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Optimization of Zinc Phosphating Process using Statistical Tool

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ABSTRACT: *This paper reports an investigated to evaluate the corrosive resisted characteristics of Zinc Phosphating coated mild steel. Phosphating is the process of dipping or immersing the oil seal made of cold rolled mild steel in the stock solution to resist the effects made by the engine such as corrosion resistance, rubber to metal bonding, abrasion etc. Now by making time study in the Hi Tech Arai Company, according to that the statistical tool used to quality and the process can be optimized. 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 method. The pieces are tested by salt spray method, and the results are analysis the quality of the oil seals was improved. That's the tested material was investigated by SEM Analysis for optimization, which is used for purpose of achieving best designed components. The electrochemical corrosion method to corrosive rate of the Phosphate conversion coated material is analyzed. The aim of the present work is to control the iron concentration in the Phosphating bath in order to improve the quality and adhesive properties of zinc Phosphating coating on mild steel.*

Keywords*- Zinc Phosphate, corrosion resistance, electrochemical corrosion, Salt spray test, Taguchi method.*

I. Introduction

Phosphating is a conversion coating treatment largely used in many industries as a surface preparation for coating by paints and to increase corrosion resistance. Phosphating is the metal pre-treatment process for the surface treatment and finishing of ferrous and non-ferrous metals. Due to its economy, speed of operation and ability to afford excellent corrosion resistance, wear resistance, adhesion and lubricate properties, it plays a significant role in the automobile, process and appliance industries. Phosphate coatings serves as a conversion coating in which a dilute solution of phosphoric acid and phosphate salts is applied via spraying or immersion and chemically reacts with the surface of the part being coated to form a layer of insoluble, crystalline phosphates. During the process of Phosphating, problem is overheating of the bath solution, which causes an early conversion of the primary phosphate to tertiary phosphate before the metal has been treated which results in an increase in the free acidity of the bath and consequently delays the precipitation of the phosphate coating. The low temperature Phosphating processes have become more significant today due to the escalating energy costs. However, low temperature Phosphating processes are very slow and need to be accelerated by some means. Acceleration of the Phosphating process could be achieved by chemical, mechanical and electrochemical methods. Phosphate conversion coatings can also be used on aluminum, zinc, cadmium, silver and tin. Phosphate coatings are often used to provide corrosion resistance, however, phosphate coatings on their own do not provide this because the coating is porous. Therefore, oil or other sealers are used to achieve corrosion resistance. This coating is called a phosphate and oil (P&O) coating.

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. The corrosion protection characteristics of zinc and manganese phosphate coating results shows 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 zinc phosphate coating was found to be able to be formed in short times with chemically stable and fine-crystallized film structures, which was quite suitable to be applied as the primer for the purpose rust-proofing of the surface of steel substrate.

II. Experimental work

In Hi tech Arai Company they are having the main problem of low production rate and less quality in Zinc Phosphating of oil seals. To analyse the problems in the company to alternative solution was determined for Phosphating process. By making of the zinc Phosphating process the degreasing is important to remove dust, grease and any other contaminates in the materials. Pre-treatment are conducted to material becomes suitable to form corrosion resistance and metal to rubber bonding. Phosphating process to corrosion resistance of phosphate conversion coating is applied on the material. Rinsing is the process of cleaning/washing the materials between the each process between the treatments. The making solution are taken from different bucket/measuring flask.

Cold Rolled Mild Steel Sheet is cut into pieces of 1 X 1 cm2 of cross sectional area shows in Fig 1. Cold Rolled Mild Steel to buildings corrosion resistant solutions for the process. In Degreasing process one litre of deionized water is taken in the bucket/measuring flask and to mix the 15g of sodium hydroxide, 70g of tri-sodium phosphate, 45g of sodium carbonate. The small piece of mild steel is taken with clamp to immerse into the degreasing solution with appropriate timing shows in Fig 2. Pre-treatment is otherwise called as surface treatment. The mild steel was pre-treated before the Phosphating process. Surface treatments are conducted by two different baths. First 1% of HCl solution is prepared in 1000ml of deionized water and that the solution is heated at 60^{o}C. Second 1% of Oxalic solution is prepared in 1000ml of deionized water and each solution is kept in separate flask/bucket. After the decreasing process the material are immerse into pre-treatment process in appropriate time shows in Fig 3.

In entire process deionized water is used for better coating. Water rinsing is kept in between the each process shows in Fig 4. Phosphating solution was prepared by adding 142ml of nitric acid (HNO_3) in 67%, 380ml of orthophosphoric acid (H_3PO_4) in 75%, 160g of zinc oxide (ZnO) and some amount of trisodium phosphate tetrahydrate ($Na_3PO_4.12H_2O$) was taken in the bucket/flask to make exact one litre of stock solution. During the Phosphating process 75 ml of stock solution is diluted by 6 litre of deionized water. Finally the materials are immersing in a Phosphating solution with proper timing and temperature shows in Fig 5. Fig 6 shows the Phosphating process to zinc Phosphate is coated on the material.

By changing the production of Phosphating process parameter with different levels to zinc Phosphate process are investigated. Change the Dipping time and temperature in different Phosphate process is easily achieved. Different factors are namely decreasing dipping time, Surface conditioning temperature and dipping time, Phosphating process time and temperature. Three levels of the parameter factors were involved during this study of investigating the corrosion protection capability of phosphate conversion coating values are tabulated in TABLE - 1. In these factors, number of parameter is 6 and number of level is 3. By using Array selector from the Taguchi method to L18 Array is selected. Based on the L18 array to this factors are arranged in sequence order shown in TABLE - 2. Set of each process to the metal are coated and the weight of the materials are taken by using measuring machine in terms of milligram.

1.1. Electrochemical corrosion test

Corrosion can be defined as the deterioration of materials by chemical processes. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process $M \rightarrow M^+ + e^-$ is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a depolarizer. Zinc phosphate conversion coating was also analysed to evaluate the film's corrosion protection performance using the electrochemical impedance spectroscopy (EIS) technique in the 5% NaCl test solution shows in Fig 7.

2.2. Salt spray test

The salt spray test is a standardized test method used to check corrosion resistance of coated samples shows in Fig 8. 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 Salt Spray Test using 5% of neutralized salt solution (NaCl) in deionized water (NSS) at the temperature of 35°C. This produces a corrosive environment of dense saline fog in the chamber so that parts exposed in it are subjected to severely corrosive conditions. The zinc Phosphate coated material is tested in a salt spray test at 48 hrs. Each on hour 5% of NSS solution in a one litre of deionized water is used. P^H value of the solution is 7.2 and working temperature of test is 27^{o}C.

III. Results and discussion

The results in evaluating the corrosion protection performance of the phosphate conversion coatings using electrochemical corrosion technique were shown in the diagrams Fig 9. Corrosion can be defined as the deterioration of materials by chemical processes. Both the coated and non-coated materials are conduct the electrochemical corrosion test based on the result in the test to the zinc Phosphate coated materials have more corrosive resistance than non-coated material. Linear polarization resistance is higher in coating material. Based on the electrochemical corrosion test to the I_{corr} values is better than without coating. Obtained results from the Potentiodynamic polarization curve to the materials are compared and their values are tabulated in TABLE - 3. The effect of processing parameters on the salt spray test results of zinc phosphate conversion coated samples were analysed by using the Taguchi method.

After complete the salt spray test, the set of metals are again weighted and difference between the before and after weight are noted. It's shown in TABLE – 4. In Taguchi method, the difference to SN value (Signal to Noise ratio) is calculated for each experiment by Eq 1.The SN values are tabulated by each level of SN values are averaged to entered in TABLE – 5

$$SN_i = -10log\left(\sum_{u=1}^{N_i} \frac{y_u^2}{N_i}\right) - - - - - - - - (1)$$

Fig 10. Displays the signal to noise (S/N) ratio response curve, which was summarized and drawn with reported data of TABLE - 5. It is noted that the degreasing dipping time levels with their S/N ratio relationship to performance of the each levels are calculated. 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 S/N ratio value and the three levels for each parameter is analysed based on the experimental results shown in Table 5. Based on that, the analytic results of other parameters are shown in Fig 11-15. In the TABLE - 5 to best level of the each parameter are obtained by using the Taguchi method. Based on that, TABLE – 2 No 5 arrangements are suitable method to improve the product quality of metals. So keep the degreasing dipping time 3 minutes, HCl solution dipping temperature 60°C with 3 minutes dipping time, oxalic acid dipping time 5 minutes also Phosphating dipping time 25 minutes & temperature 60°C to better coatings are obtained.

Scanning Electron Microscope (SEM) is an electron microscope. SEM to focus the material structure up to Nano level. Conducting the SEM analysis on the both zinc Phosphate coated material and after salt spray tested material. Coated material to understand the crystalline structure of the material in Fig 16. SEM analysis on salt spray tested material to effect of the salt reaction on the material and deposition of salt on the material are checked in Fig 17.

IV. Figures and tables

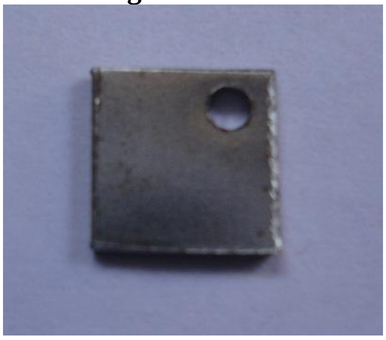

Fig. 1 Before Phosphating process

Fig. 2 Degreasing process

Fig. 3 Surface conditioning

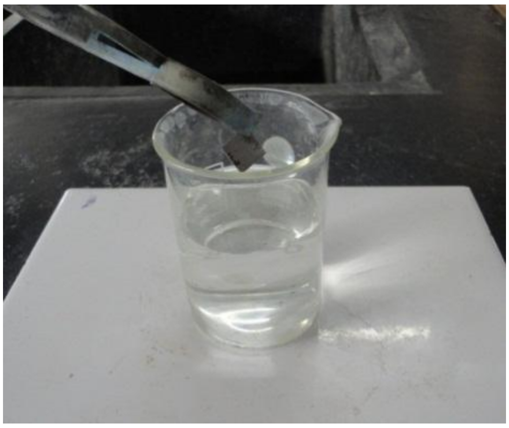

Fig. 4 Water Rinsing

Fig. 5 Phosphating process

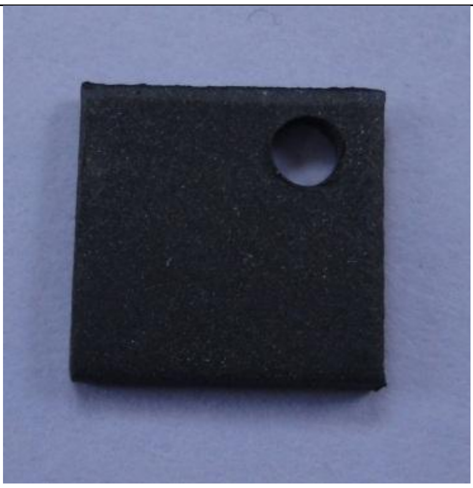

Fig. 6 After Phosphating process

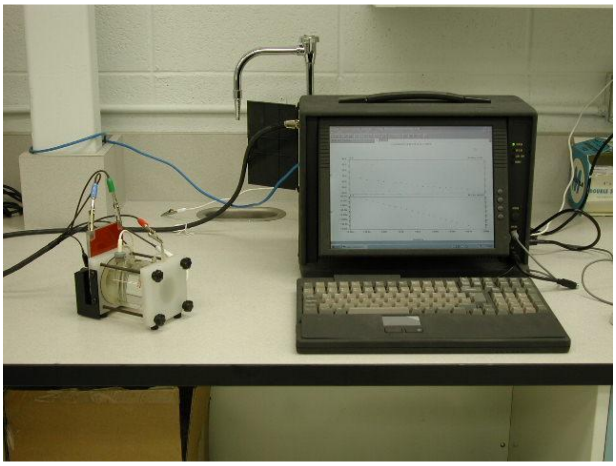

Fig. 7 Electrochemical Corrosion Test

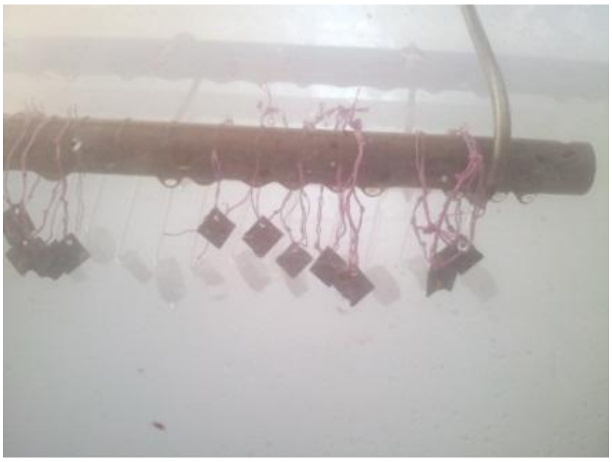

Fig. 8 Salt spray Test

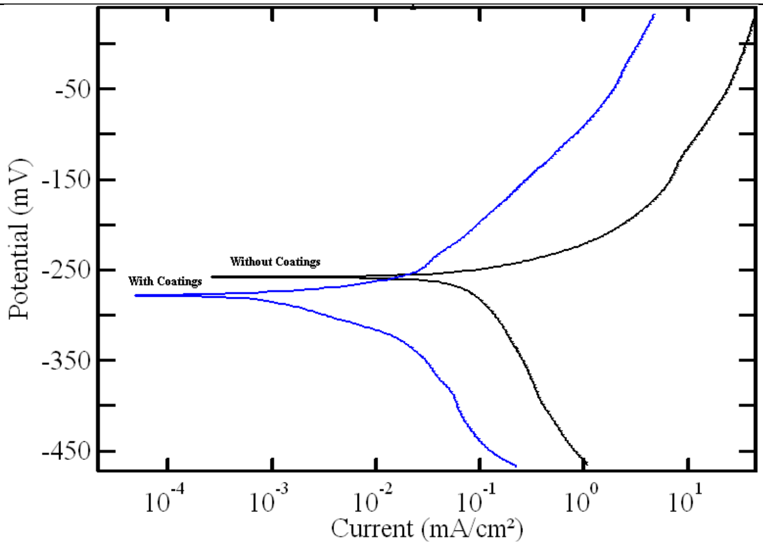

Fig. 9 Potentiodynamic polarization curve

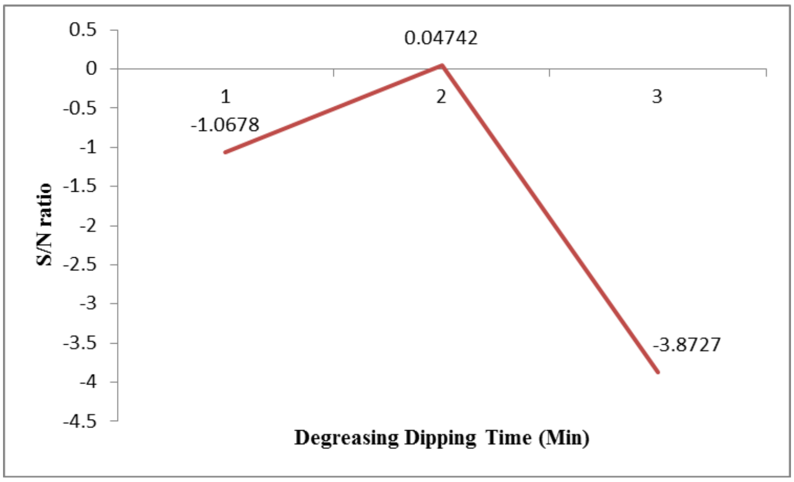

Fig. 10 S/N ratio Vs Degreasing dipping time

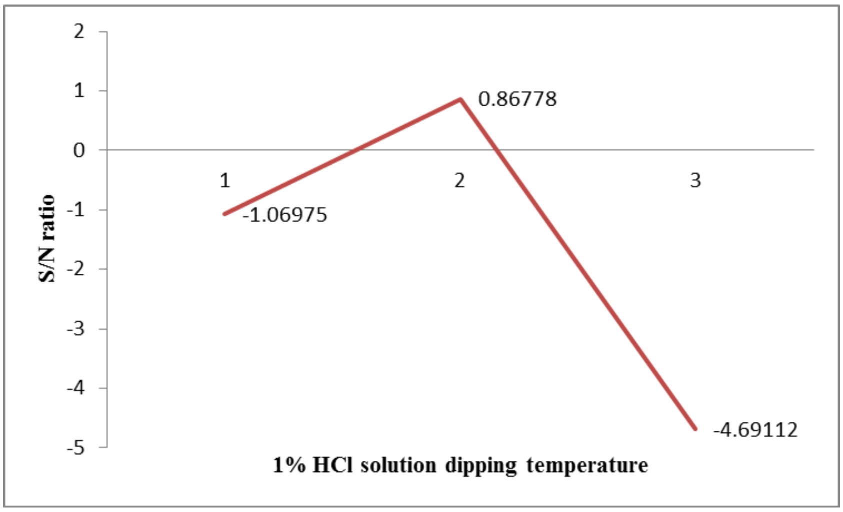

Fig. 11 S/N ratio Vs 1% HCl solution dipping temperature

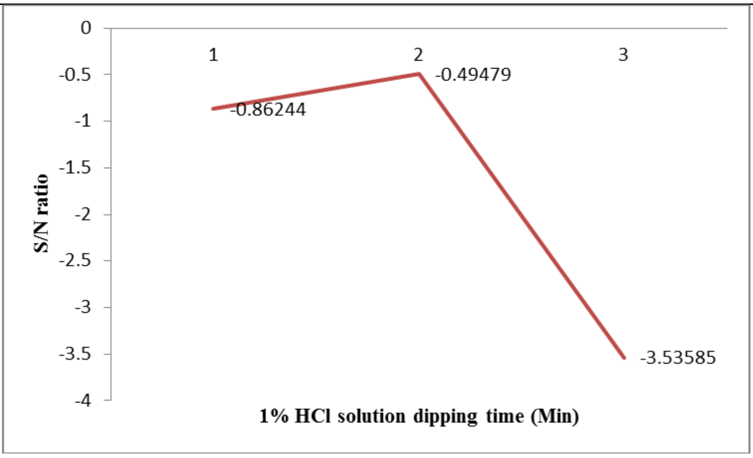

Fig. 12 S/N ratio Vs 1% HCl dipping time

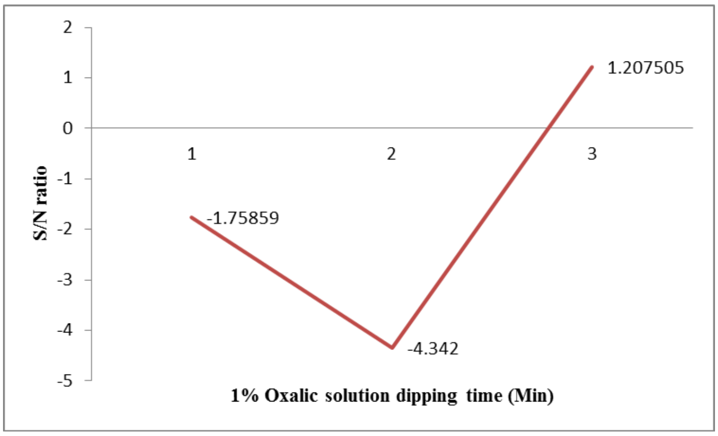

Fig. 13 S/N ratio Vs 1% oxalic solution dipping time

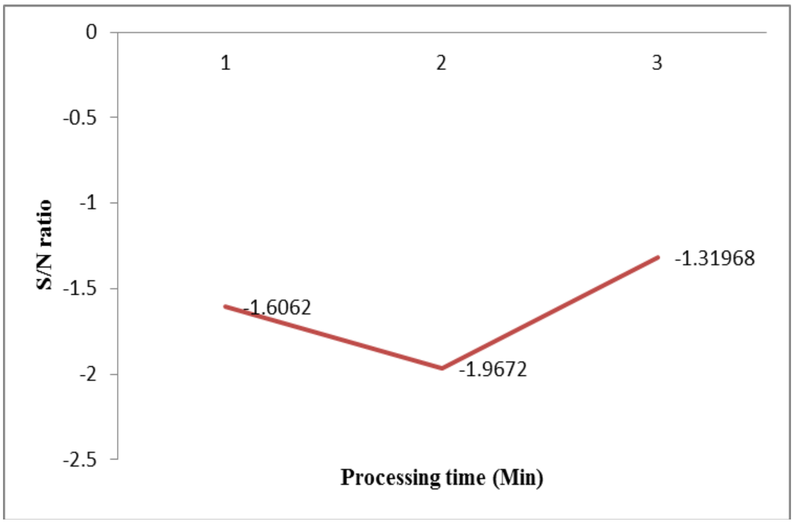

Fig. 14 S/N ratio Vs Processing time

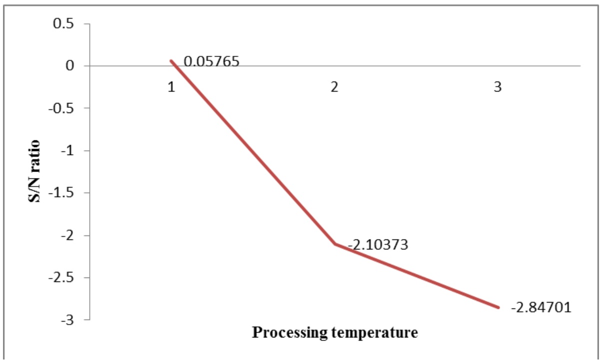

Fig. 15 S/N ratio Vs Processing temperature

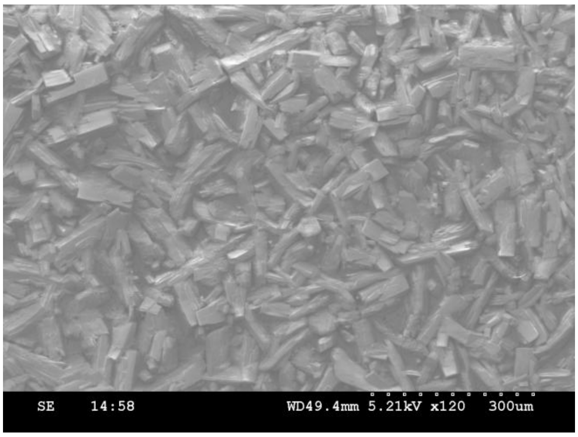

Fig. 16 SEM analysis for after Phosphating

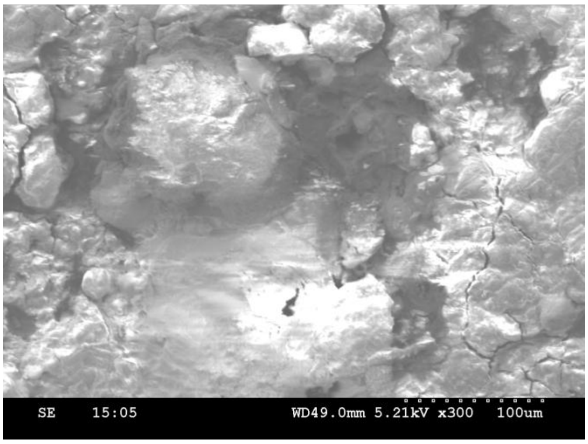

Fig. 17 SEM analysis for after salt spray test

TABLE – 1Factors for phosphate conversion coating

FACTOR		LEVEL		
		A	B	C
P1	Degreasing dip. Time (Mins)	1	3	5
P2	1% Hcl Soln. Dip. Temp.(^{o}C)	50	60	70
P3	1% Hcl Soln. Dip. Time(Mins)	1	3	5
P4	1% Oxalic Soln. Dip.Time(Mins)	1	3	5
P5	Processing Time (Mins)	15	20	25
P6	Processing Temperature (^{o}C)	60	65	70

TABLE – 2L18 array for phosphate conversion coating

No.	P1	P2	P3	P4	P5	P6
1	1	50	1	1	15	60
2	1	60	3	3	20	65
3	1	70	5	5	25	70
4	3	50	1	3	20	70
5	3	60	3	5	25	60
6	3	70	5	1	15	65
7	5	50	3	1	25	65
8	5	60	5	3	15	70
9	5	70	1	5	20	60
10	1	50	5	5	20	65
11	1	60	1	1	25	70
12	1	70	3	3	15	60
13	3	50	3	5	15	70
14	3	60	5	1	20	60
15	3	70	1	3	25	65
16	5	50	5	3	25	60
17	5	60	1	5	15	65
18	5	70	3	1	20	70

TABLE - 3Comparison b/w coated and uncoated material

Property	With coating	Without coating
Corrosion rate (mm/year)	0.764903	9.1173
LPR (Ohm.cm^2)	126.29	10.595
I_{corr} value	0.0659968	0.7866558

TABLE – 4Weight of the material

Material Details			
No.	Coated material (mg)	After salt spray test (mg)	Difference (y_u)
1	543.9	543.4	0.5
2	533.1	532.0	1.1
3	605.6	604.0	1.6
4	594.9	593.7	1.2
5	591.9	591.7	0.2
6	569.5	567.9	1.6
7	590.4	588.9	1.5
8	545.4	543.8	1.6
9	549.6	548.2	1.4
10	583.0	582.1	0.9
11	589.1	587.9	1.2
12	536.3	534.1	2.2
13	527.9	527.5	0.4
14	604.3	603.0	1.3
15	565.0	563.2	1.8
16	572.4	570.0	2.4
17	577.3	576.3	1.0
18	593.9	592.1	1.8

TABLE - 5S/N ratio value for each parameter

Level	1	2	3	Δ (Range)	Rank
P1	-1.0677	0.04742	-3.87274	3.920158	3
P2	-1.0698	0.86778	-4.69112	5.558895	1
P3	-0.8624	-0.49479	-3.53585	3.04106	4
P4	-1.7586	-4.342	1.207505	5.549502	2
P5	-1.6062	-1.9672	-1.31968	0.647515	6
P6	0.0577	-2.10373	-2.84701	2.904657	5

V. Conclusion

Based on the Taguchi method to better sequence of the process is evaluated. Salt spray test to corrosion resistance and weight loss of the material is calculated. Weight difference to SN value and Range of each parameter are calculated using the S/N equation. Averaging the S/N ratio for each parameter to Range and rank of the parameter are obtained and to that Better Phosphating parameter is determined. Electrochemical corrosion test to corrosive rate of the coated and non-coated materials are analyzed. The results in testing the corrosion protection performance of the phosphate conversion coatings are discussed for both the material. SEM Analysis to crystalline structure of the material is obtained. Based on that, material behaviour is discussed. ANOVA table to Taguchi method result are compared and to give the better processing parameter value.

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