Evaluations of Automotive Paints Coating Performance Using Electrochemical Impedance Spectroscopic Method

Dr. Haider Hadi Jasim,
Chemical Engineering Department, University of Basrah / Basrah.
Raed Abdul-Hussain
Chemical Engineering Department, University of Basrah / Basrah.
Email: raidhani73@yahoo.com
Shaima Al-Bazaz
School of Chemical Engineering and Advanced Material, Newcastle University/UK.

ABSTRACT

The aim of this paper is to study the corrosion rates and porosity of industrial paints used for car body coating. Seven types of industrial paints were used for car body structures included 2K clear coat (Lacquers), Auto Paint 2K top coat, TS 16949 (Easi coat), Clear coat (Palinal), National Numix top coat, DENSO and ICI 2K solvent based (Tinters P420) were tested and studied using the electrochemical impedance spectroscopic (EIS) method. The liquefaction potable water solution was used as electrolyte for test. The obtained results showed that the Palinal paint has high impendence and lower porosity while TS 16949 (Easi coat) shows lower impedance and high porosity. Other types showed moderates values. Microscopic inspection of the surface coatings after EIS test showed that most paints had pitting corrosion except Auto paint shows blisters.

Keywords: porosity, EIS method, Bode plot, polarization resistance, paint impedance, Nyquist plot.

تقييم الأداء في طلاءات السيارات باستخدام طريقة المقاومة الكهروكيميائية الطيفية

الخلاصة

الهدف من هذا البحث هو دراسة معدلات التآكل والمسامية للأصباغ الصناعية المستخدمة في طلاء السبائك المستخدمة في هياكل السيارات. سبعة أنواع من الطلاءات الصناعية المستخدمة في طلاء هياكل سيارات وتشمل: 2K Clear coat (Lacquers), Auto Paint 2K top coat, TS 16949 (Easi coat), Clear coat (Palinal) , National Numix top coat, DENSO and ICI 2K solvent based (Tinters P420) تم اختبارها ودراسة التآكل فيها باستخدام طريقة المقاومة الكهروكيميائية الطيفية. أظهرت النتائج من الاختبار في ماء الاسالة إن إصباغ Palinal هي الأفضل حيث انها امتلكت اعلى قيمة للممانعة واقل قيمة للمسامية، بينما اصباغ (Easi coat) TS 16949 امتلكت اقل قيم للممانعة واعلى قيمة من المسامية، بقية الأنواع أظهرت قيم

متوسطة من معدلات الممانعة والمسامية. الفحص المايكروسكوبي للسطح المغطى بالأصباغ بعد الاختبار بين تكون تآكل نقري في الطلاء باستثناء Auto Paint بين تكون بثور على السطح المطلي.

INTRODUCTION

The problem of metallic corrosion is one of significant proportions to any nation. In economic terms it has been estimated that approximately 5% of an industrialized nation's income is spent on prevention and the replacement of products lost or contaminated as a result of corrosion reactions [1].

Modern automotive paint systems perform two main functions: corrosion protection and appearance enhancement. Corrosion protection is achieved by layers of painting system. Because of their proximity of the surface, the paints are exposed to rain, heat, moisture and sunlight. Each of these can cause paint degrade. Liquid water provides a mechanism of material removal such as low molecular weight species from the paint and leading to reduce the paint resistance to corrosion process [2].

Various types of painting methods are used by car manufacturers to produce better car bodies and fulfill the customers need includes: dipped into a vat of paint, electroplated painted, electroplated using a cathodic process and paintings using organic coatings by different methods such as brush , spray cans and air-brush [3]. The brush is suited for painting small parts. The spray paint is the most widely used for the painting sources for the model cars. The airbrush is a great tool for painting small scale car models [4].

Electrochemical impedance spectroscopy (EIS) is a techniques used to determine the numerical values of the degree of corrosion protection provided by coatings. This numerical value is called impedance of the paint and represents the ability of the coating to resist the corrosion through barrier properties [5]. Porosity is an important parameter that should be assessed to estimate their quality of paintings. Porosity of the coating is strongly related to the corrosion resistance of paint [6].

Ahmed [7] indicated that one car out of every seven cars has noticeable corrosion damage, with an average age of about 4.65 years. Xu et al. [8] used the electrochemical impedance spectroscopy (EIS) to evaluate of vehicle coating performance on-site of car body. The study shows that performance of the same coating varies significantly from one part of the vehicle to another even though it appears identical on the surface. Sauy et al. [9] investigated the corrosively of two different types of epoxy coating used for automotive surface by using EIS test method. It shows that the primers have excellent behavior when applied on phosphate steel and poor on electrozincated steel. Derun et. al. [10] study car body's corrosion performances coated with and without nickel immersion type zinc phosphating and then compared with that are coated by spray and immersion methods. Results show the corrosion performance of specimens coated by no nickel and low nickel processes are as good as that coated by spray and immersion processes. Hamzah et. al. [11] compared the corrosion behavior between coated and uncoated steel sheets used in car body manufacturing. It was found that the uncoated samples were attacked by uniform corrosion, while the coating system able to protect the steel substrate from corrosive environment. Walsh et al. [12] reviewed the electrochemical techniques for the assessment of porosity in electrodeposited metal coatings. It shows that linear polarization resistance measurements are good tools to determine porosity of coating compared with EIS method due to complexity of achieving EIS test. Debnath [13]

evaluated using salt spray test and electrochemical impedance spectroscopy (EIS) the corrosion protections of the phosphated and painted steel panels. He shows the mechanism of superior corrosion resistance provided by the modern tricationic phosphating formulations and conventional high zinc phosphating formulations. Al-Atia [14] listing of electrochemical methods used to evaluate porosity of Nano ceramic coating. The nine electrochemical parameters were calculated, adopted to set a comprehensive evaluation map for protective properties of the coatings obtained based on occurrence degree of cracks, porosity, general and localized corrosion. Perez et *al.* [15] investigated the corrosion resistance of acrylic paint system containing zinc phosphate pigment using electrochemical impedance spectroscopy (EIS) method. They show an efficient protection against corrosion provided by the coating containing zinc phosphate pigments when it was applied as a multilayer system.

   The goal of this paper is to study and test experimentally seven different types of paints in a liquefaction water solution using the electrochemical impedance spectroscopic method. The porosity of the paint films was electrochemically determined using the Nyquist plot.

Types of Car Paints

   There are several types of coatings used for car body structures differ in terms of features offered by each type. The first thing is that some of these differs are related to resistance of various weather conditions (temperature, humidity and sunlight). The second is related to the ability of maintain a color and shine. The third is related to the high resistance to chemicals (kerosene and benzene). Finally, it is related to resistance of mechanical elements such as scratching and bending. Table 1 shows seven types of commercial paints and manufacturing company which is commonly used in Iraq market.

Table (1) Types of car paints.

No.	Paint Type	Manufactures Company	Origin
1	2K Clear Coat (Lacquers)	Refinish System LTD	UK
2	Auto Paint 2K Top Coat	Orbay Kimmya Imalat Sanayi Vetic LTD STI	Turkey
3	TS 16949 car paint (Easi coat)	Guangdong Yatu Chemical Co., Ltd.	China
4	Clear coat (Palinal)	Palinal Vernici S. r. l.	Italy
5	National Numix Top Coat	National paint company	UAE
6	DENSO	DENSO paints manufacture company	China
7	ICI 2K Solvent Based (Tinters P420)	NEXA Autocolor Company LTD	UK

Experimental Procedure
Specimen Preparation and Coats
    The uses of high strength steel (HSS) and Ultra High Strength Steel (ULSAB) are for more than 90 % of the car body structure [16]. These are due to challenge the car requirement such as reduce the car weight and maintaining their performance and affordability. The samples of (2*2) cm dimensions with thickness (3mm) for the EIS test were used. Fig.1 shows specimens before and after paints. A total 75 specimens were used for testing. Table 2 shows the chemical composition of H220Y high strength steel grade used for test [17].
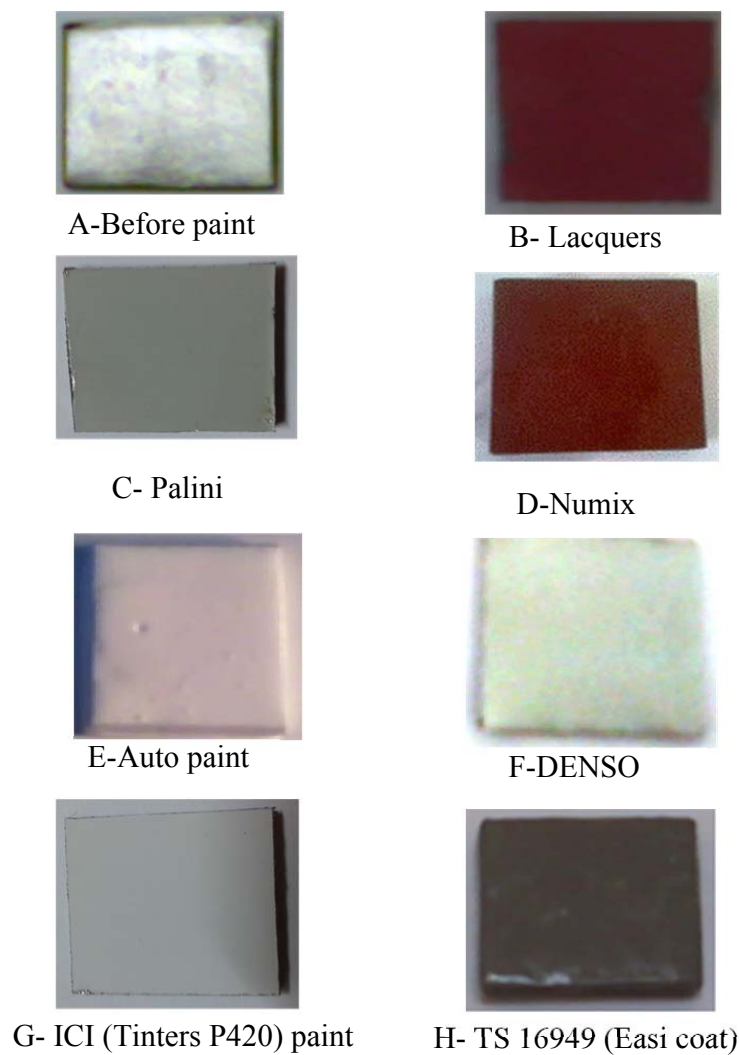
A-Before paint

B- Lacquers

C- Palini

D-Numix

E-Auto paint

F-DENSO

G- ICI (Tinters P420) paint

H- TS 16949 (Easi coat)

Figure (1) Specimens before and after paints.

Table (2) Chemical composition of H220Y high strength steel [17].

Element	Percent wt %
C	0.003
P	0.04
Nb	0.02
Si	0.01
Mn	0.40

Electrochemical Impedance Spectroscopic (EIS) Test and Porosity of Paints

EIS is a well laboratory technique for evaluating the corrosion protection of coatings. The technique uses AC (Alternating Current) electricity to measure the impedance of a coating [5]. The electrochemical system is submitted to a sinusoidal voltage perturbation of low amplitude and variable frequency. At each frequency, the various processes evolve with different rates, enabling to distinguish them.

A weak amplitude sinusoidal perturbation is generally superimposed to the corrosion potential or open circuit potential:

$$\Delta U = |\Delta U_o| \sin \omega t \qquad \qquad \dots (1)$$
$$\omega = 2\pi f \qquad \qquad \dots (2)$$

Where,
f : The frequency in (Hz) of the applied signal.
U: Voltage of electrical resistance.
U_o : Amplitude of perturbing signal.
t: Time in second.

This perturbation induces a sinusoidal current ΔI superimposed to the stationary current I and having a phase shift ϕ with respect to the potential:

$$\Delta I = |\Delta I_o| \sin(\omega t - \phi) \qquad \qquad \dots (3)$$

These values can be represented in the complex plane:

$$\Delta U = \Delta U_{re} + j \, \Delta U_{im} \qquad \qquad \dots (4)$$
$$\Delta I = \Delta I_{re} + i \, \Delta I_{im} \qquad \qquad \dots (5)$$

The complex impedance is defined as:

$$\Delta Z = \frac{\Delta U}{\Delta I} = Z_{re} + Z_{im} \qquad \qquad \dots (6)$$

The impedance can be represented by a modulus $|Z|$ and a phase angle shift φ:

$$|Z| = \sqrt{Z_{re}^2 + Z_{im}^2} \qquad \qquad \dots (7)$$
$$\tan \phi = \frac{Z_{im}}{Z_{re}} \qquad \qquad \dots (8)$$

The impedance data can be represented in two ways:
- Nyquist spectrum: - Z_{im} as a function of Z_{re}
- Bode spectrum: log $|Z|$ and phase angle φ as a function of log f.

The EIS corrosion test was achieved by connecting the Auto-lab instrument to glass cell having three electrodes as shown in Fig.2. A three-electrode glass cell configuration was set up with a paints specimen as the working electrode; a (Ag/AgCl) saturated solution as the reference electrode and a concentric platinum ring as the counter

electrode. The glass cell was filled with 0.5 liters of water and put in heater to control the temperature. The experiments were carried out at atmospheric pressure in a glass cell. The materials composition of liquefaction water is analysis by using the Spectrophotometer. Table 3 shows their material and physical properties of the liquefaction water. The coating surfaces were observed using a computerized Carl Zeiss Jena imaging system, provided by microscope and camera smart technical have 22 Mega pixels illustrated in Fig.3.
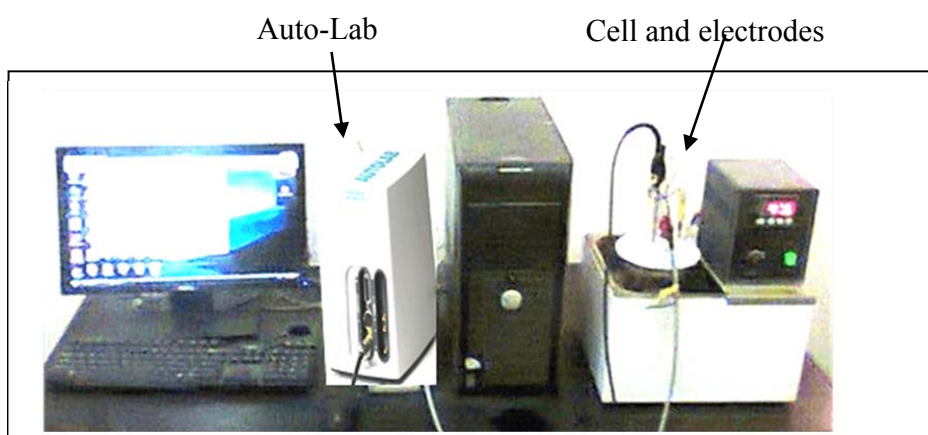
Figure (2) EIS test arrangement.

Table (3) Materials analysis and properties liquefaction water.

Elements	Concentration
Cr	12 ppm
Cu	0.01 ppm
Ni	0.76 ppm
Al	0.19 ppm
Fe	0.01 ppm
Cl	715.09 mg/l
TDS	1150. mg/l
pH	8.47

Figure (3) Computerized Carl Zeiss Jena imaging system.

The porosities (P %) of the coatings were calculated to assist in comparison and to determine the effective barrier properties of the coatings. The porosities represent the uncoated surface fractions i.e. the surface exposed to surrounding environment through the defects in the coating. The porosity of coatings was determined using the following formula [18]:

$$P = \frac{R_p^o}{R_p} * 100 \% \qquad\qquad … (9)$$

Where

R_p^o : Describes the polarization resistance of the metal substrate.

R_p: The polarization resistance of the coated substrate under evaluation.

Results and Discussion

EIS measurements were carried at a temperature (25°C). EIS measurements were carried out at the $E_{corr.}$ potential of the samples in the frequency range (0.1–500) Hz. The amplitude of the applied voltage was 10 mV.

The impedance of the painted specimens is measured at intervals during exposure to the liquefaction water solution. The initial impedance and the decrease in impedance as a function of time are used to assess coating protection and deterioration. The way the impedance changes with time enables a better prediction of long-term performance of the coating.

Figure 4 shows the variation of the impedance with time for 6 h of EIS test at 0.1 Hz. As shown the Palinal paint initially has very high impedance, typical of high performance coatings. However, its impedance has small drops consistently with time. So, the paints provide significant corrosion protection in demanding service.

Lacquers and Numix paints show a similar trend. In contrast, DENSO paints initially has high impedance but well below that of Palinal paints; however, the impedance of DENSO paint drops faster during the first 2hr. of time of exposure. This paints is presumably absorbed the water and results of physical-chemical deterioration of paint.

Paints Lacquers, Numix and ICI Tinter P420 similarly stabilize, at LogZ between 7 and 9, although at lower impedances than Palinal paints. TS 16949 (Easi coat) has the lowest

impedance, but it appears to stabilize at Log Z between 5 to 6, Based slowly decreasing on impedance with time.

Figures 5 and 6 comparisons the experiment Bode plot i.e., Log impedance and the phase angle with Logf for the seven specimens paints after 6 h of the EIS immersion test.

Initial impedance values in the low frequency range i.e. 0.1 Hz of the impedance spectra amounting for Palinal, Lacquers, Numix, auto paint, ICI Tinter P420, DENSO, and TS 16949 paints are 15.5, 14, 13.11, 11.47, 10.11, 12.5 and 9 at first hr. of test of time Fig.5. While the maximum phase angle occurred at approximately values 74, 68, 63, 61, 57, 53, and 48 respectively. At a small frequency range with phase angles less than 30° could be observed in the Bode-phase diagrams. Despite these observations, phase angles were always smaller than 90°, which would be an indication of a resistance behavior. When the phase angle closes to 90°, the sample tends to have good physical barrier properties. This Palinal has good corrosion resistance properties compared to others.

The polarization resistance R_p can be used as a quantitative parameter to compare the corrosion resistance of paints under conditions. High R_p of paint implies high corrosion resistance and low R_p implies low corrosion resistance. The values of R_p for paints are determined from Nyquist plots.

The Nyquist plots showing the imaginary versus real impedance of the seven sequential samples took on the characteristic semicircle shape for the lower frequency values Fig. 7. Given the normality of the shape, the polarization resistance R_p can be estimated as the point at which the semicircle crosses the X-axis.

To anticipate the X-intercept of the Nyquist plots, an approximate radius was estimated by taking the average of the real and imaginary impedance values at the visually observed center point. The paints sample gave slightly different values of average radius (3.85, 3.75, 3.65, 3.51, 3.42, 3.34, and 3.25) kΩ. cm^2.

Using average radius a semicircle was plotted in Fig.7 along with the impedance values showing a good fit, which, therefore, the x-intercept of the semicircle is approximately that of Nyquist plots. As a result the R_p values are determined and given in table 4.

Table (4) Polarization resistance of paints.

Paint type	Polarization resistance (Ω. cm^2)
Palinal	7700
Lacquers	7500
Numix	7300
ICI Tinters (P 420)	7020
Auto Paint	6840
DENSO	6680
TS 16949 (Easi coat)	6500

In the same method the polarization resistance of H220Y high stainless steel was determined and shown in Fig.8 which was a value of 564 (Ω. Cm^2). Than use eq.9 to calculate the porosity of coatings and the porosity values are given in table 5.

Table (5) Porosity of paints.

Paint type	Porosity %
Palinal	7.32
Lacquers	7.52
Numix	7.73
ICI Tinters (P 420)	8.03
Auto Paint	8.25
DENSO	8.44
TS 16949 (Easi coat)	8.68

From table 5, it's clear that the Palinal paint has lower degree of porosity in the painted layer 7.32 % while that for TS 16949 Easi coat is 8.68 %. Thus, it is clear that the corrosion resistances was determined by both the chemical compositions and paint properties especially its porosity level.

Through the paint porosity; the chloride ions in water permeate through the paints and reach the interface between paint and metal. When the water solution meets the contact part of a steel, the galvanic cell is formed and increase the reaction rate between molecular structures of paints and steel surface which contributes to increases the corrosion rates. The high porosity contributes to lower the values of the hardness of coating and leads to generate the coating fragments that break a way and become cutting agents.

Figs. 9 A to G show the microscopic inspection of specimens painted surface after 6 h. of EIS test at 0.1 Hz. Figs.9-A for DENSO paint, it was observed that corrosion causes damage surface coating, as illustrated by small, dark locations. Also it can be seen some of pits and small cavities covered the entire surface. Optical micrographs of the Auto paint samples in water solution are shown in Figure 9-C and Blisters are seen in the surface coating compared to other types of paints. The water absorption by coats leads to swelling of the coating and when this occurs locally, blisters may form and water may accumulate at the interface. These water accumulations are increased the charge transfer during test and reduced the impedance of paint. Figure 9-D shows of the TS 16949-coated systems. As shown it can be detected that the film coating appears to be more pitting and damage compared to other types of paints. All other types of paints show pitting and some cavities of surface as indicated in Figs. 9 B, E, F and G.
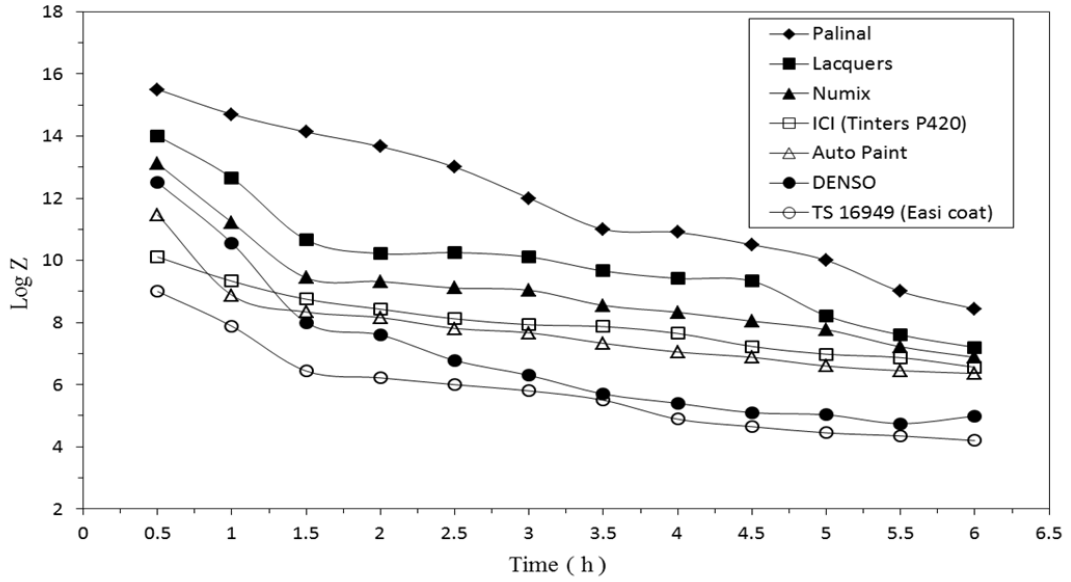
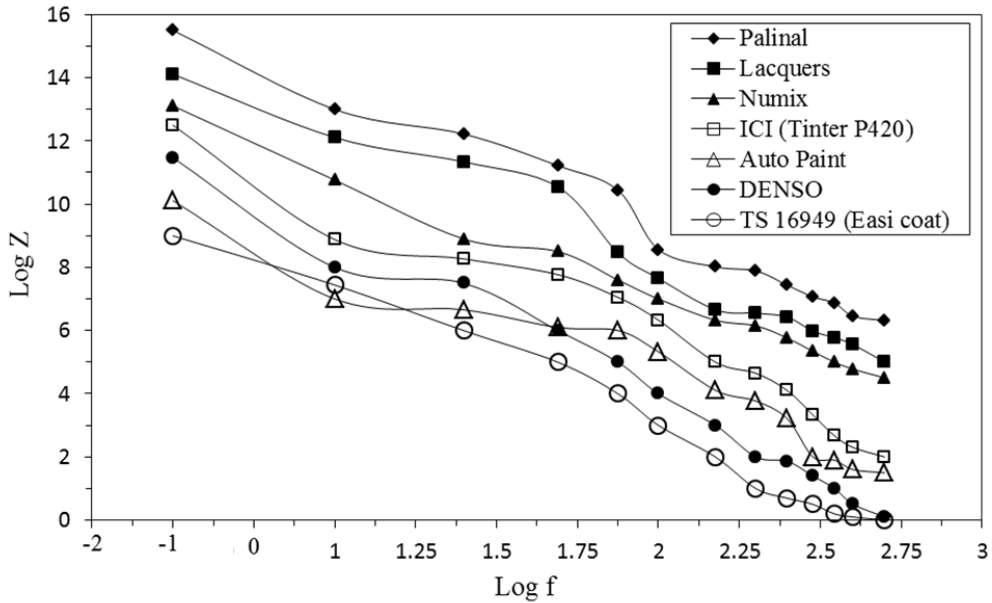**Figure (4) Coating impedance as a function of time at 0.1 Hz and 25°C .**

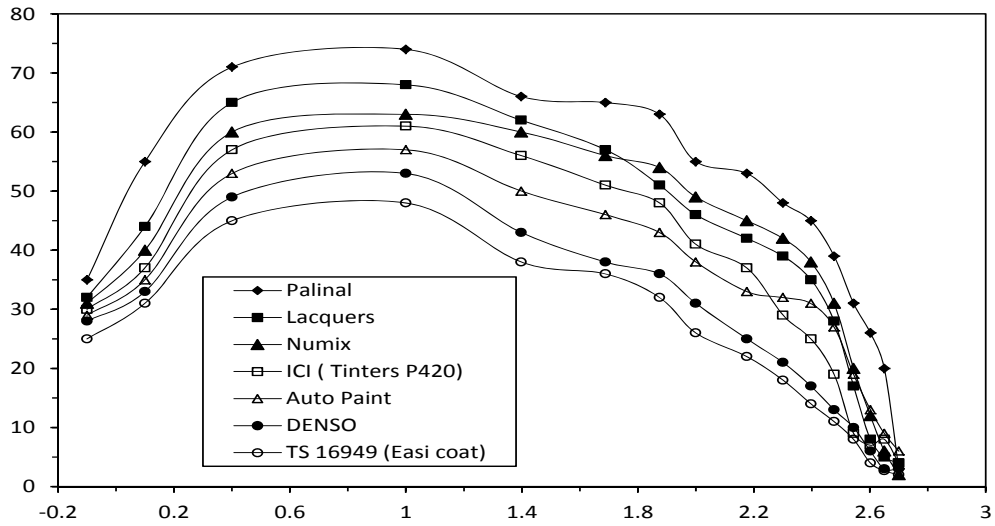**Figure (5) Coating impedance as a function of log f for seven paints at 25°C.**

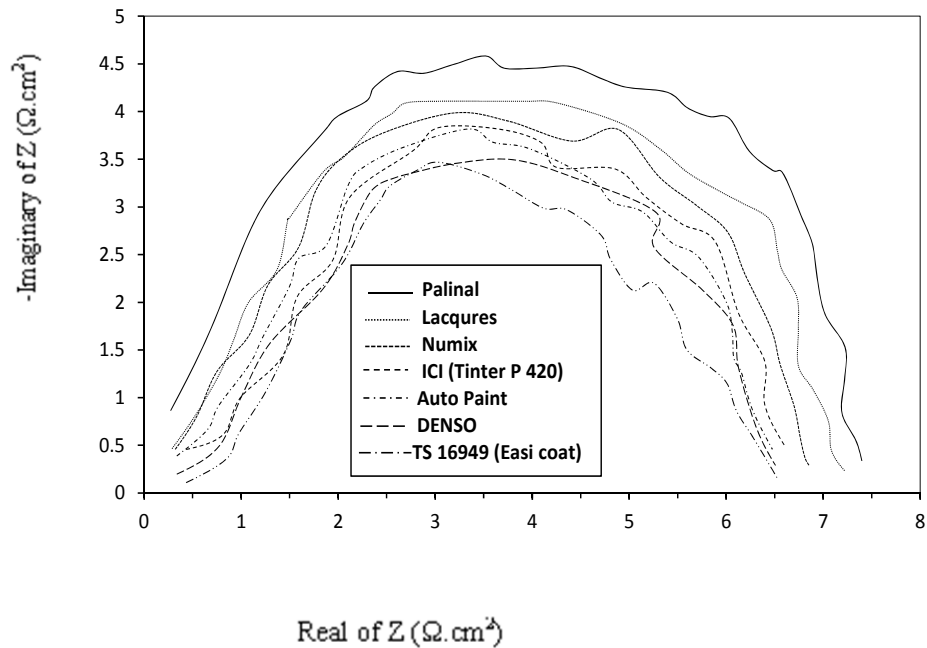**Figure (6) Phase angle as a function of Log f at 25°C.**

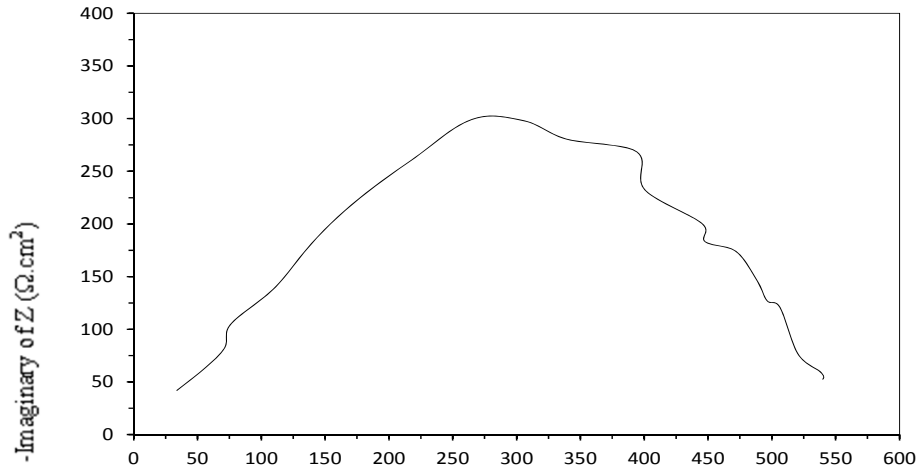**Figure (7) Nyquist plot of the imaginary versus real impedance for the seven paints.**

Figure (8) Nyquist plot of the imaginary versus real impedance for H220Y steel.
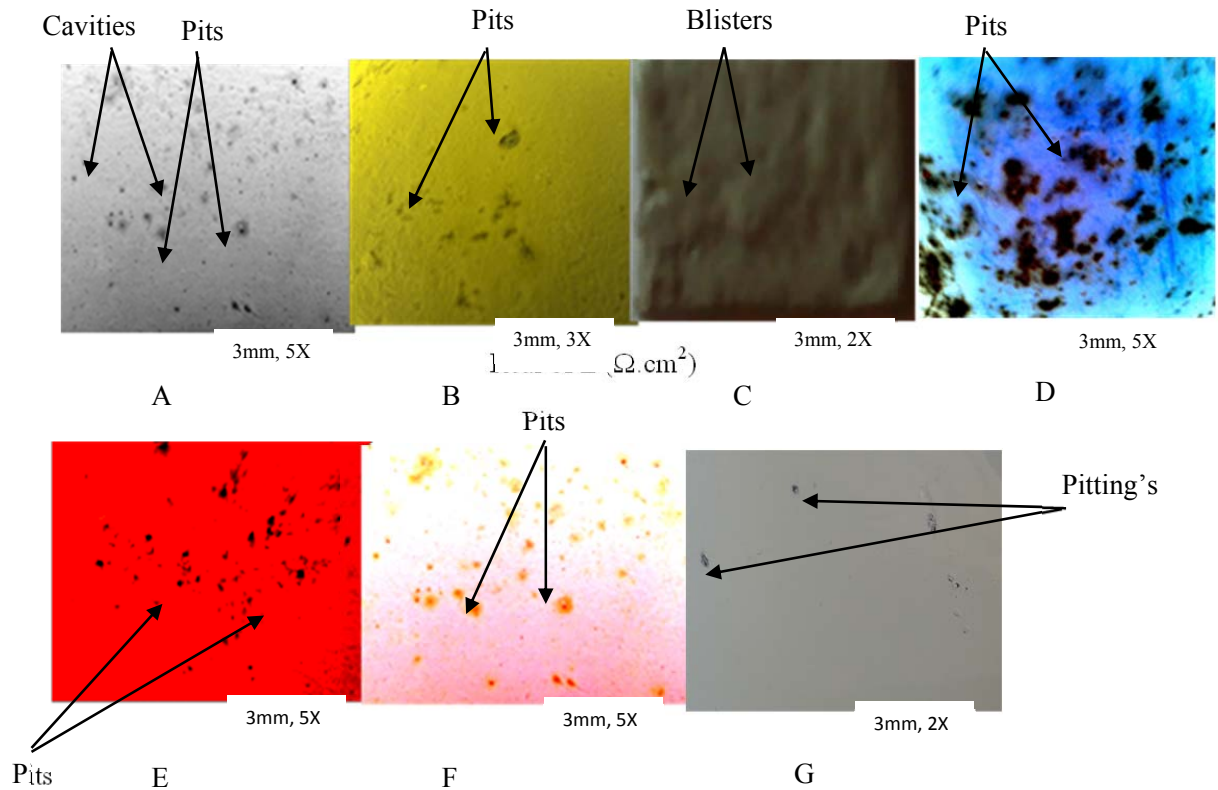

**Figure (9) Surface morphologies for: A- DENSO   B- ICI (Tinter P420)   C-Auto paint
D- TS 16949 (Easi coat) E-Lacquers   F-Numix   G-Palinal paint   at f = 50Hz and T = 25°C.**

CONCLUSIONS

From pervious discussion the following conclusions can be made:

1-The information obtained from Bode plots illustrates a significant difference in protection provided by coatings and there are various degrees of progressive failure over frequency and time.

2-The corrosion protection of paints is inversely proportional with porosities of paints i.e. that the porosity of Palinal paint lower than others paints and the TS 16949 Easi coat has a largest value.

3- EIS measurements have shown that the Palinal paint has higher corrosion resistance than other types of coatings systems and TS 16949 paint (Easi coat) show lower value of corrosion protection.

4-Microscopic observations show that the Auto paints have blistering and discoloration after test while other surface of paints shows pitting and cavities.

Acknowledgements

REFERENCES

[1] I. A. Mahmood, J. H. mohmmed and B. A. Khalaf, "Modeling of the corrosion behavior of enamel coatings in different aggressive media", Eng. & Tech. Journal, Vol.32, Part (A), No.6, 2014.

[2] T. Misovski, Mark E. Nichols, H. K. Hardcastle, "Service life prediction of polymeric materials", pp.295-308, 2009.

[3] Peter Sutcliffe, "The surface coating of car body", X-Polymers F-Car Bodies-11, 2012.

[4] D. M. Berger and Wint R. F., "New concepts for coating protection of steel structures", ASTM Special Technical Publication 841; American Society for Testing and Materials; 1984.

[5] M. Olivier and M. Poelman, "Use of electrochemical impedance spectroscopy (EIS) for the evaluation of electro-coating performance", Recent Researches in Corrosion Evaluation and Protection, Intech Publisher, 2012.

[6] B. Elsener, A. Rota and H. Bohni, "Impedance study on the corrosion of PVD and CVD titanium nitride coatings" Mat. Sci. Forum, Vol.45, pp. 29-38, 1989.

[7] Z. Ahmed, "Damage to automobiles in the eastern coast area of Saudi Arabia", Ph.D. Thesis, King Fahd University of Petroleum and Minerals, K.S.A, 1994.

[8] A. Xu, X. Wu, H. Xu, F. Jin and G. Wang, "Electrochemical impedance spectroscopy (EIS) study of vehicle protective coating performance", ICCTP 2011, pp.3827-3834, Washington, 2001.

[9] J. J. Sauy, M. T. Rodriguez, K. A. Razzaq, J. J. Carpio, and J. J. Saura, "The evaluations of anticorrosive automotive epoxy coating by means of electrochemical impedance spectroscopic", Progress in organic coating, Vol.46, pp.121-129, 2003.

[10] E. M. Derun, T. Demirozu, M. B. Piskin and S. Piskin, "The analysis of corrosion performance of car bodies coated by no nickel and low nickel zinc phosphating processes", Mat. and Cor., Vol.56, No.6, pp.412- 416, 2005.

[11] E. Hamzah and M. Kanniah, "Corrosion behavour of low carbon steel sheets for car bodies", Journal of the Mekanikal Malaysia, No.19, 2005.

[12] F. C. Walsh , C. Ponce de Leon , C. Kerr, S. Court and B. D. Barker, "Electrochemical characterization of the porosity and corrosion resistance of electrochemical deposited metal coating", Surface and Coating Technology, Vol.202, pp.5092–5102, 2008.

[13] N. C. Debnath, "Importance of surface preparation for corrosion protection of automobiles", Journal of Surface Engineered Materials and Advanced Technology, Vol.3, pp. 94-105, 2013.

[14] M. H. Al-Atia, "Comprehensive electrochemical evaluation of protective coatings properties by Sol-Gel route for stainless steel corrosion", Eng. and Tech. Journal, Vol.31, No.2, 2013.

[15] B. M. F. Perez, J.A. Gonzalez-Guzman, S. Gonzalez and R. M. Souto "Electrochemical impedance spectroscopy investigation of the corrosion resistance of a waterborne acrylic coating containing active electrochemical pigments for the protection of carbon steel", Int. J. Electro. Sci., Vol.9, pp. 2067-2079, 2014.

[16] Ultra-Light Steel Auto Body, Report of American Iron and Steel Institute Washington, D.C. 1998.

[17] Specification sheet, Report by Hubei Hongda Sunrise Trading Co., Ltd., 2014.

[18] E. Harkonen, B. Dıaz, J. Swiatowska, V. Maurice, A. Seyeux, M. Vehkamaki, T. Sajavaara, M. Fenker, P. Marcus and M. Ritalaa, "Corrosion protection of steel with oxide nano-laminates grown by atomic layer deposition", J. of the Electrochemical Society, Vol.158, No. 11, 2011.