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Investigating of Factors Affecting the Corrosion Protection of Epoxy Primer containing Calcium Hydrogen Orthophosphate and Nano Silica Using Taguchi Method

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ABSTRACT

The current essay analyzes the anti-corrosion properties of epoxy primers including anti-corrosion pigment calcium hydrogen orthophosphate and hydrophobic nano silica with various percentages optimized by Taguchi experimental design. The impact of influential factors such as the percentage of anti-corrosion pigments, percentage of nano silica and pigment to binder ratio on anti-corrosion properties of epoxy primer based on model L9 Taguchi method was considered and analyzed. The anti-corrosion pigments and nano silica were initially dispersed into epoxy resin, the samples for corrosion testing were practiced on metal panels. Furthermore, a main sample is identified to be compared with the samples chosen by Taguchi experimental method. Electrochemical impedance spectroscopy (EIS) is applied to study the corrosion inhibition performance of the primers in 3.5% NaCl aqueous solution and salt spray test. To figure out the distribution of nano silica, particles in epoxy resin were detected by scanning electron microscope (SEM). The outcomes achieved in this work revealed that solubility of pigment and corrosion inhibition are significant factors influencing corrosion resistance of the epoxy primer. Generally, it is proved that adding nano silica to epoxy primer made the number of blisters and corrosion products diminish after being exposed to corrosion test. The most appropriate results of the corrosion resistance tests presented in the sample embracing the epoxy primer loaded with 6.5% calcium hydrogen orthophosphate, 3% nano silica and pigment to binder ratio of 1. Prog. Color Colorants Coat. 10 (2017), 149-162© Institute for Color Science and Technology.

1. Introduction

Applying organic coating is recognized as one of the key methods for protecting metal structures against corrosion [1-7]. These organic coatings are being utilized in wide range in different metal industries because they are benefitable form both economic and technical aspects [2-5]. Since epoxy resin holds a good adhesion, good acid/alkali and solvent resistance, high mechanical properties and cross-linking density, it is exceedingly applied in metal protection through releasing inhibiting chemicals from the pigment to form a strong passive or barrier film [6, 7]. One

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prominent way to achieve a reliable and long term corrosion protection performance is utilizing inorganic pigments such as zinc chromate and zinc phosphate pigments with capability of releasing corrosion inhibiting species. Although zinc chromate based pigments have been used for long in industry for the sake of their excellent anticorrosive properties, these compounds are terribly toxic and make severe environmental pollution. Phosphates compounds containing zinc, aluminum and strontium have been substituted for zinc chromate pigment [1, 5, 8]. These pigments can be dissolved in water slightly and they release free ions such as phosphate, zinc or strontium in the coating matrix. These ions can participate in anodic and cathodic reactions. Conclusively, insoluble compounds can make a passive layer on the metal surface creating a metal surface protection against corrosion. This passive layer can slow down the speed of electrochemical reactions rate in the active zones on the metal surface. The pigment solubility in water plays a leading role in metal surface passivation [1, 3]. The emergence of nano technology has drawn attention of researchers to give a good consideration to polymer nano-composites within the past few years. Due to their structure or surface energy in comparison to pure polymers, nano particles can improve the physical, mechanical and chemical specifications of organic coating. Moreover, nanoparticles-based coatings are able to improve resistance against corrosion. Nano silica coatings reveal outstanding barrier properties against gases and moisture [4, 9, 14]. The surface of nano silica also affects the electrochemical behavior of the coatings [10]. A wide range of materials such as SiO_2 [4, 10, 14], TiO_2 [11], ZnO [12], nano clay have been studied in this regard [13]. Calcium hydrogen orthophosphate has not been used in anti-corrosion coatings. This pigment can be a good alternative for anti-corrosion pigments such as chromates, phosphates and other anticorrosion pigments. This work newer in corrosion industry.

The present work aims at optimizing the corrosion inhibition performance of calcium hydrogen orthophosphate and nano silica in epoxy primer by Taguchi experimental design. L9 Taguchi design was performed by selecting three important parameters including percentage of anti-corrosion pigment, percentage of nano silica and pigment to binder ratio with three levels for each parameter. The electrochemical impedance spectroscopy (EIS) and salt spray test were used to investigate corrosion inhibition performance of the coatings. In addition, corrosion inhibition properties of calcium hydrogen orthophosphate will be compared with that of zinc phosphate.

2. Experimental

2.1. Taguchi Design of Experiments

Taguchi method reduces the great number of tests using orthogonal array. The simultaneous studies of a large number of parameters can decrease the research and development expenses. The Taguchi method chooses the factors and levels for the first place [15]. Three operating factors are considered in this paper: percentage of calcium hydrogen orthophosphate, percentage of nano Silica, and pigment to binder ratio (Table 1). Taguchi method chooses standard L9 orthogonal array (Table 2) based on the number of factors and levels.

Table 1: Factors and their levels.

Factors	Symbol	Level 1	Level 2	Level 3
Percentage of anticorrosion pigment	A	8.5	7.5	6.5
Percentage of nano silica	B	3	2	1
Ratio of pigment to binder	C	2	1.4	1

2.2. Analysis of Variance (ANOVA)

A statistical measurement is used by Taguchi method to perform the analysis of variance (ANOVA). The source of variation was assessed by the analysis of variance (ANOVA) on the experimental outcomes during corrosion process. The standard method (ANOVA) measures each impact in accordance with the equations below. Herein after, the variation is referred as factor (A) and the sum of its squares is measured as the following [16]:

$$S_A = \frac{\sum_{i=1}^{NA1} Y_{A1}^{2}}{N_{A1}} + \frac{\sum_{i=1}^{NA2} Y_{A2}^{2}}{N_{A2}} + \ldots + CF \qquad (1)$$

where Y_{An} and N_{An} are the response value and the experiments number in which the parameter A has its n^{th} level, respectively. Correction function (CF) is:

$$CF = \frac{\sum_{i=1}^{N} Y_i}{N} \qquad (2)$$

where N is the total number of the experiment according to orthogonal array and Y_i is the value of the response in i^{th} experiment. By considering the degree of freedom of the factor A, f_A, the variance of factor A (V_A) is calculated from:

$$V_A = \frac{S_A}{f_A} \qquad (3)$$

So, the portion of the effect of factor A (P_A) could be calculated according to the following equations:

$$P_A(\%) = \frac{S_{A'}}{S_T} \qquad (4)$$

$$S_{A'} = S_A - (V_e \times f_A) \qquad (5)$$

$$S_T = \sum\nolimits^{N}_{i=1} (Y_i - Y) \qquad (6)$$

where V_e is the variation of error and Y is the average of response. The Fisher ratio (F_A) which determines the meaningfulness of a factor can be calculated by the equation below:

$$F_A = \frac{V_A}{V_e} \qquad (7)$$

2.3. Materials

EPIRAN01X-75 type of epoxy resin (epoxy equivalent 434-555 g/eq) was supplied by Khuzestan Petrochemical Company. Aradur 115 Polyamidoamine curing agent (amine value 240-260 mg KOH/g) was obtained from Huntsman Company. Aerosil R812 nano sized hydrophobic silica was purchased from Evonik with the specifications given in Table 3. Different types of pigments including Nanoguard ACP®DCP (calcium hydrogen orthophosphate) and Zinc Phosphate were taken from Sensopolis and Heubach Ltd Company. Dispersing agent (Byk 2152) was supplied from BYK Company.

Table 2: L9 orthogonal array of Taguchi method.

Sample	A	B	C
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

Table 3: Nano silica specification.

Type	pH	Average particle
AEROSIL® R 812	5.5-8	8 nm

2.4. Preparation of coating systems and application

The epoxy primers were prepared according to array L9 Taguchi method (Table 2). The mixture of resin, particles, dispersing agent and solvents were gradually poured under stirring for 45 min with high shear mixer and then milling by 1 mm zirconium pearls for 60 min. Metal panels were degreased chemically by acetone and then polished mechanically with 400 emery paper. The primers were mixed with a stoichiometric value of a polyamidoamine curing agent. At the end, the final primers were applied on the cleaned metal panels using a gun spray. The thickness of the dry film after curing the primers at 80 ˚C for 40 min was 30-35 µm.

2.5. Methods

The corrosion inhibition performance of the epoxy primers was studied by a salt spray and electrochemical impedance spectroscopy (EIS) analysis. The salt spray test was conducted on 3×3 cm^2 areas of the samples in a salt spray cabin S78 V301 (made by Pars Horm Co.) according to ASTM B117. The NaCl 5% w/w solution was directly sprayed to the samples for certain times. The corrosion resistance of the coated samples was also studied by an AUTOLAB PGSTAT12 type EIS. The disturbance and frequency range of the measurement were ±10 mV and 10 kHz–10 Hz, respectively. The electrochemical system included platinum electrode (auxiliary electrode), KCl (3 N) Ag/AgCl electrode (reference electrode) and metal sheet (working electrode). The experiment was carried out on 4 cm^2 area after 7 and 35 days immersion times. A frequency response analysis (FRA) program was utilized in order to analyze the results obtained from the Nyquist and Bode plots.

3. Results and Discussion

3.1. Morphology investigation by SEM

Initially, the Mira 3 TESCAN scanning electron microscope (SEM) with a Link Systems X-ray energy dispersive spectrometer (EDS) was used to identify nano silica into epoxy primer films. The dispersion of nano silica in epoxy resin is illustrated in Figure 1. In fact, the accumulation of nano silica inside the coating decreases the corrosion resistance [4].

3.2. Assessing the Corrosion protection by EIS

An EIS technique is used to assess the electrochemical performance. Figures 2 and 3 display the Nyquist and Bode plots of the samples. These Nyquist plots actually contain two semi-circles showing electrolyte penetration to the interface of coating and metal. Figures 2 and 3 indicate the capacitive behavior in high frequencies. The impedance at low frequencies reflects an almost resisting. R_{ct}, R_c, C_c, C_{dl} values from the Nyquist and Bode plots are achieved through hiring the

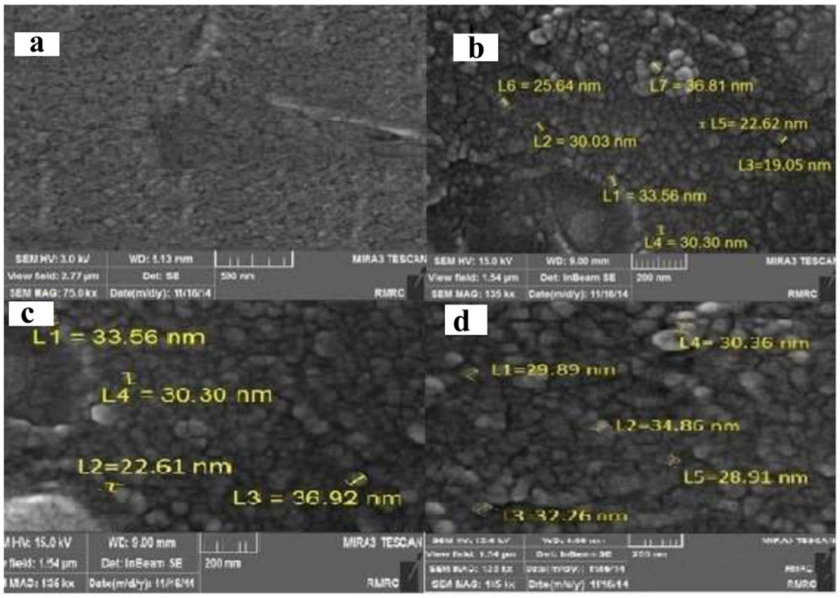

Figure 1: a) Epoxy primer without nano silica, b) Epoxy primer containing 3% nano silica, c) Epoxy primer containing 2% nano silica and d) Epoxy primer containing 1% nano silica.

electrochemical circuits (Figure 4). R_s, R_c, R_{ct}, C_c, C_{dl} and W represent solution resistance, coating resistance, charge transfer resistance, coating capacitance, double layer capacitance and Warburg effect, respectively, as shown in Figure 4. After immersion for 7 and 35 days, the parameters of coating capacitance (C_c) and double layer capacitance (C_{dl}) of the coatings are compared with each other. Coating capacitance (C_c) indicates the permeation of water into the coating. The eco-efficiency of water dielectric is more than that of the coating. Therefore, the penetration of water into the coating makes the capacitance of the coating enhance [1]. After 35 days immersion, samples 2, 3, 1 and the sample containing ZP yield the highest amount of coating capacitance (C_c). On the other hand, samples 5, 7, 8 and 9 had the lowest coating capacitance. Higher coating capacitance value demonstrates more water penetration into the coating. These are essential for the sake of their high solubility of calcium hydrogen orthophosphate in water. Eventually, the presence of nano silica and the high solubility of calcium hydrogen orthophosphate impede water penetration into the coating and bonds hydrolysis. As observed in Table 4, the double layer capacitance (C_{dl}) values increased after 35 days of immersion. Obviously, the C_{dl} is identified as a suitable factor indicating the corrosion under the film and coating delamination [1]. The lowest amount of C_{dl} f was achieved for samples 5, 7, 8 and 9 which implies that less water permeates into the coating interface in these samples. In fact, calcium hydrogen orthophosphate forms the passive layer and nano network by Aerosil R812 into the epoxy matrix makes the barrier properties better against the penetration of water and electrolyte. This nano network makes the way of reaching to the metal surface longer [4, 10]. Figure 5 shows the schematic models of the transportation of water and electrolyte in epoxy primer. In case which a suitable passive layer is not formed, water permeation takes place easier and the corrosion products are simply formed in the coating/metal interface. Moreover, this led to C_{dl} reduction. It should be considered that either the increase or decrease of C_{dl} can occur due to the progress of corrosion at the metal surface. In other words, a constant C_{dl} is an indication of a stable interface [19].

Table 5 shows the values of R_{ct} and R_c taken from electrochemical circuits. This table shows it also features lower values of R_c and R_{ct} of the coating containing ZP and samples of 1 to 4 and 6. The highest R_c and R_{ct} values were obtained for samples of 5, 7, 8 and 9. It is observed that the amounts of R_c and R_{ct} decreased in all samples after 35 days. It is essential to make a balance between water permeation into the coating and forming a suitable passive layer to access high corrosion inhibition [20, 21]. Higher Rct value is another result formation surface passivation and nano network on the metal. As the immersion time increases, the coating resistance decreases because of ions permeation into the interface through the polymer pores while the coating resistance is high, it seems that there is no simple moving direction for the ions and there are many touched areas over the coating surface [10].

Table 4: The C_c and C_{dl} values obtained from the impedance data.

Sample	C_c (x10^2)(µF.cm $^{-2}$)		C_{dl}(x10^2) (µF.cm $^{-2}$)	
	7 days	35 days	7 days	35 days
Zinc Phosphate	0.18	16.00	0.55	0.82
1	0.59	17.30	0.86	1.16
2	0.65	20.03	0.93	1.29
3	0.72	18.90	0.78	1.37
4	0.65	11.82	0.7	0.98
5	0.44	4.78	0.5	0.8
6	0.49	14.52	0.73	1.02
7	0.86	1.12	0.36	0.43
8	0.60	2.86	0.25	0.71
9	0.53	9.25	0.59	0.96

Table 5: Charge transfer resistance (R_{ct}) and coating resistance (R_c) values for different samples immersed.

Sample	R_{ct}(Ω cm^2)		R_c (Ω cm^2)	
	7 days	35 days	7 days	35 days
Zinc Phosphate	2.48×10^{4}	7.98×10^{3}	7.36×10^{5}	8.9×10^{4}
1	0.84×10^{4}	2.76×10^{2}	6.23×10^{5}	8.2×10^{4}
2	0.68×10^{4}	10.91×10^{2}	4.65×10^{5}	5.96×10^{4}
3	0.49×10^{4}	1.68×10^{2}	5.12×10^{4}	7.94×10^{3}
4	2.25×10^{4}	5.98×10^{2}	13.25×10^{5}	7.56×10^{4}
5	7.12×10^{5}	8.65×10^{4}	7.04×10^{6}	8.23×10^{5}
6	3.48×10^{4}	5.47×10^{2}	3.26×10^{6}	1.89×10^{5}
7	3.25×10^{7}	1.55×10^{6}	1.89×10^{7}	7.08×10^{6}
8	9.86×10^{5}	5.73×10^{4}	9.59×10^{6}	6.45×10^{5}
9	4.58×10^{4}	5.82×10^{3}	6.85×10^{6}	2.28×10^{5}

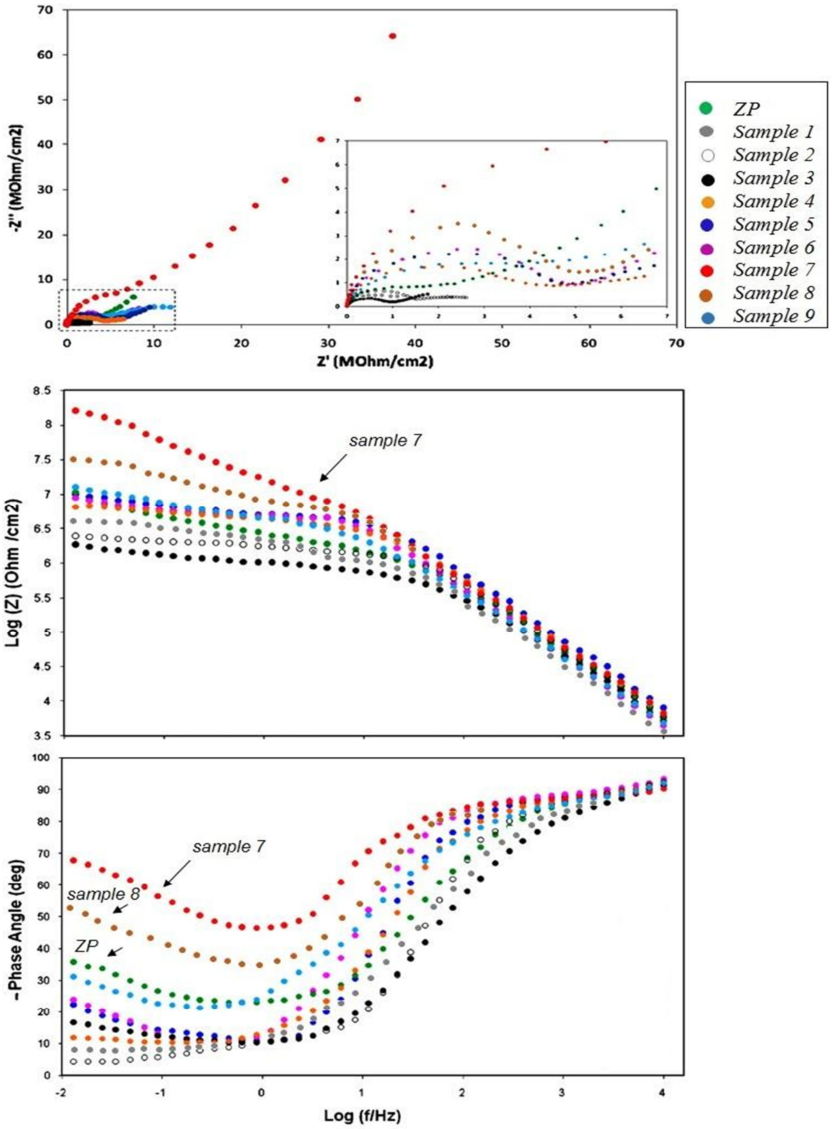

Figure 2: The Nyquist and Bode plots obtained from EIS analysis after 7 days of immersion in NaCl 3.5%.

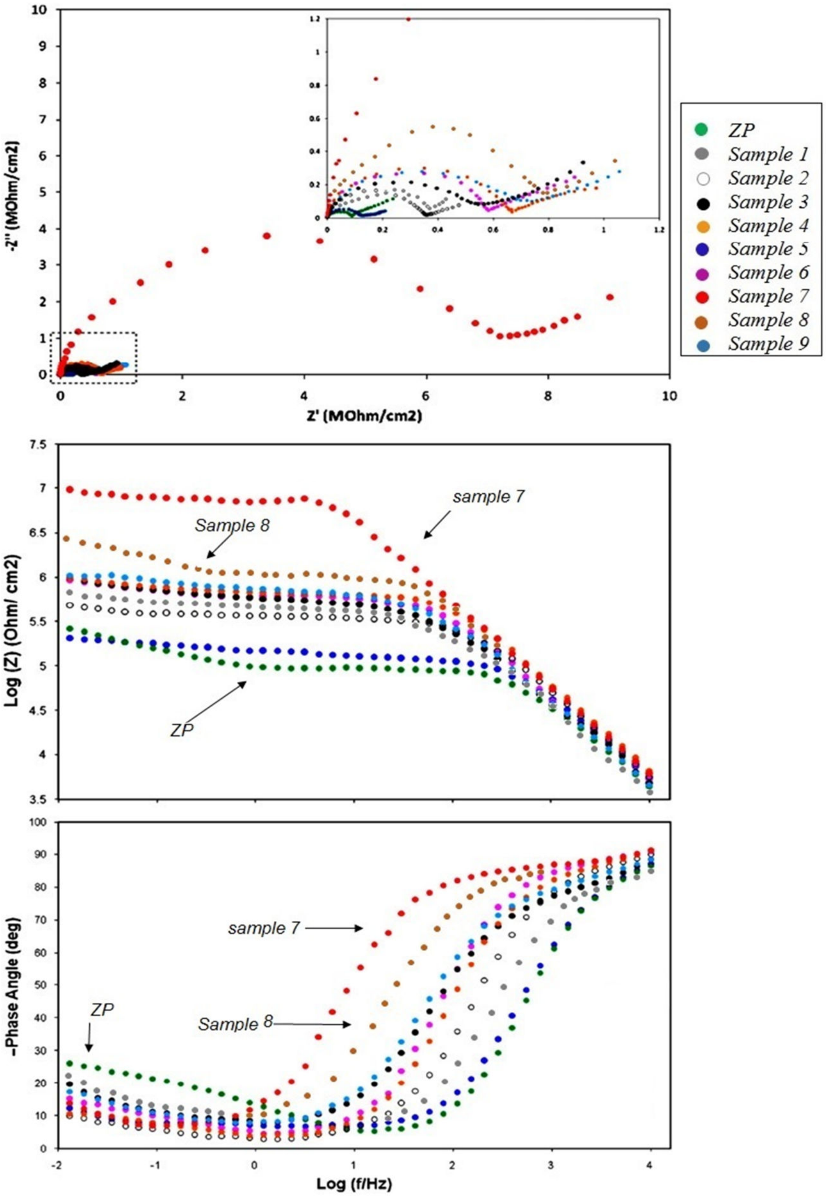

Figure 3: The Nyquist and Bode plots obtained from EIS analysis after 7days of immersion in NaCl 3.5%.

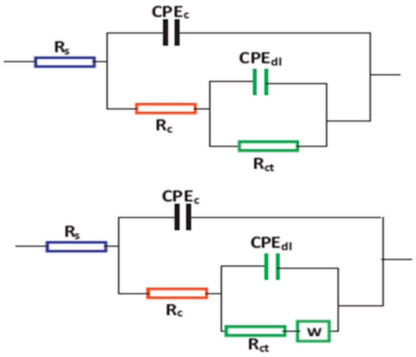

Figure 4: The equivalent electrical circuits used to analyze the results obtained from EIS analysis.

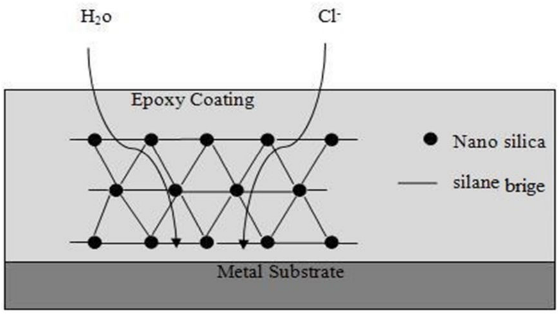

Figure 5: Schematic models of the transportation of H_2O and Cl^- in epoxy primer.

The EIS results show that coatings loaded with calcium hydrogen orthophosphate and hydrophobic nano silica (samples 5, 7, 8 and 9) have a much more effective influence on improving corrosion prevention compared with sample loaded with ZP.

3.3. Corrosion inhibition mechanisms of ZP and calcium hydrogen orthophosphate

ZP and calcium hydrogen orthophosphate are active pigments with high solubility in water. They can release Zn^{2+}, Ca^{2+} and PO_4^{3-} ions when exposed to corrosive electrolyte. Zn^{2+}, Ca^{2+} and PO_4^{3-} ions could reach the anodic and cathodic regions on metal surface causing a significant decrease of metal oxidation and reduction reactions rates. The released anions and cations by pigments could reach the metal substrate both through defects and porosities. Solubility of the pigments is important factor affecting the corrosion inhibition performance [1]. The dissociation of such pigments in water is mentioned by Esq. (8), (9):

$$Zn_3(PO_4)_2 \leftrightarrow 3Zn^{2+} + 2PO_4^{-3} \quad (8)$$

$$CaHPO_4 \leftrightarrow Ca^{2+} + PO_4^{-3} + H^+ \quad (9)$$

When the corrosive electrolyte reaches the coating/metal interface, the following reactions may occur (Eqs. (10) and (11)):

$$Fe \leftrightarrow Fe^{2+} + 2e^- \quad (10)$$

$$H_2O + O_2 + 2e^- \leftrightarrow 2OH^- \quad (11)$$

The ferrous ions can also be oxidized to ferric ions (Eq. (12)).

$$Fe^{2+} \leftrightarrow Fe^{3+} + e^- \quad (12)$$

The pigments can reveal species to reach the interface of the metal and the coating and they can interact with OH^- and Fe^{2+} ions. Thus, the passive layer holds various metal complexes such as $Fe_3(PO_4)_2$, $FePO_4$ and $Ca(OH)_2$ formed on the metal surface as indicated by Esq. (13 to 15) [1].

$$Ca^{2+} + 2OH^- \longrightarrow Ca(OH)_2 \quad (13)$$

$$3Fe^{2+} + 2PO_4^{3-} \longrightarrow Fe_3(PO_4)_2 \quad (14)$$

$$Fe^{3+} + PO_4^{3} \longrightarrow FePO_4 \quad (15)$$

3.4. SEM Studies after 24 h immersed in pigments extract solutions

Metal panels are prepared and kept for 24h inside a pigment extract solution containing 3.5 wt% NaCl solution to study the formation of passive layer by ZP and calcium hydrogen orthophosphate. Metal panels are removed from solutions after 24 h and then the formation of passive layer was studied by SEM. The results represented that the passive layer formed by ZP is very thin and it is very hard to be identified as shown in Figure (6a). Figure (6b) actually specifies that an appropriate passive layer has been formed in the presence of calcium hydrogen orthophosphate. The passive layer analysis by SEM/EDX confirms the presence of Ca, Al, Si, O and P. This pigment consists of Ca^{2+} and PO_4^{3-} ions and it seems that Ca^{+2} ions has more capacity of the passive layer.

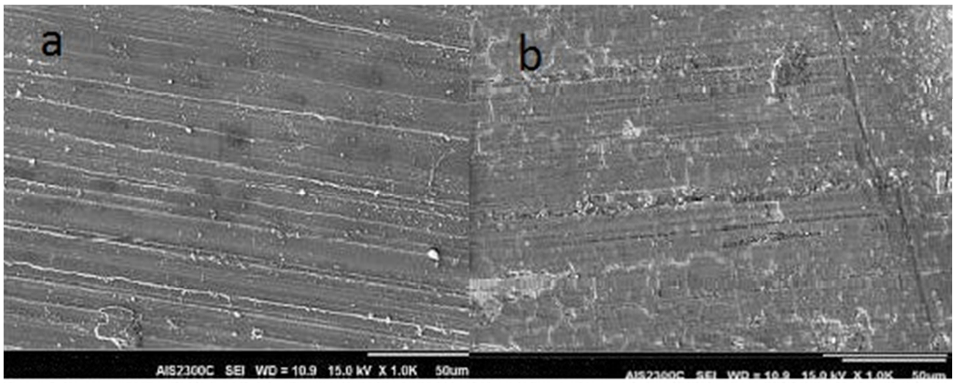

Figure 6: SEM micrographs of the samples immersed in pigment extracted Solutions (24 h) containing 3.5wt% NaCl solution; a) containing Zinc phosphate and b) containing calcium hydrogen orthophosphate.

3.5. Salt spray test and Adhesion measurements

The salt spray is recognized as a suitable test for simulating corrosive environment in order to visually analyze the anti-corrosive performance. Table 6 illustrates the test results. Figure (7) indicates the anti-corrosive performance of samples up to 200 h. Samples 1 to 6 exhibit the growth of blister and corrosive products on the coating. The number of the blisters and the produced corrosive products are remarkably reduced around the scratch in samples 7 and 8. These observations demonstrate that the pigment of calcium hydrogen orthophosphate represents a better anti-corrosive performance than zinc phosphate pigment. This is concluded by the passive layer formation by the metal complexes as well as the nano-network created by nano silica. The presence of nano-particles inside the epoxy resin prevents blister formation and coating delamination. The increased corrosion resistance is related to the final network structure which increases the moving length of the corrosive factors [11, 14]. As a result, the superior corrosion protection performance is the result of the passive layer and nano-network. The factors improving the anti-corrosive epoxy resistance include: 1) a compact coating formed by the nano-silica increases the resistance against water penetration and Cl^- ion. 2). The long direction of penetration makes the water and Cl^- ion reach the interface more difficult [11]. This theory has also been improved in similar works and the conclusions of this research have the same results as the previous works. This observation again shows lower passivation properties of ZP as it has low solubility compared with calcium hydrogen orthophosphate.

The adhesion strength of the primers were measured according to ASTM D3359-2 and displayed in Table 6. Due to the results, adhesion of the epoxy coating containing the calcium hydrogen orthophosphate and nano silica are considerably higher than the sample loaded with ZP and other samples. The least value of adhesion was observed in the sample 1 to 6 and samples 8 and 9. The best adhesion after salt spray test was observed in sample 7. As it is obvious when the electrolyte reaches the interface of the metal coating, it makes the hydrolysis of the coating bonds. Consequently, it diminishes the coating adhesion strength. The formation of corrosive products like iron hydroxides and OH^- ion decline the adhesion strength. Reduction in the adhesion of coating on the metal substrate is caused by the corrosive electrolyte diffusion into the coating/metal interface [19, 20].

3.5. Taguchi analyses

3.5.1. Taguchi analyses for coating capacitance (C_c) and double layer capacitance (C_{dl})

Coating capacitance (Cc) and double layer capacitance (C_{dl}) of the samples are given in Table 4 as electrochemical parameters. The relative contribution percentage (P) and F-value of each factor obtained by the ANOVA method are presented in Tables 7 and 8 which reveals the significance of factors based on the participation percentage (P%): (1) anti-corrosion pigment percentage; (2) nano silica percentage; (3) pigment to binder ratio.

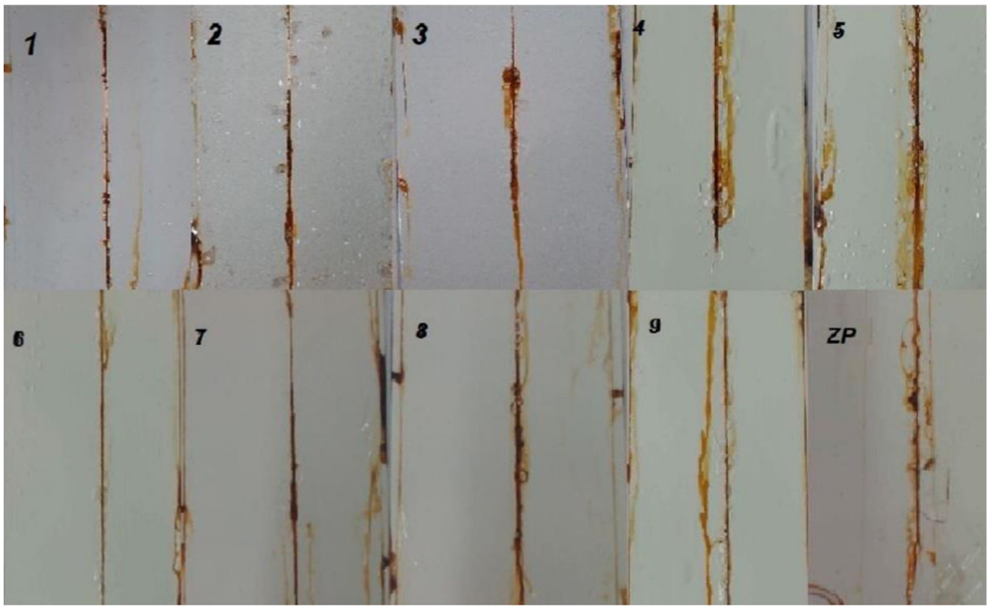

Figure 7: Macroimages of the samples after salt spray test.

Table 6: Salt spray and adhesion test results.

Samples	Salt Spray (h)	Adhesion before salt spray	Adhesion after salt spray
ZP	350	5B	2B
Sample 1	276	4B	1B
Sample 2	224	4B	1B
Sample 3	208	4B	1B
Sample 4	348	5B	1B
Sample 5	386	5B	2B
Sample 6	350	5B	1B
Sample 7	548	5B	4B
Sample 8	420	5B	2B
Sample 9	370	5B	2B

Table 7: ANOVA analysis for coating capacitance (C_c).

Factors	DOF (f)	Sum of squares (S)	Variance (V)	F-Ratio (F)	Pure Sum (S')	Percent P (%)
% Anticorrosion pigment	2	387.52	193.76	128.72	348.509	94.449
%Nano silica	2	9.518	4.759	3.161	6.507	2.949
Pigment/Binder ratio	2	7.058	3.529	2.344	4.407	0.994
Error	2	36.01	1.505	-	-	1.725
Total	8	407.104				٪100

Table 8: ANOVA analysis for double layer capacitance (C_{dl}).

Factor	DOF (f)	Sum of squares (S)	Variance (V)	F-Ratio (F)	Pure Sum (S')	Percent P (%)
% Anticorrosion pigment	2	0.554	0.277	30.004	0.536	76.614
%Nano silica	2	0.079	0.039	4.313	0.061	10.567
Pigment/Binder ratio	2	0.049	0.023	2.539	0.028	4.067
Error	2	0.017	0.008	-	-	8.752
Total	8	0.699				٪100

Table 9: Optimum conditions for coating capacitance (C_c).

Factors	Level Description	Level	Contribution
% Anticorrosion pigment	6.5	3	8.843
%Nano silica	3	1	4.256
Pigment/Binder ratio	1	3	1.226

Table 10: Optimum conditions for double layer capacitance (C_{dl}).

Factors	Level Description	Level	Contribution
% Anticorrosion pigment	6.5	3	0.292
%Nano silica	3	1	0.102
Pigment/Binder ratio	1	3	0.092

The most significant factor is anti-corrosion pigment percentage; the contribution percentage of that parameter to coating capacitance was 94.449 %. The next important factor is nano silica percentage with the participation percentage of 2.949 %, and the third significant factor is the error with the contribution percentage of 1.725 % and pigment to binder ratio with the contribution percentage of 0.994 %.

The optimum level of each factor is the level which gives the highest average value of coating capacitance. Considering maximum values, the optimum levels of significant parameters are as follows: anti-corrosion pigment percentage, level 3; nano silica percentage, level 1; pigment to binder ratio, level 3. Therefore, the predicted optimum condition is the sample which was prepared at 6.5% anti-corrosion pigment with nano silica percentage of 3% and pigment to binder ratio of 1 in the current study. The assessment of performance at any arbitrary condition can be also calculated by Taguchi method. The special performance with the lowest coating capacitance (optimum) and double layer capacitance were chosen as confirmation experiments. The predicted optimum coating capacitance of the epoxy primer is calculated as 1. 12 µF cm $^{-2}$ and 0.43 µF cm $^{-2}$ after 35 days immersion in NaCl 3.5% solution. The optimum condition for coating capacitance and double layer capacitance suggested by Taguchi method are given in Table 9 and 10.

3.5.2. Taguchi analyses for salt spray

As corrosion protection parameter, resistance against salt spray of the samples is represented in Table 6.

Table 11: ANOVA analysis for salt spray.

Factor	DOF (f)	Sum of squares (S)	Variance (V)	F-Ratio (F)	Pure Sum (S')	Percent P (%)
% Anticorrosion pigment	2	66976.91	33488.455	18.517	63360.015	72.716
%Nano silica	2	10011.571	5005.785	2.768	6394.676	12.262
Pigment/Binder ratio	2	6670.177	3335.088	1.844	3053.282	3.222
Error	2	3616.894	1808.447	-	-	11.8
Total	8	82275.555				100

Table 12: Optimum conditions and performance.

Factors	Level Description	Level	Contribution
% Anticorrosion pigment	6.5	3	98.222
% Nano silica	3	1	42.888
Pigment/Binder ratio	1	3	32.888

The relative contribution percentage (P) and F-value of each factor obtained by the ANOVA method are carried out in Table 11. Table 11 reveals the significance of factors based on the participation percentage (P %): (1) Percentage of anticorrosion pigment; (2) percentage of nano silica and (3) ratio of pigment to binder.

The most significant factor is the percentage of anticorrosion pigment; the contribution percentage of that parameter to salt spray resistance was 72.714 %. The other significant factor is percentage of nano silica with the participation percentage of 12.262 %, and the third important factor is the error with contribution percentage of 11.802 % and pigment to binder ratio with contribution percentage of 4.67 %.

The optimum level of each factor is the level which gives the highest average value of salt spray resistance (Table 12). Regarding the maximum values, the optimum levels of significant parameters are as the following: percentage anticorrosion pigment, level 3; percentage nano silica, level 1; ratio of pigment to binder, level 3. Therefore, the predicted optimum condition is the sample which was prepared at 6.5 % anticorrosion pigment with nano silica of 3 % and ratio of pigment to binder of 1, in this study. The optimum condition suggested by Taguchi method was applied and the sample's salt spray resistance is given in Table 12.

4. Conclusion

In this study, Taguchi method was applied to investigate the significance of corrosion protection properties. It has been attempted to investigate corrosion protection properties of an epoxy primer loaded with nontoxic anti corrosive pigment (calcium hydrogen orthophosphate) and hydrophobic nano silica. It gets to the following conclusions:

- SEM results showed the full dispersion of nano silica in epoxy resin.
- The results indicated that the addition of calcium hydrogen orthophosphate and nano silica to the epoxy resin could decrease the corrosion generation rate, as well as the corrosion growth probability of the metal underneath.
- Electrochemical results revealed that calcium hydrogen orthophosphate could behave like an active pigment to passive metal surface. In fact, corrosion inhibition and passivation properties of calcium hydrogen orthophosphate were considerably higher than ZP.
- The electrochemical results showed that hydrophobic nano silica particles within the epoxy primer are effective in improving the corrosion resistance of the metal.

- Using calcium hydrogen orthophosphate along with hydrophobic nano silica caused an increase in corrosion resistance of the coating that greater than corrosion inhibition properties than ZP.
- Calcium hydrogen orthophosphate and nano silica reduced the number of blisters and corrosive products on the coating surface. The coating barrier properties against electrolyte diffusion reduced in the presence of low loadings of calcium hydrogen orthophosphate.
- The adhesion loss diminished in the presence of the calcium hydrogen orthophosphate and nano silica (Sample 7). After salt spray test, the sample containing calcium hydrogen orthophosphate and nano silica had better adhesion than other samples and the sample containing ZP.
- The optimum condition for resistance against corrosion suggested by Taguchi method includes 6.5% anti-corrosion pigment, 3 % nano silica and pigment to binder ratio 1. This condition was observed in sample 7.

5. References

1. M. R. Heydarpour, A. Zarrabi, M. M. Attar, B. Ramezanzadeh, Studying the corrosion protection properties of an epoxy coating containing different mixtures of strontium aluminum polyphosphate (SAPP) and zinc aluminum phosphate (ZPA) pigments, *Prog. Org. Coat.*, 77(2014), 160-167.
2. Sh. Pashapour Yeganeh, M. R. Kalaee, Optimization of Mechanical Properties of Polyurethane/SiO_2 Nanocomposite on Polypropylene for Automotive Clear Coating by Taguchi Method., *Prog. Color Colorants Coat.*, 8(2015), 295-307.
3. R. Naderi, M. Mahdavian, A. Darvish, Electro-chemical examining behavior of epoxy coating incorporating zinc free phosphate based anticorrosion pigment, *Prog. Org. Coat.*, 76(2013), 302-306.
4. Z. Ranjbar, Sh. Ashhari, A. Jannesari and Sh. Montazeri, Effects of Nano Silica on the Anticorrosive Properties of Epoxy Coatings, *Prog. Color Colorants Coat.*, 6(2013), 119-128.
5. Pedro de Lima-Neto, Alexsander P. de Ara´ujo, Walney S. Ara´ujo, Adriana N. Correia, Study of the anticorrosive behavior of epoxy binders containing non-toxic inorganic corrosion inhibitor pigments, *Prog. Org. Coat.*, 62(2008), 344-350.
6. A. K. Malviya, S. P.Tambe, Accelerated Test Metods for Evaluation of WB coating system comprising of epoxy primer and poly urethane top coat., *Prog. Color Colorants Coat.*, 10(2017), 93-104.
7. Na. Wang, K. Chenga, H. Wu, Ch. Wang, Q.Wang, Fuhui Wang, Effect of nano-sized mesoporous silica MCM-41 and MMT on corrosion properties of epoxy coating, *Prog. Org. Coat.*, 75 (2012), 386- 391.
8. A. Kalendov, P. Kalenda, D. Vesel´y, Comparison of the efficiency of inorganic nonmetal pigments with zinc powder in anticorrosion paints, *Prog. Org. Coat.*, 57(2006), 1-10.
9. R. Joseph Rathish, R. Dorothy, R. M. Joany, M. Pandiarajan and Susai Rajendran,Corrosion Resistance of nano particle incorporated nano coatings, *Eur. Chem. Bull.*, 12(2013), 965-970.
10. F. Dolatzadeh, S.Moradian, M. M. Jalili, Influence of various surface treated silica nanoparticles on the electrochemical properties of SiO_2/polyurethane nano coatings, *Corros. Sci.*, 53(2011), 4248-4257
11. H. Shi, F.Liu, L. Yang, E. Han, Characterization of protective performance of epoxy reinforced with nano meter sized TiO_2 and SiO_2, *Prog. Org. Coat.*, 62(2008), 359-368
12. B. Ramezanzadeh, M. M. Attar, Studying the corrosion resistance and hydrolytic degradation of an epoxy coating containing ZnO nanoparticles, *Mater. Chem. Phys.*, 130(2011), 1208-1219.
13. M. R. Bagherzadeh, F. Mahdavi, Preparation of epoxy clay nanocomposite and investigation non its anti-corrosive behavior in epoxy coating, *Prog. Org. Coat.*, 60(2007), 117-120.
14. H. Dastmalchian, S. Moradian, M. M. Jalili, S. M. Mirabedini, Investigating changes in electrochemical properties when nano-silica is incorporated into an acrylic-Based polyurethane clear coat, *J. Coat. Technol. Res.*, 9(2014), 195-201.
15. N. Amini, M. Kalaee, S. Mazinani, S. Pilevar, S. O. Ranaei-Siadat, Morphological optimization of electrospun polyacrylamide/MWCNTs nanocomposite nanofibers using Taguchi's experimental design., *Int J Adv Manuf Tech.*, 69(2013), 139-146.
16. P. Patil, A.I Wasif, S.V. Anekar, J.R. Naglaes, Butea frondosa flower dye extraction optimization through Taguchi design, *Prog. Color Colorants Coat.*, 8(2015), 25-35.
17. Y. Shao, C. Jia, G. Meng, T. Zhang, F. Wang, The role of a zinc phosphate pigment in the corrosion of scratched epoxy-coated steel, *Corros. Sci.*, 51(2009), 371-379.
18. E. Legghe, E. Aragon, L. Bélec, A. Margaillan, D. Melot, Correlation between water diffusion and adhesion loss Study of an epoxy primer on steel, *Prog. Org. Coat.*, 66(2009), 276-280.
19. M. J. Gimeno, S. Chamorro, R. March, E. Or´o, P. Pérez, J. Gracenea, J.Suay, Anticorrosive properties

enhancement by means of phosphate pigments in an epoxy 2k coating. Assessment by NSS and ACET, *Prog. Org. Coat.*, 77(2014), 2024-2030.

20. E. AliBakhshi, E.Ghasemi, M. Mahdavian, Corrosion inhibition by lithium zinc phosphate pigment, *Corros. Sci.*, 77(2013), 222-229.
21. E. Alibakhshi, E. Ghasemi, M. Mahdavian, Optimization of potassium zinc phosphate anti-corrosion pigment by Taguchi experimental design, *Prog. Org. Coat.*,76(2013), 224- 230.

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