The Study on Optimizing the Zinc Phosphate Conversion Coating Process and Its Corrosion Resistance

Ta-Tung Chen[*], Shih-Tsung Ke[**], Yih-Ming Liu[*], Kung-Hsu Hou[***]

[*]*Department of Mechanical Engineering,*
[**] *Electrochemical Microfabrication Lab.*, *Department of Applied Chemistry,*
[***] *Department of Vehicle Engineering*
Chung Cheng Institute of Technology, National Defense University

ABSTRACT

This research aims at the surface treatment of low carbon steel using zinc phosphate conversion coating technique. The influence of the phosphate processing parameters on the corrosion resistance of zinc phosphate conversion coatings and the optimization of the process are investigated using the Taguchi robust experimental design method. The corrosion protection characteristic of the zinc phosphate conversion coatings is found would be strongly affected by the concentration of total acid (TA) and free acid (FA). The results showed that the salt spray resistance of the phosphatic coatings increased up to 190 minutes can be obtained using the optimized processing parameters of TA – 90 point, acid ratio (TA/FA) – 12, accelerate concentration – 8 point, surface modification agent concentration – 1 g/L, processing temperature - 70°C and processing time – 12 minutes.
Keywords: zinc phosphate, conversion coating, corrosion resistance

磷酸鹽處理製程最佳化及耐蝕性研究

陳大同[*] 柯世宗[**] 劉益銘[*] 侯光煦[***]

[*]機械工程學系 **應用化學系 電化學微細製造實驗室 [***]車輛工程學系
國防大學中正理工學院

摘 要

本研究係以磷酸鋅系為轉化膜處理液對低碳鋼試件進行表面處理，並藉助田口實驗法來探討磷酸鹽各種參數對皮膜之耐蝕性的影響，以尋求最佳耐蝕性之操作條件。實驗結果顯示最佳條件為全酸度 90 point，酸比 12，促進劑 8 point，表面調整劑 1 g/L，溫度 70 °C，時間 12 min，其磷酸鹽皮膜耐鹽霧時間可達 190 min。
關鍵詞：磷酸鋅、轉化膜、腐蝕阻抗

文稿收件日期 94.05.05; 文稿修正後接受日期 94.10.17.
Manuscript received May 5, 2005; revised Oct. 17, 2005.

I. INTRODUCTION

The phosphate conversion coating technique is widely applied for the surface pretreatment of both ferrous and non-ferrous metals [1]. The purposes of this process are mainly served as the metal surface prime coating for the corrosion protection, lubrication, abrasion resistance, insulation and decoration applications. As a result of its low processing cost, simple operation procedures and good performance on surface protection, the phosphate conversion coating plays a significant role in various industries such as automobile, manufacture and tool fabrication. The surface protection performance of the metal after the phosphating process is improved without degrading its intrinsically promising physical and mechanical properties such as strength, hardness, elasticity, magnetism and elongation due to the formation of the uniform and dense phosphate conversion film on the surface.

Zinc, manganese and iron phosphate conversion coatings are the most widely used phosphating processes. Zinc phosphate coating is commonly used for the purposes as the primer before applying paint, electrical insulation coating or other organic pigments. Manganese phosphate coating is mainly applied for the decoration and improvement of the wear resistance. Basically, these (zinc, manganese and iron) phosphate conversion coatings have good corrosion resistance and superior adhesion with the metal substrate [2-4]. Weng et al. investigated the corrosion protection characteristics of zinc and manganese phosphate coatings [5]. The results showed that the insulation capability of zinc phosphate film is better than that of manganese phosphate film, however, the zinc phosphate film was shown to have higher porosity than that of manganese phosphate film. It was found that the failure of zinc phosphate coating was primarily due to the chemical dissolution process, which would be speeded-up by the electrochemical corrosion of the metal substrate. The protection performance of zinc phosphate was considered to be dependent upon its barrier capability according to the results of Weng's study [6]. Because the zinc phosphate coating was found to be able to be formed in short times with chemically stable and fine-crystallized film structures [7-10], which was quite suitable to be applied as the primer for the purpose rust-proofing of the surface of steel substrate [11].

The phosphate conversion coating is theoretically a complex chemical reaction process [12-14]. The process for the formation of the phosphate coating is thought to be dominated by two essential factors – film growth extent and film growth speed, which are related to the thermodynamics of chemical reactions and reaction kinetics. Basically, the process for forming the phosphate coating can be divided into four steps – ionization, hydrolysis, oxidation and crystallization, which can be derived according to the analysis results of the formulation of the phosphating bath and the chemical composition of the phosphating conversion film.

According to the above statement, it is indicated that the microstructure of the phosphate conversion coating has great influence on its corrosion protection properties and the adhesion ability to the subsequent painting. Therefore, the objectives of this study are to develop the optimum phosphate conversion coating parameters, such as total acid (TA) concentration, free acid (FA) concentration, acid ratio, accelerator concentration, surface modification agent concentration, temperature and time of the processing bath and investigate the effect of film microstructure on the phosphate conversion coating's corrosion protection characteristics using Taguchi robust experimental designed method (three levels of experimental parameters shown in Table 1).

Table 1. Three levels of the Taguchi robust experimental designed factors were involved during this study of investigating the corrosion protection capability of phosphate conversion coating.

Factors	Level		
	1	2	3
Total acid concentration (point)	30	45	60
Acid ratio	4	12	20
Accelerator concentration (point)	4	6	8
Surface modification agent concentration (g/L)	0	1	2
Processing temperature (℃)	50	70	90
Processing time (mins)	6	12	18

II. EXPERIMENTAL PROCEDURES

2.1 Configuration of Zinc Phosphate Conversion Coating Bath

The configuration of the materials used for preparing zinc phosphate conversion coating bath solution is summarized in Table 2.

Table 2. The configuration of materials was used to preparing zinc phosphate conversion coating bath.

Surface modification agent: $TiOSO_4 \cdot 2H_2O$
Zinc phosphate: $Zn_3(PO_4)_2 \cdot 2H_2O$
Accelerator: $Pb_5(PO_4)_3Cl$
Indicator: phenolphthalein, bromophenol blue
Titrant：0.1N NaOH
Acid ratio modification agent: Na_2CO_3, HNO_3 or H_3PO_4

2.2 Zinc Phosphate Conversion Coating Process

The zinc phosphate conversion coating process for surface treating low carbon steel was mainly conducted as the following steps：

(i) Alkaline degreasing and acid cleaning: The surface of the low carbon steel was degreased to remove the oil or soil deposits in alkaline (for example, carbonate, phosphate or silicate) aqueous solution before the zinc phosphate conversion coating process. The acid cleaning process was followed to remove the rust using 15-25 % hydrochloride acid or 15-20 % sulphuric acid at 45-55°C.

(ii) Water rinsing: The sample was water-rinsed at room temperature to reduce the concentration of the pollutants induced during the degreasing and acid cleaning processes in order to increase the lifetime of the phosphate coating bath.

(iii) Surface modification: The metallic surface was modified by immersing in the 0.2-2 % titanate aqueous solution under stirring. This process is aiming to reduce the time for forming the phosphate conversion coating with fine-grained structures and improve the film's corrosion resistance.

(iv) Phosphate conversion coating: The grey phosphate conversion coating was formed on the surface of the low carbon steel by the immersion of the samples in the aqueous solution of phosphate and nitrate at the temperature of 50-90°C for 6-18 minutes with the addition of the accelerator of 0.5-3 g.

(v) Drying: The sample was then rinsed in water and dried at the temperature of 120-180°C.

2.3 Titration Processes Were Involved During The Preparation of The Zinc Phosphate Conversion Coating Solution

(i) Total acid concentration: The zinc phosphate conversion coating bath was prepared by diluting the concentrated phosphating solution of 10ml with the addition of 3-5 drops of the indicator – phenolphthalein and the titrant of 0.1N NaOH under stirring to give the total acid concentration with 25-65 points, which is considered to be equal to the quantity of the volume of the titrant.

(ii) Free acid concentration: The zinc phosphate conversion coating bath was also prepared by diluting the concentrated phosphating solution of 10ml with the addition of 2-3 drops of the indicator – bromophenol blue and the titrant of 0.1N NaOH under stirring to give the free acid concentration with 1-15 points, which is considered to be equal to the quantity of the volume of the titrant.

(iii) Accelerator concentration: The concentration of the accelerator was calculated as the volume of the gas being diffused out of the solution during the preparation process by the addition of concentrated phosphating solution with 2-3g of sulfamic acid.

(iv) The alteration of the free acid concentration: The concentration of the free acid has to be modified by adding acid ratio modification agent, while altering the total acid concentration involved during the phosphating coating process, in order to ensure a better quality of produced phosphating conversion film. The addition of 0.43 g/L of Na_2CO_3 is needed for reducing 1 point of free acid concentration. On the contrary, the addition of 0.23 g/L of H_3PO_4 or 0.16 g/L of HNO_3 is needed for increasing 1 point of free acid concentration.

(v) Acid ratio: The dependence of the ratio of total acid to free acid, altered in the ranges of 5-20, on the phosphate conversion coating processing parameters was investigated in this study.

Here, the point is a droplet liquid of the titrant - 0.1N NaOH, a point is about 0.35 ml.

Table 3. Taguchi robust experimental designed was related to phosphate conversion coating parameters.

No.	Total acid (point)	Acid ration	Accelerator concentration (point)	Surface modification agent concentration (g/L)	Processing temperature (℃)	Processing time (mins)	Salt spray test time (mins)
1	30	4	4	0	50	6	8
2	30	12	6	1	70	12	120
3	30	20	8	2	90	18	20
4	45	4	4	1	70	12	26
5	45	12	6	2	90	6	23
6	45	20	8	0	50	12	95
7	60	4	6	0	90	12	102
8	60	12	8	1	50	18	186
9	60	20	4	2	70	6	179
10	30	4	8	2	70	12	15
11	30	12	4	0	90	18	30
12	30	20	6	1	50	6	68
13	45	4	6	2	50	18	12
14	45	12	8	0	70	6	168
15	45	20	4	1	90	12	52
16	60	4	8	1	90	6	60
17	60	12	4	2	50	12	110
18	60	20	6	0	70	18	28

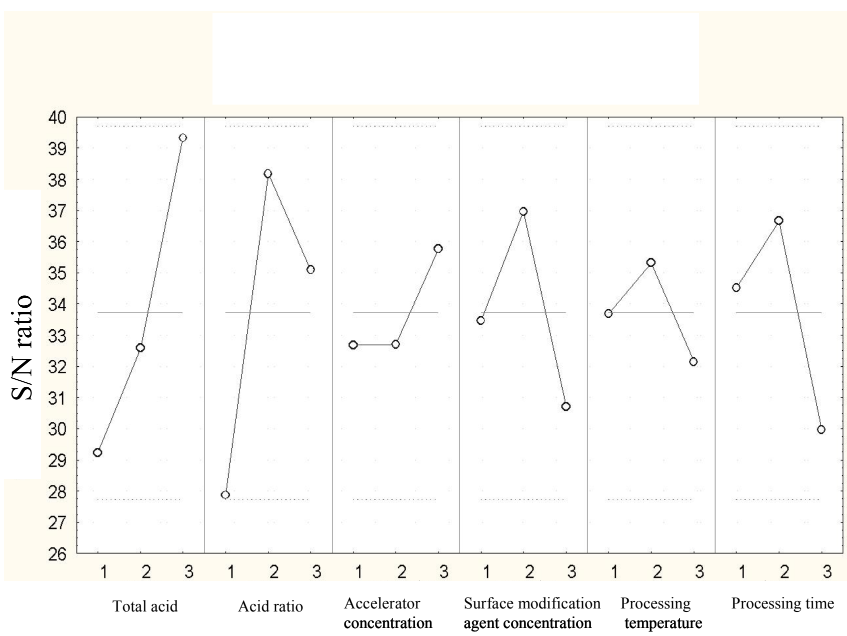

Fig. 1. The S/N response curve of the CRPC coatings were tested by salt spray method.

2.4 Salt Spray Test

The corrosion resistance of zinc phosphating coating on low carbon steel samples were investigated by conducting the salt spray test, based on the ASTM B-117 standard, with the Elite Salt Spray Tester using 5 wt % of neutralized salt solution (NSS) at the temperature of 35 ± 1°C. When the red rust occur on the sample, the salt spray test will stop and record the test time.

2.5 AC Impedance Analysis

The AC impedance behavior of zinc phosphate conversion coating was also analyzed to evaluate the film's corrosion protection performance using the electrochemical impedance spectroscopy (EIS) technique in the 5 wt % NaCl test solution.

III. RESULTS AND DISCUSSION

The effect of processing parameters on the salt spray test results of zinc phosphate conversion coated samples were analyzed by using the Taguchi robust experimental design method, which is shown in Table 3. The right column shows the time for the red rust to be occurred, ranged from 8 to 186 minutes, representing the ability of resisting the salt spraying. It means that the "corrosion resistance of the phosphate conversion (CRPC)" coatings were strongly dependent upon the phosphating processing parameters. Figure 1 displays the signal to noise (S/N) ratio response curve, which was summarized and drawn with reported data of Table 3. It is noted that the total acid and acid ratio are the primarily influenced processing parameters affecting the CRPC coating. The other parameters considered to be the secondarily influential are concluded as the processing time, concentration of the surface modification agent, processing temperature and concentration of the accelerator.

In order to have a clear understanding of the influence of phosphating operation parameters on the salt spray resistance capability of phosphate conversion coated samples, the relation between the average salt spray resistance time and the three levels processing parameters is analyzed based on the experimental results shown in Table 3. The analytic results are shown in Figures 2-7.

The effect of total acid concentration on the corrosion protection characteristics of the phosphate conversion coating is shown in Figure 2. The CRPC coating displayed to be increased with the increasing of the total acid concentration. Therefore, it is better to control the total acid in the upper limit of the required ranges of the concentration involved during the phosphate process. Because the higher total acid concentration results in faster speed of phosphoric reaction involved during the phosphating coating process, which will lead to the formation of fine-grained film structure.

Figure 3 shows the influence of the acid ratio on the corrosion resistance capability of the phosphating coating. With the acid ratio to be increased, the CRPC performance is found to be improved due to the faster phosphoric reaction resulting in thin phosphate film with fine microstructure, however, it leads to the difficulty in forming the film and the degradation of the coating's corrosion protection ability while using too high acid ratio of the phosphating solution. As the acid ratio used is too low, the phosphate coating with coarse-grained microstructure is produced due to the slow phosphoric reaction occurred during the coating process. Therefore, in order to achieve better CRPC coatings, the acid ratio of the phosphating solution needed to be optimized.

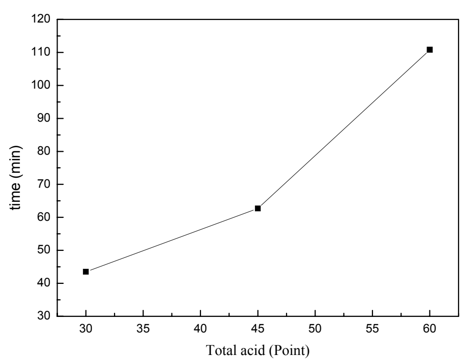

Fig. 2. The related curve is "TA concentration" vs. the red rust happen timing of CRPC coating.

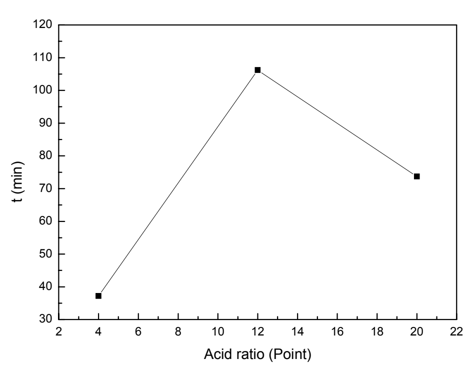

Fig. 3. The related curve is the "acid ratio" vs. the red rust happen timing of CRPC coating.

The effect of adding free acid, which dominates the reaction of the dissolution of iron normally occurred during the phosphating process resulting in more nuclei with the formation of fine-grain-structured coating, on the corrosion resistance of phosphate coating is considered to be relevant to the total acid concentration and acid ratio of the used phosphating bath solution. However, it is observed that the higher the free acid concentration, the faster dissolution of iron occurred leading to the formation of lots of hydrogen gas, which makes it difficult for the nuclei to be formed due to the production of non-saturated phosphate in the interface between the coating and the metal substrate. The corrosion protective ability of the coatings is degraded because of the formation of the coarse-crystallized film structure with variety porosities sparsely distributed on the film surface. There are thin or no phosphate coatings noted to be formed while too low free acid concentration is involved during the phosphating process.

The CRPC of coatings is shown (see Figure 4) less affected by the accelerator with the concentration set from 4 to 6 point. However, it is still required that the accelerator should be controlled at higher concentration in order to inhibit the formation of the hydrogen gas, promote the anodic oxidation reaction occurred on the work-piece surface during the coating process and prevent from the occurrence of the cathodic polarization process, resulting in the formation of fine crystallized phosphate conversion coating with improved corrosion protection.

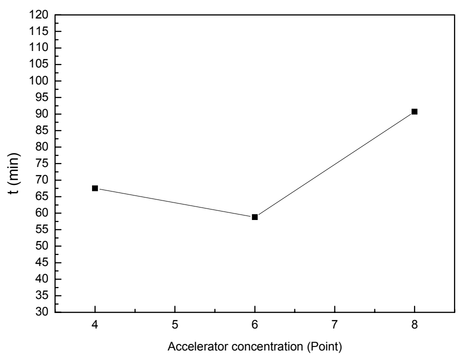

Fig. 4. The related curve is the "accelerator concentration" vs. the red rust happen timing of CRPC coating.

As shown in Figure 5, in order to obtain coatings with better corrosion protection, the surface modification agent concentration should be adequately controlled (not very high) at the concentration around 1g/L. The reason for preventing using too high concentration of the surface modification agent is probably related to the possibility of resulting in the over-activated surface during the coating process.

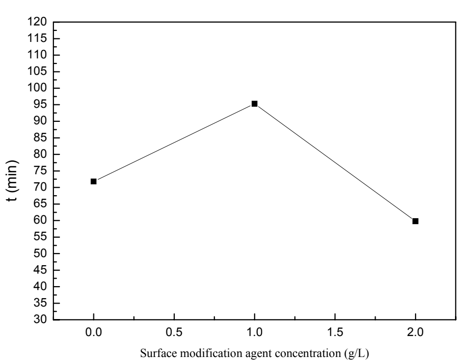

Fig. 5. The related curve is the "surface modification agent concentration" vs. the red rust happen timing of CRPC coating.

It is shown in Figure 6 that the temperature involved during the phosphating process should be carefully set at about 70°C in order for obtaining better CRPC coating. As the temperature is too high, it induced a very fast phosphoric reaction leading to the formation of coarse-grained coating with poor corrosion resistance. On the contrary, as the temperature is too low, it was also found that the produced phosphate coating was thin with poor resistance to the corrosion environment due to the resulted slow phosphoric reaction involved during the phosphating process.

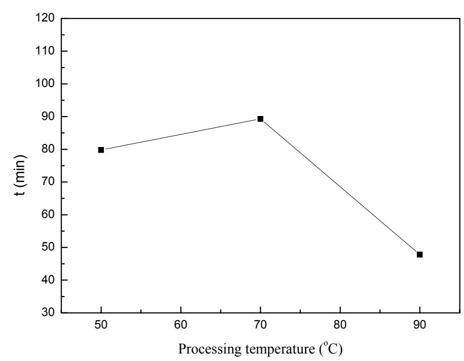

Fig. 6. The related curve is the "processing temperature" vs. the red rust happen timeing of CRPC coating.

Figure 7 shows the influence of the processing time on the resulted CRPC coatings, which indicates that the processing time and used during the phosphating process has better to be controlled at around 12 minutes. Basically, the thickness of the conversion coating is increased with the increasing processing time that leads to the longer phosphoric reaction process. However, as the selected processing time is too long, the thickness of the coating is found to stop being thickened due to reaching the equilibrium state of the 'crystallization ⇔ dissolution' reaction involved during the phosphating process. The longer processing time also causes the poor stability of the formed conversion coatings due to the over-etching by the free acid resulting in too many Fe^{2+} ions. While the processing time used is too short, the quality of the phosphoric reaction becomes poor, which will produce the thin and non-uniform phosphate conversion coatings with poor corrosion protection.

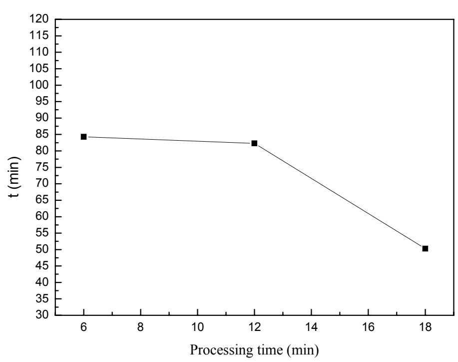

Fig. 7. The related curve is the "processing time" vs. the red rust timing of CRPC coating.

Based on the results of the level analysis of the average maximum S/N ratio of various phosphating processing parameters, the best corrosion protective phosphate conversion coatings was obtained with no clear indication of rust formation observed after 190 minutes of salt spray test using the optimum parameters of TA ＝ 90 point, acid ratio (TA/FA) ＝ 12, accelerator additive ＝ 8 point, surface modification agent additive ＝ 1 g/L, temperature of bath ＝ 70°C and processing time ＝ 12 minutes. The obtained surface morphology is shown in Figure 9, which is finer and smoother than the surface morphology of the phosphlating coating obtained using the processing parameters of level 1 (see Figure 8).

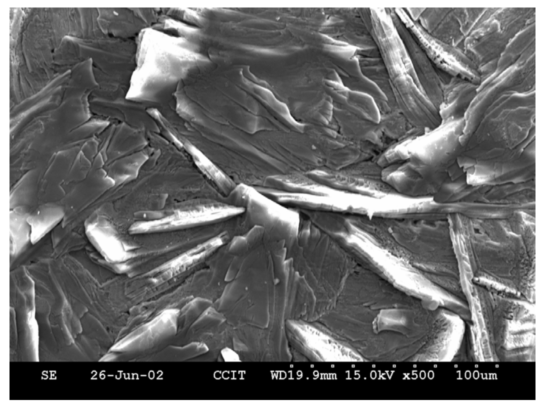

Fig. 8. The surface morphology of the phosphlating coating obtained using the processing parameters of level 1.

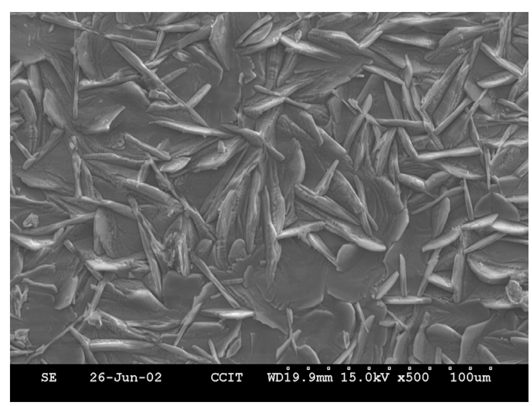

Fig. 9. The surface morphology of the phosphlating coating obtained using the optimum processing parameters (TA – 90 point, acid ratio – 12 , accelerator concentration – 8 point, surface modification agent concentration - 1g/L, processing temperature - 70 ℃ , processing time – 12 mins).

The results in evaluating the corrosion protection performance of the phosphate conversion coatings using electrochemical impedance spectroscopy technique were shown in the Nyquist diagrams (see Figures 10 and 11), which are shown to have good correlation with the experimental results by the salt spray test. To compare the Nyquist plots for the phosphate conversion coatings using the optimum processing parameters on the analysis results of the salt spray test (Figure 11) and the processing parameters of level 1 (Figure 10).

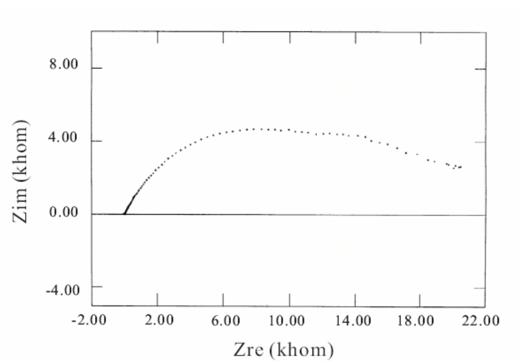

Fig. 10. The Nyquist diagram obtained for the phosphate conversion coating using the processing parameters of level 1.

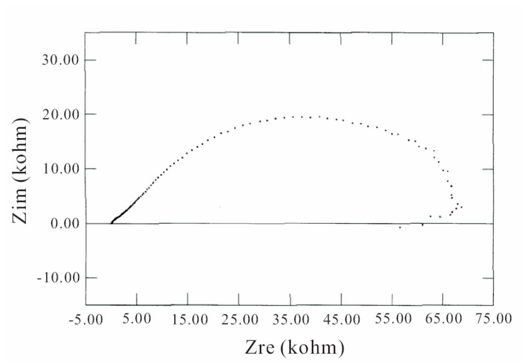

Fig. 11. The Nyquist diagram obtained for the phosphate conversion coating using the optimum processing parameters.

It is clearly indicated that the phosphate coating with optimum corrosion resistance that is shown to have AC impedance (~ 65kohm) higher than the one with inferior corrosion resistance (obtained using the parameters of level 1) having lower AC impedance of ~ 20Kohm.

IV. CONCLUSIONS

Based on the experimental results using Taguchi robust experimental design method, it is noted that the total acid and acid ratio are the primarily influenced processing parameters affecting the corrosion resistance of the phosphating conversion coating. The other parameters considered to be the secondarily influential are concluded as the processing time, concentration of the surface modification agent, processing temperature and concentration of the accelerator.

The parameters for obtaining optimum corrosion protective phosphate conversion coating with no clear indication of rust formation observed after 190 minutes of salt spray test are TA – 90 point, acid ratio (TA/FA) – 12, accelerator additive – 8 point, surface modification agent additive – 1 g/L, temperature of bath - 70°C and processing time – 12 minutes.

It is noted that the phosphate conversion coating with the optimum corrosion resistance is shown to have higher AC impedance (~ 65kohm) than the one with inferior corrosion resistance (obtained using the parameters of level 1) having lower AC impedance ~ 20Kohm. The results in testing the corrosion protection performance of the phosphate conversion coatings using electrochemical impedance spectroscopy technique were shown to have good correlation with the evaluation results by the salt spray test.

REFERENCES

[1] Narayanan, T.S.N.S., "Influence of Various Factors on Phosphatability - An Overview," Metal Finishing, Vol. 94, No. 6, pp. 86-90, 1996.

[2] Di Giampaolo, A.R., Medina, M., Reyes, R., and Velez, M., "Zinc Phosphate Interlayer for Sol-Gel-Derived Aluminosilicate Coating on AISI-1010 Carbon Steel," Surface and Coatings Technology, Vol. 89, No. 1-2, pp. 31-37, 1997.

[3] Lazzarotto, L., Maréchal, C., Dubar, L., Dubois, A., and Oudin, J., "The Effects of Processing Bath Parameters on The Quality And Performance of Zinc Phosphate Stearate Coatings," Surface and Coatings Technology, Vol. 122, No. 2-3, pp. 94-100, 1999.

[4] Sugama, T., Kukacka, L. E., Carciello, N., and Warren, J. B., "Chemisorption Mechanism and Effect of Polyacrylic Acid on The Improvement in Bond Durability of Zinc Phosphate-to-Polymer Adhesive Joints," Journal of Materials Science, Vol. 22, No. 2, pp. 722-736, 1987.

[5] Weng, D., Jokiel, P., Uebleis, A., and Boehni, H., "Corrosion and Protection Characteristics of Zinc and Manganese Phosphate Coatings," Surface and Coatings Technology, Vol. 88, No. 1-3, pp. 147-156, 1997.

[6] The ASM Committee on Phosphate Coating, "Metals Handbook," American Society for Metals, 9th ed., Vol. 5, pp. 434, 1982.

[7] Cape, T.W., "Metals Handbook," American Society for Metals, 9th ed., Vol. 13, pp. 383, 1982.

[8] Di Giampaolo, A.R., Puerta, M., Ruiz, H., and Olivares, J. L., "Thick Aluminosilicate Coatings on Carbon Steel via Sol-Gel," Journal of Non-Crystalline Solids, Vol. 147-48, pp. 467-473, 1992.

[9] Kelly, R., "Principles Of Fastener Pretreatment," Metal Finishing, Vol. 86, No. 4, pp. 15-19, 1988.

[10] Scislowski, S., "Phosphating," Metal Finishing, Vol. 89, No. 4, pp. 29-30, 1991.

[11] Guenbour, A., Benbachir, A., and Kacemi, A., "Evaluation of the Corrosion Performance of Zinc-Phosphate-Painted Carbon Steel," Surface and Coatings Technology, Vol. 113, No. 1-2, pp. 36-43, 1999.

[12] Amirudin, A. and Thierry, D., "Corrosion Mechanisms of Phosphated Zinc Layers on Steel as Substrates for Automotive Coatings," Progress in Organic Coatings, Vol. 28, No. 1, pp. 59-76, 1996.

[13] Vasovic, D.D., Stojakovic, D.R., and Zec, S.P., "Metal Phosphate Preparation Using Boron Phosphate," Materials Research Bulletin, Vol. 32, No. 6, pp. 779-784, 1997.

[14] Kouisni, L., Azzi, M., Zertoubi, M., Dalard, F., and Maximovitch, S., "Phosphate Coatings on Magnesium Alloy AM60 Part 1: Study of the Formation and the Growth of Zinc Phosphate Films," Surface and Coatings Technology, Vol. 185, No. 1, pp. 58-67, 2004.