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Optimization of Process Parameters of Manganese Phosphate coating developed on En-36 Steels by Statistical Design of Experiments

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Abstract: Phosphate is a chemical conversion process in which constituents of a metal surface with a view to produce thin adherent protective coating of insoluble crystalline phosphate by reaction with phosphoric acid solution. This conversion coating should have strong interfacial adhesion and porous enough. The growth of phosphate coating is influenced by method of cleaning of metal surface to be treated before treatment, use of surface activating rinses and acid or alkaline content of phosphate solution. Manganese phosphate coating can produces a dark grey black phosphate layer in combination with suitable post treatments on En-36 steel samples. The quantitative assessment of coating was done by stripping method and corrosion resistance was evaluated qualitatively by salt spray test according with ASTM B 117 Standard. The process parameters employed to produce phosphate have been optimized using statistical design of experiments. The regression equations were derived for each set of experiment and depending on the numerical value of the coefficient of each parameter its influence was assessed. The parameters like The moil Grenadine 112 content, steel wool content and process time showed the synergetic effect on the resulting phosphate quality.

Keywords: Manganese Phosphate coating, stripping method, salt spray testing, statistical design of experiments ,regression equations, acid ratio, process time, steel wool content, The moil ran dine 112 content, etc.

I. INTRODUCTION

Phosphate coating is the treatment of iron steel, galvanized steel, or aluminum with dilute solution of phosphoric acid and other chemicals to produce mildly protective layer of insoluble crystalline phosphate[1-3]. Manganese phosphate coating is used as an oil base, which can intensify the black colour to reduce friction by providing lubricity , as a buffer to prevent galling on the heavy loaded gears ,as a corrosion protection of Nd Feb. magnet and as base for paint.

Various factors such as process time, extent of water rinsing, bath temperature, acid ratio and bath composition, acid content, accelerators used and iron content of electrolyte affect the quality of phosphate coating [4-7].Many researcher had used classical methods involving large number of trials to study their effect .However, by using the Statistical design of Experiments the number of experiments could be reduced drastically [8-10]. In the present research work manganese phosphate coating was adopted as corrosion protection method for selected En-36 steel samples.

Coating weight was calculated by stripping method which covers under IS 3618: 1966 while coating thickness was measured by magnetic induction coating thickness gauge. Corrosion study of phosphate coating was carried out with salt spray test with a period of 24, 48 and 72 hour. The result shows that phosphate coating developed on En-19 steel has good corrosion resistance and uniform thickness.

II. EXPERMENTAL WORK

En – 36 steel content 0.184%C, 0.223%Si, 0.694%Mn, 3.589%Ni & 0.816% Cr. En -36 steel sample were subjected to Carburized at 930^{o} C for 4 hours followed by air cooling. Then Stabilized at 900^{o} C for 45 minutes. Hardening at 840^{o} C for 45 minutes followed by oil quenching and tempered at 260^{o} C for 50 minutes.. All specimen were subjected to grit blasting to have fresh surface before phosphate. Experiments were design based on levels and interval of process variables as shown in table I.

TABLE-I: LEVELS, CODES AND INTERVAL OF VARIATION OF PROCESS VARIABLES

Process variables	Code	Upper level+1	Base level0	Lover level-1	Interval of variation
Thermion grenadine 112(g/l)	X_1	150	135	120	15
Steel wool(g/l)	X_2	6	4	2	2
Phosphate process Time (min.)	X_2	30	20	10	10

All experiments were carried out on the basis of above process variables by following as design of matrix as shown in table-II in specially fabricated phosphate cell which is schematically represented in fig.1.The process variable were chosen as levels, the upper level (+) and lower level (-) limit. Factorial design of experiments of 2^n

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type was used for carrying out the experiments where ‘n’ represent the number of variable factors. i.e. three [8].

TABLE- II: DESIGN OF MATRIX

Exp No.	Process variable		
	Thermion grenadine 112 (g/l) (X_1)	Steel wool (g/l) (X_2)	Process time (min) (X_3)
1	+150	+6	+30
2	-120	+6	+30
3	+150	-2	+30
4	-120	-2	+30
5	+150	+6	-10
6	-120	+6	-10
7	+150	-2	-10
8	-120	-2	-10
9	135	4	20

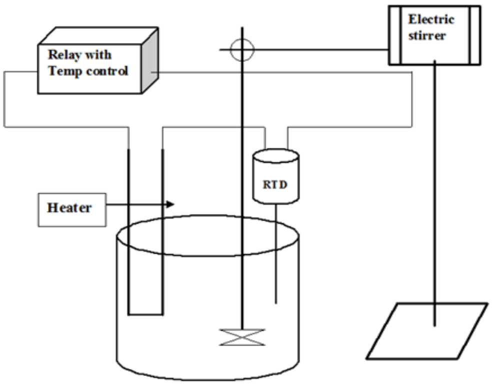

Fig.1. Schematic diagram of Experimental Setup
Fig. 1 Experimental set up of phosphate

III.TESTING & EVOLUTIONS

3.1 Determination of Coating Thickness:

The coating thickness was measured with the help of magnetic induction coating thickness gauge.

3.2 Determination of Coating Weight:

Coating weight was determined by stripping method which covers under IS 3618: 1966.

3.3 Visual inspection:

The coating obtained was visually inspected for discontinuity (patches) or to observe crystalline appearance after scratching with a finger nail.

3.4 Corrosion Testing:

Corrosion behavior of coating was studied by salt spray test as per ASTM B117-95. The exposure time was kept 24 hrs, 48 hrs and 72 hrs for each category of materials used in the investigation [11].

IV. RESULETS AND DISUSSIONS

4.1 Experimental condition and response Variables:

Experimental condition and response values are given in the table III to find out the total iron point age and acid ratio of the bath to be used for the experiments on various materials.

TABLE- III: VARIATION OF TOTAL IRON POINTAGE AND ACID RATIO FOR PHOSPHATING PROCESS

Exp. No	Process Variables			Response Variables	
	Thermion Grenadine 112 (g/l)	Steel Wool (g/l)	Process Time Min	Total Iron Point age	Acid Ratio = Total Acid Points / Free Acid Points
1	150	6	30	10.7	8.0446
2	120	6	30	10.7	5.3703
3	150	2	30	3.6	6.2668
4	120	2	30	3.6	5.5238
5	150	6	10	10.7	8.0446
6	120	6	10	10.7	5.3703
7	150	2	10	3.6	6.2668
8	120	2	10	3.6	5.5238
9	135	4	20	7.15	6.3017

Two sets of experiment were carried out for each material selected which is shown in the following tables viz Table-IV.

TABLE-IV EXPERIMENTAL PARAMETERS AND RESULTING RESPONSE PARAMETERS

Exp. No	Process parameters			Response parameters	
	Thermion grenadine 112 (g/l) X_1	Steel Wool (g/l) X_2	Process time Min. X_3	Coating weight (g/m^2) Y_1	Coating thickness µm Y_2
1	150	6	30	46.8769	29.131
2	120	6	30	45.3001	28.735
3	150	2	30	45.3422	23.911
4	120	2	30	22.7351	17.335
5	150	6	10	29.3889	20.521
6	120	6	10	37.5701	24.015
7	150	2	10	29.0149	22.205
8	120	2	10	21.6935	19.085
9	135	4	20	42.7228	23.331

From the data in Table-IV the regression coefficients were calculated and equation 1 and 2 were derived for comparative studies.

$$Y_1 = 34.7402 + 2.9155\ X_1 + 5.0438\ X_2 + 5.3434\ X_3 - 4.5666\ X_1X_2 + 0.9811\ X_2X_3 + 3.1304\ X_3X_1 - 0.6909\ X_1X_2X_3 \quad \ldots 1$$

$$Y_2 = 23.1172 + 0.8248\ X_1 + 2.4832\ X_2 + 1.6607\ X_3 - 1.5992\ X_1X_2 + 4.1717\ X_2X_3 + 0.9182\ X_3X_1 + 0.0543\ X_1X_2X_3 \quad \ldots .2$$

Where,
Y_1= Coating weight gms/m^2, Y_2= Coating thickness µm
X_1= Thermoil granodine 112 g/l, X_2= Steel wool (g/l),
X_3 = Process time, min.

The values of the factors in the above equation are shown in Table V in order to show the adequacy of the equation 1 & 2 value of coating weight (Y_1) and coating thickness (Y_2) are calculated for given combination of Thermion grenadine 112 (X_1) steel wool (X_1) and process time (Y_3).

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X_1 = (X_1 percent – 135) / 15, X_2 = (X_2 percent – 4) / 2, X_3 = (X_3 percent – 20) /10

Table-V shows the comparison between the experimental and calculated value, Thermoil granodine 112 (X_1), steel wool and process time being taken within the ranges of variation considered.

TABLE-V COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES

Properties	X1 = +1, X2 =0, X3 = -1		X1= -1, X2 = 0, X3 = +1	
	Calculated	Experimental	Calculated	Experimental
Coating weight (g/l)	29.1819	42.7228	40.2985	42.7228
Coating thickness µm	21.3631	23.331	23.0349	23.331

4.2Interpretation of Results
Two pairs of regression equations were computed from the data obtained from the three sets of experiments as shown above viz. equations 1 to 2 Equations 1 to 2 reveal the relative influences of Thermoil granodine 112 content (X_1), steel wool content (X_2) and phosphating process time (X_3) and of their interactions on the coating weight (Y_1) and coating thickness (Y_2) of phosphatized samples, within the ranges of variation considered (Refer table II).
Here positive sign of regression equation coefficient indicate significance influence of process variables on response variables, i.e. as in equation 1, X_3 has maximum positive coefficient that imply that phosphating process time play significant role in development on phosphate coating while other X1 and X_2 also has positive influence but which is lover than X_3.similarly it cal interpreted for secondary and tertiary interaction effect of process variable on response variables. The results can be shown graphically as fig.2 & 3. As shown in graph different coating weight and coating thickness were obtained with different combination of process parameters viz. content of Thermoil granodine112, steel wool & process time for all three materials. When all process parameters on upper side coating weight and coating thickness would have higher values. If all process parameters on lover side coating weight and coating thickness would have lover values.

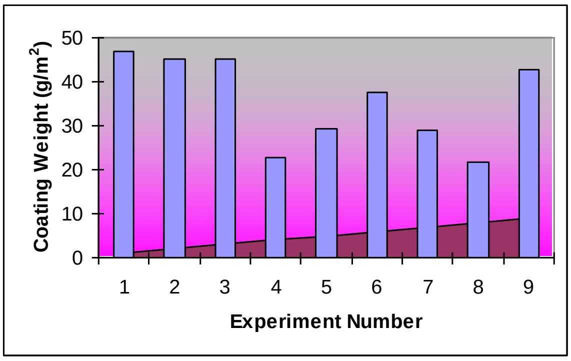

Fig. 2 Influence of process variable on coating weight

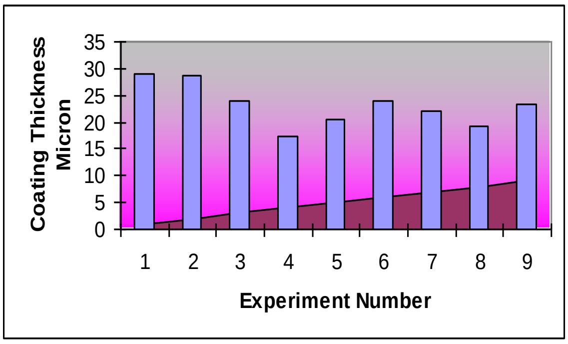

Fig. 3 Influence of process variable on coating thickness

4.3 Visual inspection after phosphating treatment
Phosphatized surfaces of En – 36 look grey in colour. After oiling, it intensify to blackish in colour , Phosphate coated sample shows crystalline characteristic mark when scratched with nail.


Fig 4 Phosphatized steel sample

4.4 Observations & remarks after salt spray tests of phosphating treatment
To evaluate the corrosion resistance of the coated samples salt spray test was performed for 24hours. En-36 steel sample shows good corrosion resistance while few of them have severe rust on the surface which treated with lower acid content. Salt spray results which performed for 24 hours was acceptable but for academic purpose the test period was extended for 48 and 72 hours which also acceptable.


Fig 5 Salt spray test of phosphatized steel sample after 24 hour

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Fig. 6 Salt spray test of phosphatized steel sample after 48 hour

Fig 7 Salt spray test of phosphatized steel sample after 72 hour

V. CONCLUSIONS

1. The review of data on manganese phosphate coating by application of design of experiments revel that the experimental values and calculated values for response variables are very closed to one another that means the statistical design of experiment used in the present case holds true.
2. Phosphate coating is found powdery type in experiments 1 and 5 which may be because of excess iron content (8.4 g/l), higher acid ratio (8.0446) & lower free acid content (8.95).
3. Salt spray results of 24, 48 and 72 hours exposure to En-36 steel shows good corrosion resistance with exception of few of them which shows one or two spot of rusting at curved surface.
4. The regression equations it can be concluded that if there was increase in Thermoil granodine112 content, steel wool content and process time coating weight or coating thickness was increased while interaction effect either binary or ternary may increase or decrease the coating weight or coating thickness according to their order of combination.
5. Higher coating weight and coating thickness is obtained with higher acid point age and with higher iron content.
6. Lower coating weight and coating thickness is obtained by excess free acid, lowering solution temperature, lowering chemical composition, lowering accelerator concentration.
7. Maximum corrosion resistance was obtained with higher acid pointage 72 point, proper adjusting acid ratio between (5.5 - 6.5) & maintaining iron content between (0.2-0.7percent).
8. The regression equations developed can now be utilized for the purpose of optimization by with the aid of a computer, incorporating the necessary constraints. However, the equations developed are valid only for the system studied and within the ranges of variation considered.

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BIOGRAPHY

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