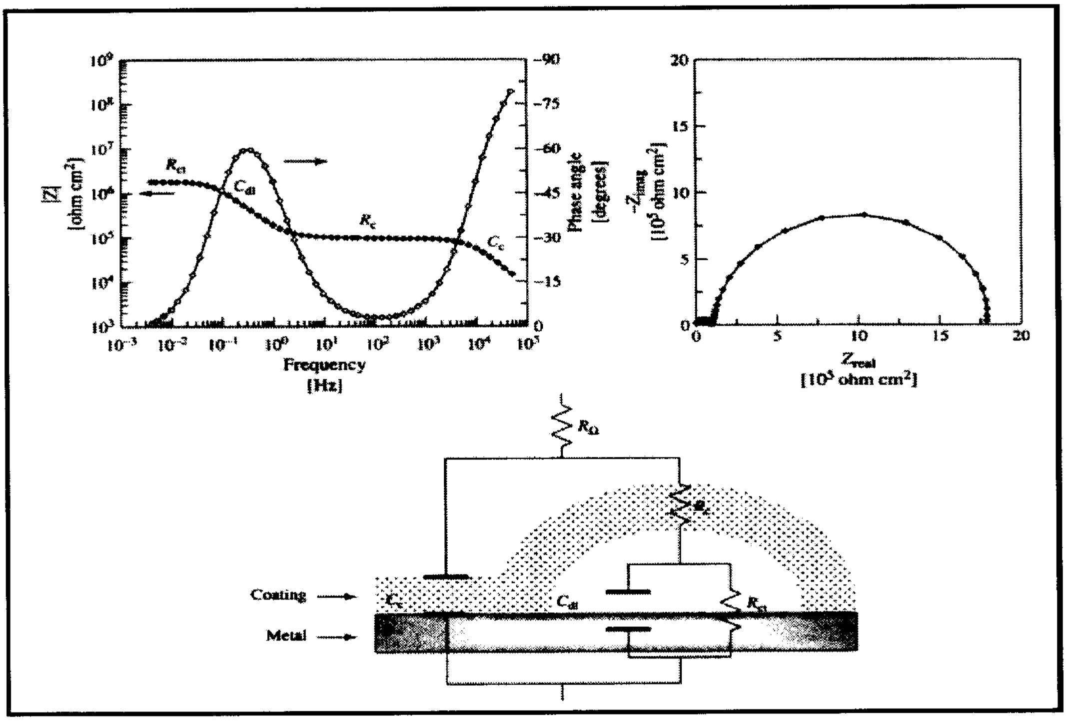
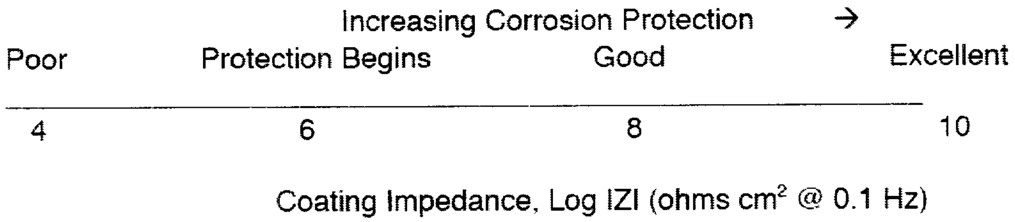


Fig. 9. Impedance spectrum and equivalent circuit for organic-coated metal, with corrosion occurring under the blisters [7].

2.4.3 Performance of Corrosion Protection by Impedance Values

The EIS testing of organic-coated steel has shown that for the perfect epoxy coating, the measured impedance values are greater than 10^8 Ωcm^{-2}, intermediate corrosion protection was found for impedance values between 10^6 and10^8 Ωcm^{-2}, and poor corrosion performance was observed for impedance values below 10^6 Ωcm^{-2} [8].

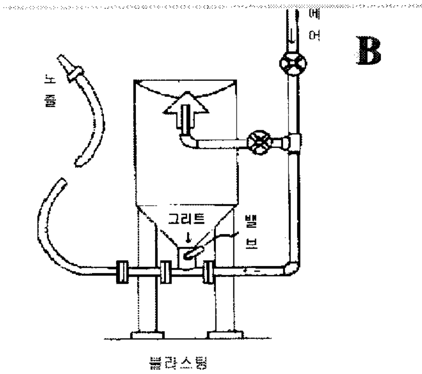


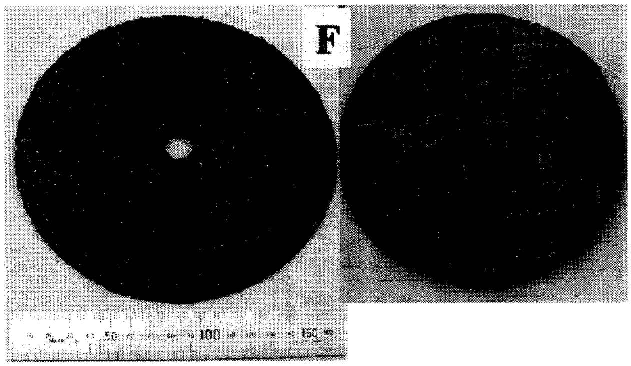
3. Experiments

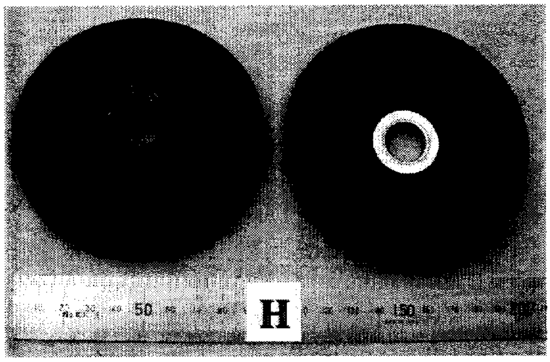
Test specimens (75mm×150mm×1.6mm, smoothed carbon steel) were prepared by employing four different types of surface preparation methods, which are an abrasive blast cleaning plus 3 different power tooling methods as shown in Table 2. The working capacity (the area can be prepared per hour) and their resultant surface profiles by 4 different surface treating methods were evaluated and used for coating applications with coated material A(CA) and B(CB) for D.F.T of 250µm(125㎛ × 2coats) and dried for 2weeks, at 25°C. The basic physical properties of coatings were summarized in Table 3 and Table 4 shows their resultant working capacity and surface profile. After complete drying of test panels, various tests such as adhesion strength, impact resistance, Erichen cupping, cathodic disbondment, salt spray and electrochemical impedance spectroscopy (EIS) tests were carried out. Table 5 shows the list of test methods used in this study.

Table 2. Properties of Surface preparation

Methods of Surface preparation	B	M	F	H
Type	Blast	Power tool	Power tool	Power tool
Material	Grit	Wire	Coated abrasive (Aluminum Oxide)	Bonded abrasive (Aluminum Oxide)







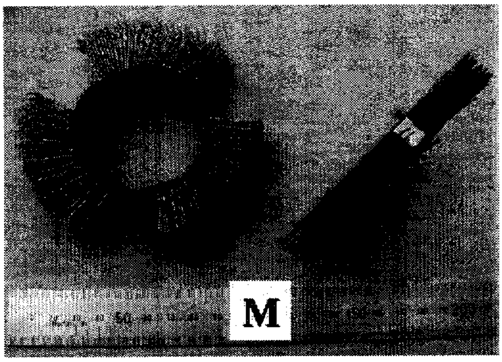


Table 3. Basic Physical Properties of Coatings

Product		Coating A	Coating B
Description		Tar free epoxy (Polyamine)	Modified tar free epoxy (Amine adduct)
Physical data	Color	Grey/Light grey	Bronze/Aluminum
	Specific gravity	1.5kg/L	1.25kg/L
	Viscosity(cP/KU)*	1237/91.8(No Thinning)	1103/88.6(No Thinning)
	Solid volume ratio(SVR)	80%	60%

* Stomer viscometer measurement(ASTM D502) was used.

Table 4. Test methods and their description with related standards

Test items	Test method	Related standards
Adhesion	A procedure for evaluating the pull-off strength of a coating by determining either the greatest perpendicular force(in tension) that a surface area can bear before a plug of material detached, or whether the surface remains intact at a prescribed force(pass/fail).	ASTM D4541
Impact resistance	A procedure for evaluating the impact resistance of a coating of paint, test were performed with impact tester of Dupont company. The weight of 1,000g was dropped to the coated face as well as to the reverse side from the specified height.	ISO 6272
Erichen cupping	A procedure for assessing the resistance of a coating of paint, varnish or related product to cracking and/or detachment from metal substrate when subjected to gradual deformation by indentation. Hold the test panel firmly between the retaining ring and the die with the coating towards the die and with the hemispherical end of the indenter. Examine the coming of the test panel for cracking and/or detachment from the substrate.	ISO 1250
Salt spray	An accelerated procedure for assessing the relative corrosion resistance of painted or coated specimens, this practices provides the information in respect to corrosion resistance, blistering associated with corrosion, loss of adhesion at a scribe mark, or other film failure. Scribe the specimens to obtain X-cut or I-cut through the coating which is being tested and than these specimens are exposed in a salt spray chamber.	ASTM B 117
Water Immersion	The method involves the immersion of samples in aerated water at 40°C. The immersion time is not specified. After immersion the panels are assessed visually for blistering and other signs of deterioration. The panels are left to air-dry at room temperature and then assessed for adhesion, rusting, color change and embrittlement.	-NACE TG 263,264 -Modified ISO 2812-2 synthetic sea water
Cathodic Disbondment	This method provides accelerated adhesion assessment and determines resistance of the coating to cathodic potential and current flow. This test method is one measure of the undercutting resistance of a coating system	ASTM G 95
AC Impedance	EIS measurements used to study the mechanisms involved in the corrosion performance of painted metals under fully immersed conditions. This technique provides quantitative kinetic and mechanistic information and is very useful for developing improved coating systems. A coating system's electrical resistance is a general indicator of its performance.	ASTM G 106

Table 5. Surface Roughness and Relative Working Time Results

Surface preparation methods		Surface roughness(㎛)		Grade (SSPC)	Relative Working Time
		Ra	Rz		
Blasting	B	14.4	61.5	SP10	1
Power tool	M	4.3	21.2	SP3	8
	F	5.7	16.2	SP3	2.8
	H	8.1	41.2	SP11	3.2

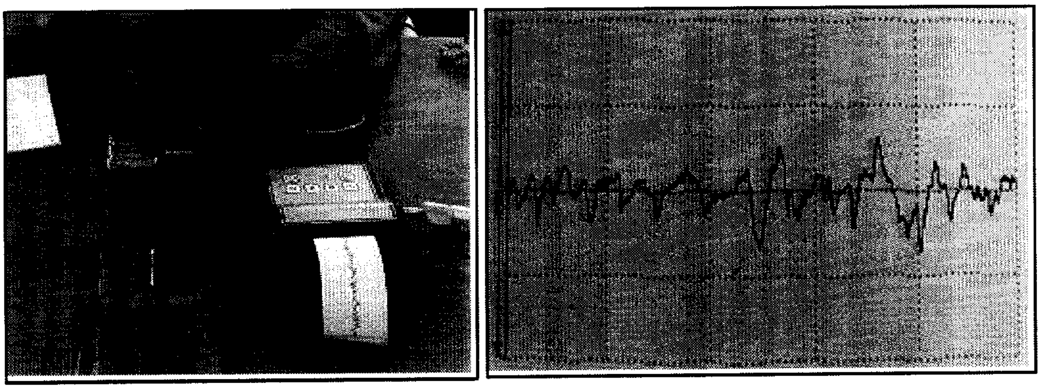


Fig. 10. Measurements of Surface Roughness (DIAVITE DH - 5).

4. Results and Discussions

4.1 Adhesive Properties

4.1.1 Adhesive Strength

The adhesion of protective coating system to the substrate is considered to be a good indicator of the coating's ability to resist corrosion and therefore represents longevity of the coating [9]. Therefore, if adhesion is weak, the coating will gradually fail by blistering, under film corrosion, or chipping and flaking [2]. Pull-off adhesion test and/or crosscut methods were employed to determine the adhesive strength of the coatings. In this study, adhesion measurements were performed according to ASTM D4541 and ASTM D 3359.

The results showed that there was no discernible difference among the adhesion strengths of all types of specimens, at least by pull-off adhesion and cross-cut tests, and as shown in Table 6 and Fig. 11. All of their adhesion strength satisfied the minimum requirement of 5MPa, as designated in an industrial standard Norsok M 501 [10].

Table 6. Adhesion Test Results

Surface preparation methods		Pull-off adhesive strength (Mpa)		Cross-cut test (ASTM D 3359)	
		CA	CB	CA	CB
Blasting	B	5.9	5.4	5B	5B
Power tool	M	5.9	5.5	5B	5B
	F	5.3	5.1	5B	5B
	H	5.1	5	5B	5B

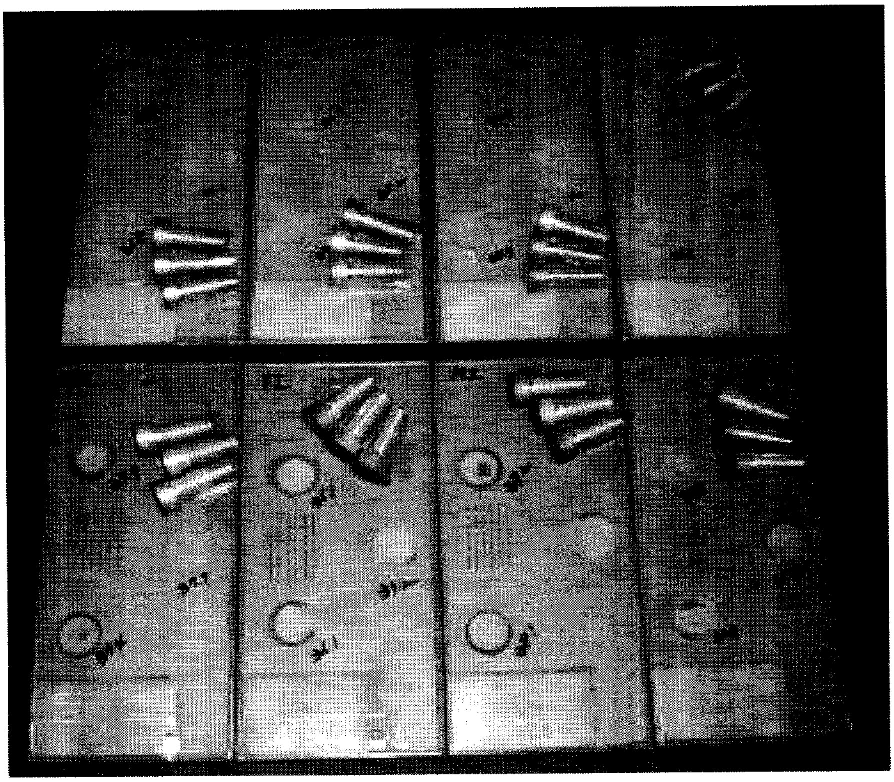


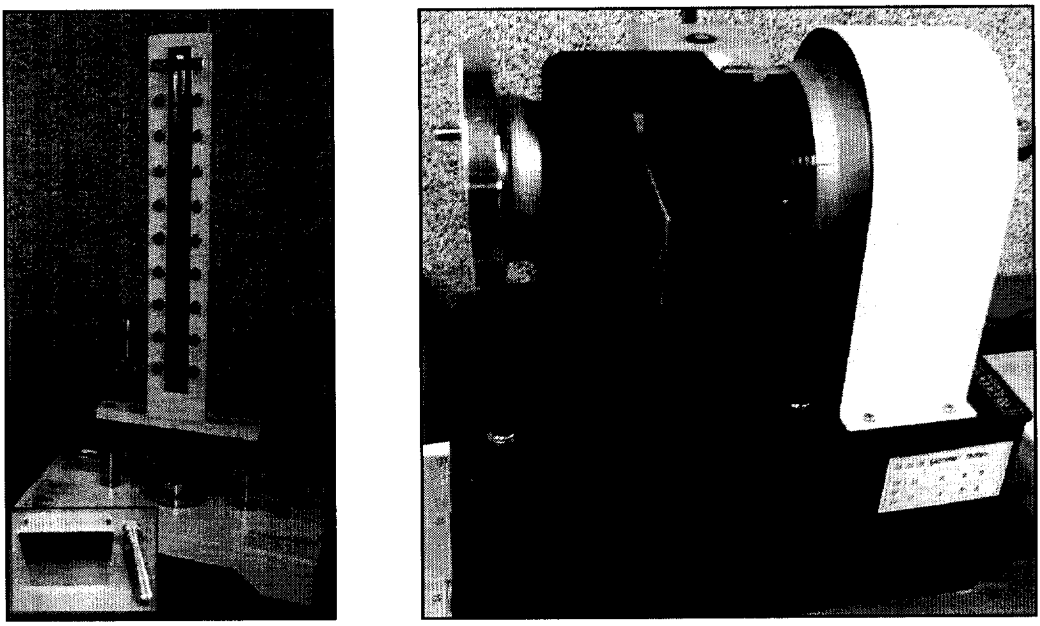
Fig. 11. Pull-off Adhesion and Cross-cut Test.

4.1.2 Impact Resistance and Erichen Cupping Test

The impact resistance test method represents the coating's ability to withstand damage to a direct impact with another object. This test method is often required for coating performance results where both impact and damage resistance are of greater importance [9].

For evaluating the impact resistance of coating system, falling-weight tests were performed with a commercial impact tester (Dupont Company). The weight of 1,000g was dropped to the reverse side of coated face from a height of 500mm in accordance with ISO 6272. Cupping tests to assess the cracking and/or detachment characteristics of coatings were conducted by applying gradual deformation by indentation.

In Table 7 – 10, the results of impact resistance on the rear side and cupping test on the coated specimens after various surface preparation were summarized. In these test results, the lower the flaked off diameter implicated the better adhesion of the coating. Therefore, the impact resistance and Erichen cupping resistance are shown as follows: B > H > F = M in order.



(a) (b)

Fig. 12 DuPont Impact Tester(a) and Erichen Cupping Tester(b).

Table 7. Impact Resistance test results by DuPont Impact tester
(reverse impact, 1,000g/50cm)

Surface preparation methods		Flaked off diameter, mm	
		Coating material, A	Coating material, B
Blasting	B	6.0	5.5
Power tool	M	7.4	7.2
	F	7.3	7.0
	H	7.2	7.0

Table 8. Results of Impact Test

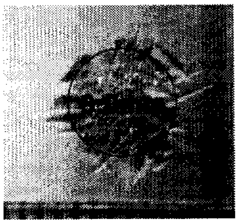
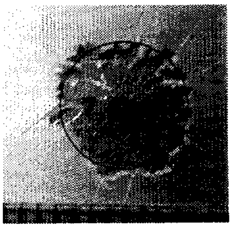
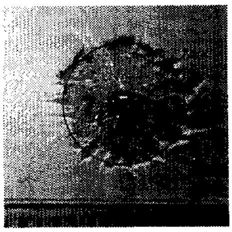
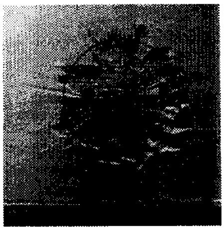
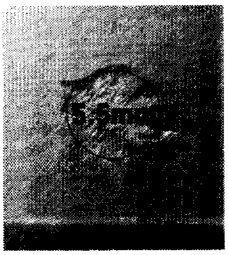
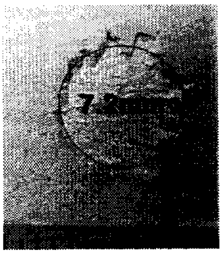
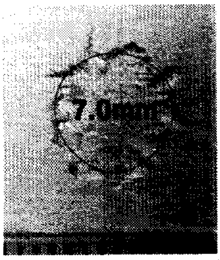
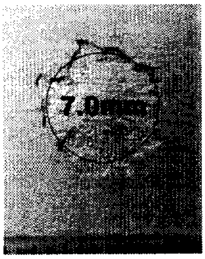
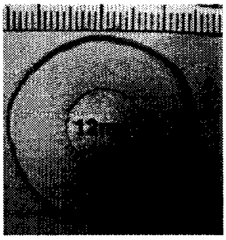
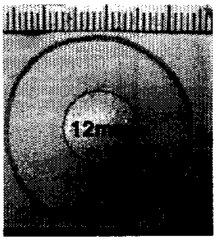
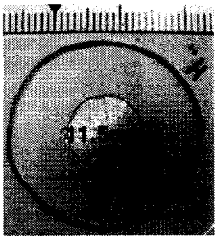
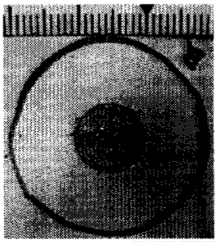
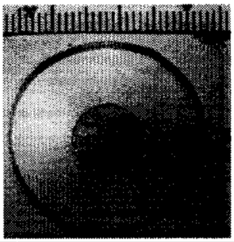
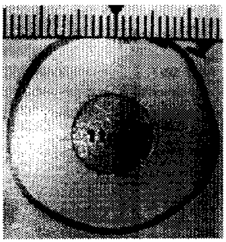
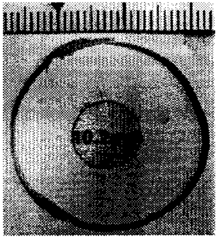
	B	**M**	**F**	**H**
CA				
CB				

Table 9. Erichen Cupping test results

Surface preparation methods		Flaked off diameter, mm	
		Coating material, A	Coating material, B
Blasting	B	10.5	10.2
Power tool	M	12	11
	F	12	11
	H	11.5	10.2

Table 10. Results of Erichen Cupping Test

	B	**M**	**F**	**H**
CA				
CB				

4.1.3 Cathodic Disbondment Test

Cathodic disbondment(CD) test provides accelerated adhesion strength assessment and determines resistance of the coating to cathodic potential and current flow. This test method is to be used to measure the undercutting resistance of a coating system. Experiences in the oil and gas pipeline industry have clearly shown that coating with better cathodic disbondment resistance have better corrosion resistance and longevity. The coating systems with good adhesion to the steel substrate tend to have a similar resistance to cathodic disbondment. If a coating is able to adhere to the steel substrate, it will therefore tend to resist the undercutting damage of corrosion, thereby offering a longer service life [9].

When a coated steel surface is subjected to a cathodic potential, disbondment will occur around holidays in the coating. This disbondment is believed to occur primarily because of hydroxyl ion formation at the coating/steel interface.

The basic experimental set-up specified in the modified ASTM G95, was used to evaluate the cathodic disbondment performance of various surface preparation and coating samples. A 6mm diameter holiday was drilled through the coatings(70×150mm) to the metal surface in the center of each specimens and the specimens were immersed in sea water tank in presence of a potential of -1.5V vs. Cu/$CuSO_4$ as shown in Fig. 13. The test temperature was maintained 25℃ for 14 days. After 14 days, the coating was peeled off to measure extent of disbondment and reported as CD in mm [11, 12].

Results of cathodic disbondment test after 2 weeks are shown in Table 11 and Fig. 14, which show that abrasive blasted surface is better than others, and coating B showed higher resistance to cathodic disbondment than coating A. On the other hand, the coatings by type F conventional power tooling method was found to have the worst resistance among them.

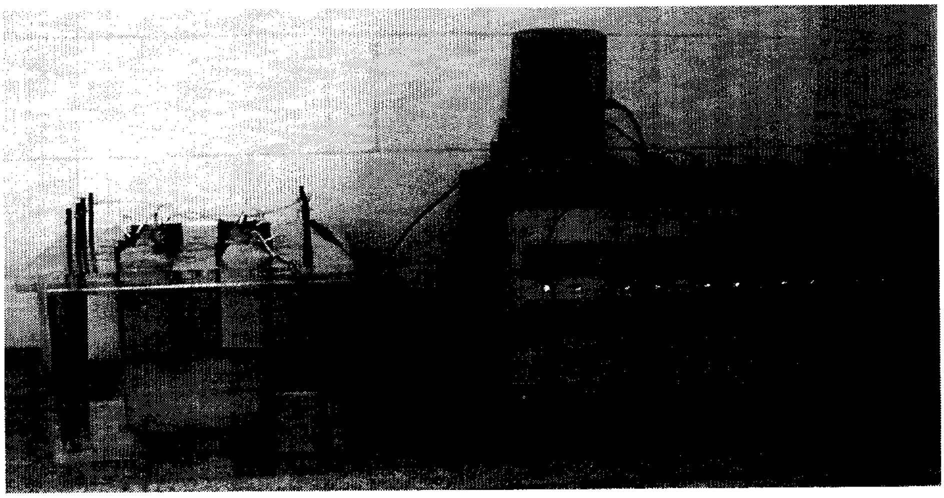


Fig. 13. Cathodic Disbondment Tester.

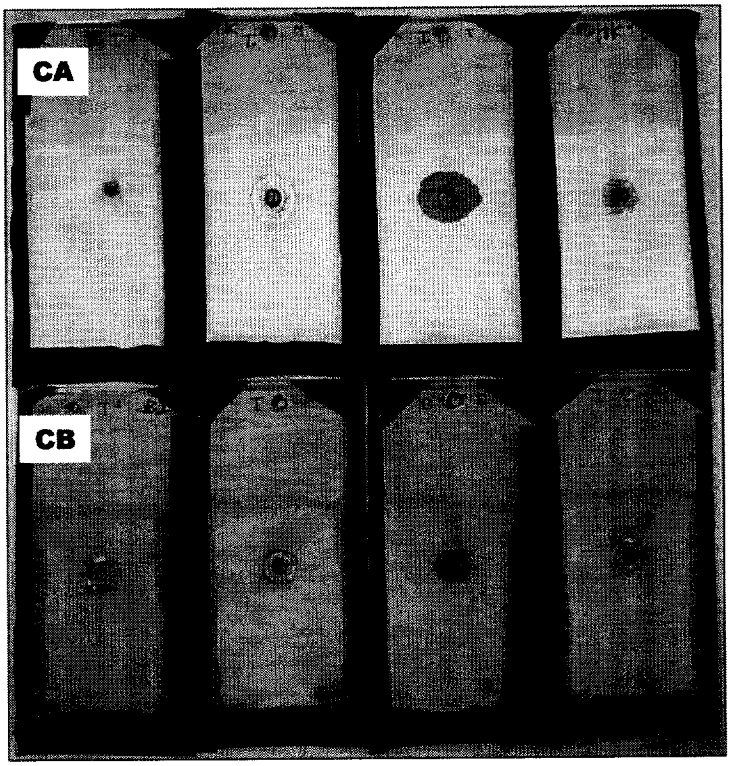


Fig. 14. Results of Cathodic Disbondment.

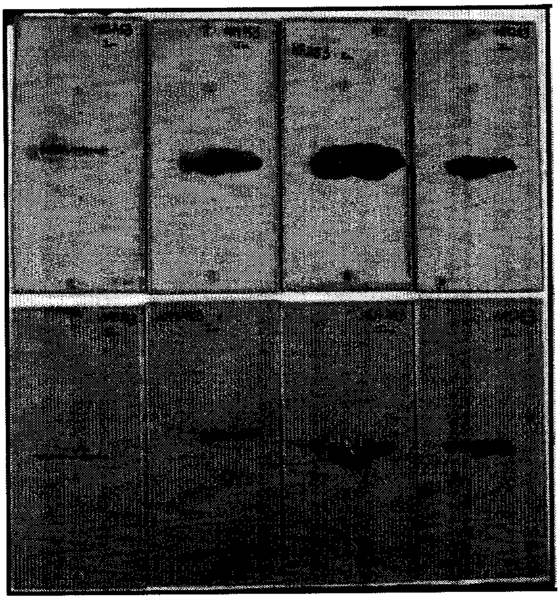
Table 11. Results of Cathodic Disbondment Test

Surface preparation methods		Average Radial Disbondment, mm	
		Coating A	Coating B
Blasting	B	1	0.5
Power tool	M	13	5
	F	16.5	8.5
	H	4.5	4

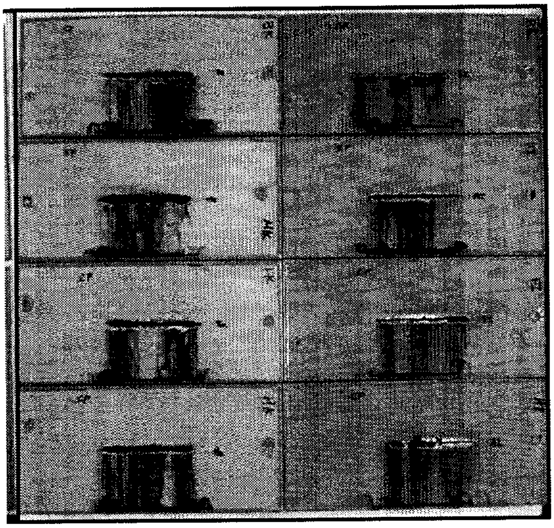
4.2 Rust Creepage by Water Immersion and Salt Spray

Rust creepage (corrosion creep) at the scribe was calculated in accordance with NORSOK M 501. Rust creepage (cutback, undercut, loss of adhesion, deterioration, disbondment) was measured from the average of measurements of the maximum width of the corrosion across the scribe. The maximum width is measured in the middle of the scribe, and in four points on each side of the middle, 5mm between each point. Corrosion creep M = (C-W)/2, where C is the average of the maximum widths of corrosion across the scribe, and W is the original width of scribe (For a 50 mm scratch line, 9 measurements are required) [10]. The average and maximum cutback was measured for each sample. Defects at the scribe having the appearance of a "blister" will be defined to be rust creepage (or cutback) [13].

In this study, specimens with and without scribe exposed to the salt spray chamber (ASTM B117) for 800 hrs and immersed in the synthetic seawater chamber at 40℃ for 12 weeks, followed by evaluation in terms of mean rust creepage (from scribe) and blistering. Table 12 and Fig. 15 show the results of relative rust creepage resistance (corrosion resistance) for corrosion test (salt spray and water immersion). In these test results, the rust creepage resistance is shown as follows: B > H > M > F in order and Coating B > Coating A.



(a) Water Immersion



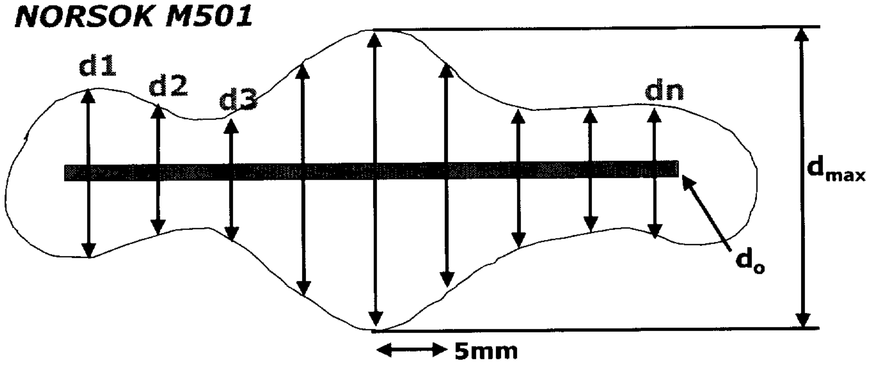
(b) Salt Spray

Fig. 15. Rust Creepage by Corrosion Test.

Table 12. Rust Creepage by Corrosion Test

Surface preparation methods		Rust Creepage of coating, mm				Visual examination remarks
		Salt Spray, 800hrs		Water Immersion, 12wks		
		CA	CB	CA	CB	
Blasting	B	2.0	1.4	2.9	2.1	No blistering
Power tool	M	3.7	2.3	4.6	3.5	No blistering
	F	2.6	2.5	6.1	5.8	No blistering
	H	2.2	2.1	3.6	3.0	No blistering

NORSOK M501



Average scribe creep : $\bar{a} = \dfrac{\bar{d} - d_o}{2}$

Where, $\bar{d} = \dfrac{(d1+d2+...+dn)}{n}$

4.3 Barrier Property by Water Immersion and AC Impedance

The Electrochemical Impedance Spectroscopy (EIS) measurements have been used to study the mechanisms involved in the corrosion performance of coatings under fully immersed conditions. EIS has proven to be an effective tool in monitoring changes of physical characteristics of organic coatings. This technique provides quantitative kinetic and mechanistic information. A coating system's electrical resistance is a general indicator of its performance. For example, coatings with initial resistance over $10^8\,\Omega cm^{-2}$ typically provide excellent corrosion protection whereas those under $10^6\,\Omega cm^{-2}$ provide poor corrosion protection [13].

All specimens have been immersed in synthetic seawater at 40℃ for up to 12 weeks (ASTM D 1141). EIS measurements were carried out every once a week after subjection of the samples to water immersion. Immediately after each impedance test, the samples were reloaded into the water immersion chamber till the next impedance experiment. EIS measurements were performed in the 100kHz ~ 0.01Hz frequency range using a commercial Frequency Response Analyzer (Solartron Mo. 1260/1296). The measurements were made at 5 points per decade, 20mV a.c. amplitude and 50mV d.c. and exposure area is $13.9cm^2$ (refer to Table 13).

After immersion, the coatings were measured by EIS once a week in order to evaluate the barrier property for water permeation. All the values in the 0.01Hz are summarized in Table 14 and plotted in Fig. 16. As the immersion time increases, the impedance values were decreased, however, their differences among various surface preparation methods were found to be negligibly small and their barrier properties are thought to be excellent because they all exceed 10^8 Ωcm^{-2} as addressed previously. Besides, coating material B(CB) was found to be a better barrier than the coating material A(CA) as shown in Fig. 17.

Table 13. The Conditions of EIS Measurement

Equipment	Solartron FRA 1260/1296
Frequency Range	100kHz ~ 100mHz
Electrolyte	0.5N-NaCl
Electrode	2 Electrode (WE, CE)
Exposed Area	13.9cm2
Applied D.C Voltage	20mV
Applied A.C Amplitude	50mV

Table 14. Impedance Variation at 0.01Hz by Water Immersion for 7 weeks (Ωcm^{-2})

Immersed Weeks	Coating A				Coating B			
	CA-B	CA-M	CA-F	CA-H	CB-B	CB-M	CB-F	CB-H
1	7.65E+08	8.29E+08	7.47E+08	7.95E+08	4.95E+09	4.74E+09	5.11E+09	5.02E+09
3	5.10E+08	4.40E+08	4.67E+08	5.69E+08	3.62E+09	3.25E+09	2.85E+09	2.81E+09
4	4.34E+08	3.49E+08	3.77E+08	4.24E+08	3.07E+09	2.80E+09	2.73E+09	2.80E+09
7	3.74E+08	3.00E+08	3.31E+08	3.59E+08	2.75E+09	2.27E+09	2.38E+09	2.51E+09
8	3.84E+08	3.98E+08	3.30E+08	3.98E+08	4.05E+09	3.80E+09	4.38E+09	3.95E+09
10	3.83E+08	4.66E+08	3.83E+08	3.83E+08	3.97E+09	3.40E+09	4.33E+09	3.57E+09
11	4.84E+08	5.38E+08	5.38E+08	5.28E+08	4.01E+09	3.64E+09	4.36E+09	3.75E+09
12	4.00E+08	4.36E+08	4.18E+08	4.02E+08	4.40E+09	3.81E+09	4.35E+09	3.81E+09

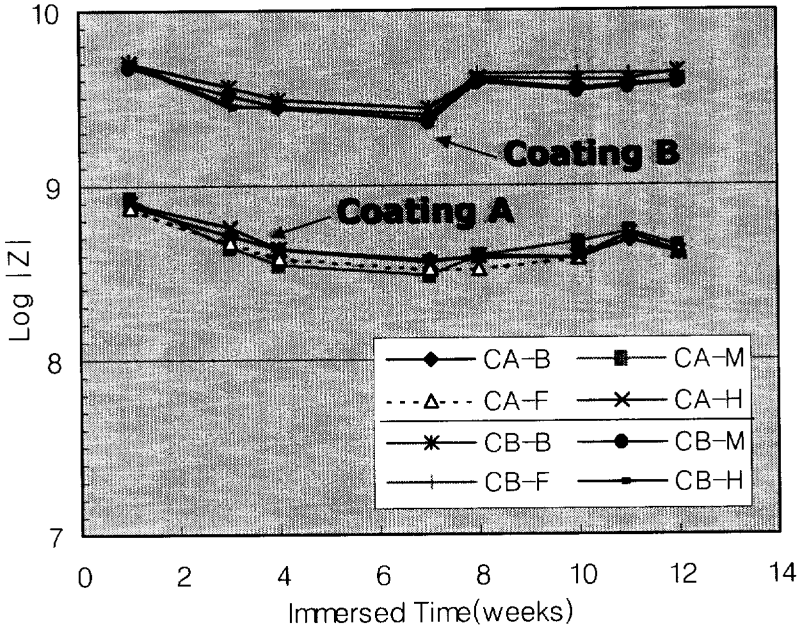
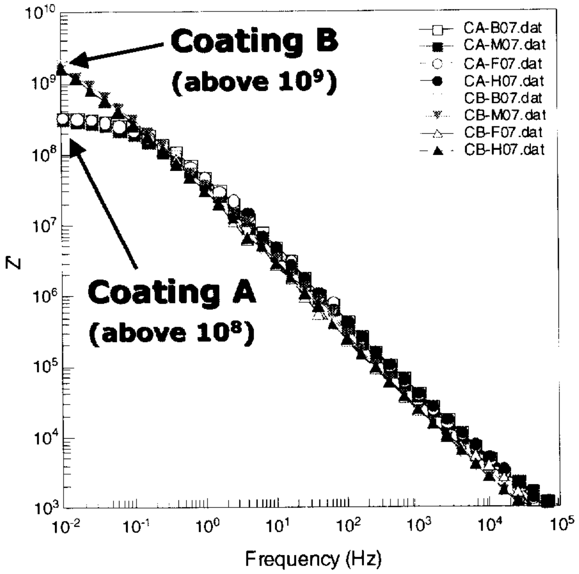
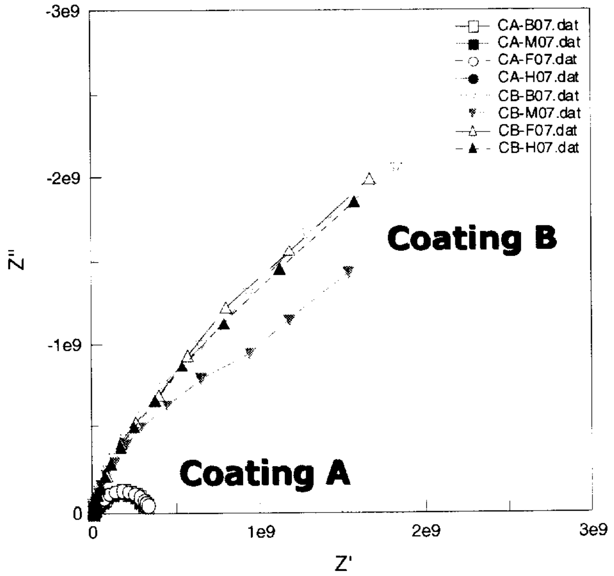


Fig. 16. Impedance Variation by Immersed Time.



(a) Bode plot



(b) Nyquist plot

Fig. 17. Comparison of Impedance between Coating A and Coating B.

5. Summary of Test Results

The performances of the coatings applied on the surface prepared by an abrasive blasting plus 3 types of power tooling surface treatment methods were evaluated in terms of adhesion properties, rust creepage resistance and film barrier property. The test results are summarized in Table 15 and the following results are obtained:

1. Surface profile ranking: B > H > M > F
2. Adhesion strength ranking: B >H > F = M > 5Mpa, and Coating B > Coating A > 5Mpa, and (B + Coating A) $\approx$ (H + Coating B)
3. Rust creepage resistance ranking: B > H > M > F, and Coating B > Coating A, and (B + Coating A) $\approx$ (H + Coating B)
4. Barrier property: B$\approx$H$\approx$F$\approx$M > $10^8\,\Omega\text{cm}^{-2}$, and Coating B > Coating A

Table 15. Summary of Evaluated Results

Items	Surface Preparation Methods				Coating Materials	
	B	M	F	H	CA	CB
Surface Profile	SP10	SP3	SP3	SP11	-	
Working capacity	◎	×	○	△	-	
Adhesion strength	◎	◎	◎	◎	>	
Impact resistance	◎	△	○	○	<	
Cupping resistance	◎	○	○	◎	<	
Cathodic disbondment	◎	△	△	○	<	
Rust creepage	◎	△	△	○	<	
Barrier property	◎	◎	◎	◎	<	
Final Rank	1	4	3	2	2	1

* ◎(Excellent) > ○(Good) > △(Fair) > ×(Bad)

6. Conclusions

(1) As expected, the coatings applied on the surface prepared by abrasive blasting method showed better coating performance in terms of overall coating properties than those applied on the surface prepared by other power tooling methods. However, some power tooling methods were found to have almost equivalent coating performance to the coating applied on the surface prepared by abrasive blasting.

(2) The power tooling method H (special abrasive disc) could be an alternative to blasting in the surface treatment of marine structures in their erection stage such as erection welding joints, for which cannot be covered by the use of abrasive blasting method is limited due to its accessibility. On the other hand, the power tooling method F could be applied with a proper selection of coating material (for example coating material B).

(3) Significant concerns should be directed to the proper control of cathodic protection system condition for the part of the surface prepared by power tooling method, even type H, because the excessive protection potential, such as -1.5V vs. $Cu/CuSO_4$, could incur unexpected earlier failure of the coatings prepared by power tooling methods.

7. References

1. US Army, Painting: New Construction and Maintenance, US Army Corps of Engineers document EM1110-2-3400, 1995
2. C.G.Munger, Corrosion protection by Protective Coatings, NACE International, pp.199-211, 1999
3. J.H.W. De Wit, Corrosion mechanisms in Theory and Practice, edited by P. Marcus and J. Oudar, Marcel Dekker, Inc., New York. pp.594-602. 1995
4. J.J. Ritter and J. Kruger, "Corrosion Control by Organic Coatings, NACE, Houston, 1981, p.78
5. J.S. Hammond, J.W. Hobluka, and R.A. Dickie, *J. Coat Technol.* pp.51~45, 1979
6. Wioleta Agata Pyc, "Field Performance of Epoxy-coated Reinforcing Steel in Virginia Bridge Decks", Dissertation to the Faculty of the Virginia Polytechnic Institute and State Univ., p.24, 1998
7. Bard-Stratman, "Encyclopedia of Electrochemistry Corrosion and Oxide Films", pp.500-525, 2001
8. Clear, K.C., "Performance of Epoxy Coated Reinforcing Steel in Highway Bridges." NCHRP Report 370, Transportation Research Board National Research Council, National Academy Press, Washington, D.C., 1995
9. S.W.Guan, The selection, application and inspection of 100% solids polyurethane coatings for corrosion protection, SSPC2000, Nov. 12-16, 2002
10. NORSOK M501, Rev. 4, 1999
11. D.Roy, G.P.Simon, M.Forsyth and J.Mardel, Modification of thermoplastic coatings for improved cathodic disbondment performance on a steel substrate: a study on failure mechanisms, International J. of Adhesion & Adhesives, 22, pp. 395-403, 2002
12. Y.Korobov and D.P.Moore, Performance Testing Methods for Coatings: Cyclic, EIS and Stress, NACE International Corrosion 2004, Paper# 04005, 2004
13. AASHTO Designation, Standard Practice for Evaluation of Coating Systems with Zinc-Rich Primers, AASHTO Designation: R 31-02, 2002
14. J.M.NcIntyre and H.Q.Phan, Electrochemical impedance spectroscopy; a tool for organic coatings optimizations
15. A.U.Malik, I.Andijani, Sahmed and F.Al-Muaili, Corrosion and mechanical

behavior of fusion bonded epoxy(FBE) in aqueous media, Desalination(150), pp. 247-254, 2002

16. A.M. Berendsen, Marine Painting Manual, Kluwer Academic Publishers Group, pp. 77-93, 1989
17. NACE TG 263, Offshore Platform Ballast Water Tank Coatings, NACE International, 2002

감사의 글

1995년 대학을 졸업하고 회사생활을 한지 8년이 지난 후 또 다른 배움에 대한 부푼 꿈에 얼마나 기뻐하였던가! 설레임으로 배움에 임하면서 배움의 깊이란 것이 끝이 없다는 것과 하나의 의문점을 해결하고 나면 또 다른 의문이 생긴다는 것, 그리고 새로움에 대한 의구심을 갖고 해결하면 그 기쁨이 배가 된다는 것을 알게 되었습니다. 졸업을 앞둔 현재 지식 보따리의 무게를 달아 보려니 부끄러움이 앞섭니다.

2년 동안 학업에 많은 가르침을 주신 박진환 교수님께 진심으로 감사를 드립니다. 그리고 바쁘신 와중에도 많은 도움을 주신 서차수 교수님, 이근대 교수님, 문명준 교수님, 곽삼탁 교수님께도 감사의 말씀을 드립니다.

회사를 위해 더욱 열심히 일할 수 있는 일군이 되도록 공부할 기회를 주신 현대중공업㈜ 산업기술연구소 박동환 소장님께 충심으로 감사의 말씀을 드립니다. 또한 학업에 정진할 수 있도록 많은 배려와 도움을 주신 도장·방식연구실 백광기 실장님과 이병헌 책임연구원, 정몽규 책임 연구원, 김기홍 책임연구원 이하 여러 연구원들께 진심어린 감사의 말씀을 전합니다.

그 외에도 실험실에서 항상 열심히 하고 있는 신안섭, 하효민, 조국원, 김민홍, 양진혁 군과 먼저 졸업한 김경래 군, 윤선화 선생님에게도 고마움을 전합니다. 그리고 동주산업의 황선환 과장님과 윤영진 계장님께도 감사의 말씀을 드립니다.

끝으로 이 세상에 태어나게 해주시고 사랑의 힘과 자연의 이치를 깨닫게 해주신 부모님과 할머니 그리고 장인, 장모님께 감사의 말씀을 드립니다. 그리고 2년 동안 매주 외박(?)을 하는데도 웃으면서 힘을 실어주고 항상 함께 해준 사랑스런 아내 천애란과 항상 웃음과 희망을 주는 귀염둥이 딸 지원, 예림이와 함께 이 작은 기쁨을 나누고자 합니다.