EXPERIMENTAL ANALYSIS ON THE EFFECTS OF SODIUM HYPOPHOSPHITE CONCENTRATION, PH AND TEMPERATURE WITH THE VARYING COATING BATH PARAMETERS ON IMPACT ENERGY

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ABSTRACT

This paper discusses the effects of sodium hypophosphite concentration, pH and temperature on deposition rate. This paper also discusses the evaluation of coating strength, surface and subsurface by varying the bath parameters, percentage of phosphate, plating temperature and pH of the plating solution. Taguchi technique has been used for the analysis. In the experiment, Nickel chloride which is a source of nickel when mixed with sodium hypophosphite has been used as the reducing agent and the source of phosphate and sodium hydroxide used to vary the pH of the coating bath. The coated samples are tested for impact energy by conducting impact test.Finally, the effectsof coating bath parameterson the impact energy absorbed have been plotted and analysis has been carried out. Further, percentage contribution of coating bath parameters using Design of Experiments approach (DOE) has been analysed. Finally, it can be concluded that the bath parameters of the Ni-P coating will certainly influence on the strength of the specimen.

Key words: Bath parameters, Coatings, Design of Experiment, Fracture Toughness, Impact strength,

I. INTRODUCTION

Electroless plating is a well-established surface engineering process that involves deposition of a metal-metalloid alloy coating on various substrates. Although a variety of metals can be electroless plated, it is a chemical reduction process which depends upon the catalytic reduction process of nickel ions in an aqueous solution (containing a chemical reducing agent) and the subsequent deposition of nickel metal without the use of electrical energy. Electroless Nickel coating has received widespread acceptance as it provides high hardness and excellent resistance to wear, abrasion and corrosion. Electroless Nickel coatings are widely used for corrosion protection application in a variety of environments. It is a barrier coating, protecting the substrate by sealing it off from the corrosive environments, rather than by sacrificial action. However, in this respect, only electroless Ni–high P coating is effective in offering an excellent protection whereas electroless Ni–Low P and Ni– medium P coatings are not recommended for severe environments. Due to itsexceptional corrosion resistance and high hardness, the process finds wide application on items such as valves, pump parts etc., to enhance the life of components exposed to severe conditions of service, particularly in the oil field and marine sector.With correctpretreatment sequence and accurate process control, good adhesion and excellent service performance can be obtained from electroless nickel coating deposited on a multitude of metallic and non-metallic substrates. The properties of electroless nickel coatings depend largely on the composition of the bath used and the deposition conditions. The small amounts of additives are usually used to provide improved deposition rate, throwing power and brightness, finer grain structure and better corrosion resistance. Since electroless nickel plating process is chemical reduction of nickel ions to the nickel results from the presence of reducing agent in the solution, it always concerns with hydrogen evolution during the plating process and formation of porous surface. It greatly reduces the corrosion resistance of the coating. To remove this hydrogen from the surface of substrate and to produce pit free nickel deposits, surfactants were used as wetting agent into the plating. Pit free nickel deposits had been achieved by the addition of 150 ppm sodium dodecyl sulphate in the plating bath. The cleaning, pretreatment and the coating bath parameters play a vital role in the effectiveness of the coated surface.

II. LITERATURE SURVEY

J.P Dan., et.al, [1] have discussed the difference between two families of deposition techniques CVD and PVD and its influences on the choice of substrates and properties of the coating substrate systems.Lee Hyland., [2] hasopined that Electroless nickel prepared using sodium hypophosphite as redundant and coatings which contain phosphorus are superior compared to those of the pure metal.R C Agarwala., et.al, [3] have reviewed different electroless alloy/composite coatings with respect to its bath types, compositions, properties and its applications. They have carried out different characterisation studies on various electroless nickel-based coatings with emphasis on wear and corrosion properties.T.S.N. Sankara Narayanan, et.al, [4]have conducted experiment on Ni–P/Ni–B duplex coatings by electroless plating process and carried out evaluation of hardness, wear resistance and corrosion resistance. They have compared micro hardness, wear resistance and corrosion resistance of electroless nickel duplex coatings with electroless Ni–P and Ni–B coatings of similar thickness. R. Ramaseshan., et.al, [5] have concluded that Titanium and aluminide intermetallic coatings are gaining greater importance due to their low density, high melting temperature, good high temperature properties and oxidation resistance. They also opined that, vapour phase deposition methods can be used for coating low based carbon fibres. K. Hari krishnan et.al, [6] have discussed the development of electroless Ni-P bath their advantages, mechanisms of deposition, and applications.Linda. et.al, [7] have researched on trends of electroless nickel plating and concluded that Electroless nickel (EN) deposits are found on functional parts such as office equipment spacers to state-of-the-art multi-chip module electronic packages. H. R. Molla [8] has carried out an investigation to study the Electroless nickel–phosphorus (Ni–P) deposition with high hardness and excellent resistance to wear and abrasion. In this study, autocatalytic deposition of Ni–P alloy has been carried out on steel CK-75 sheets from bath containing nickel sulphate hexahydrate, sodium hypophosphite hydrate, thiourea, lactic acid, and sodium acetate. I.E. Ayoub [9] had discussed the characteristics of Electroless Ni-P plating treatment as applied to stainless steel substrate for improving its corrosion resistance and micro-hardness. Makoto Hino., et.al, [10] have conducted experiment to know the effects of alloying elements on zincate treatment and adhesion of electroless Ni-P coating onto various aluminium alloy substrates.

III. EXPERIMENTAL WORK

The electroless Ni–P coating is made using hypophosphite-reduced electroless nickel plating bath. Nickel chloride is taken as the source of nickel and sodium hypophosphite as the reducing agent.

3.1 Substrate material

3.1.1 Medium Carbon Steel (C-40 steel)

This steel is of particular importance because of unique combination of strength & toughness after heat treat treatment. The chemical compositions of the test material are depicted in the table 1 and the physical properties of the substrate are depicted in the Table 2.

Table 1Chemical Compositions of Mild Steel

Content	C	Si	Mn	P	Pb	S	Fe
Volume %	Max. 0.14	Max. 0.05	0.90-1.30	Max. 0.11	0.20-0.35	0.27-0.33	balance

Table 2 Physical Properties of C-40

Property	Value
Hardness	170HV max
Yield Stress	270N/mm^2 min
Tensile Strength	590N/mm^2 max
Elongation %	30 min

3.2 Specimen Preparation

Coating of metals with electroless nickel phosphorus is highly dependent on substrate surface condition. The coating specimens are prepared according to ASTM E23 standard, the corner notch is made at the centre with 2mm depth. as shown in the figure 1.The prepared samples are polished or grounded to get fine surface finish, because the coating surface depends on the texture of the substrate.

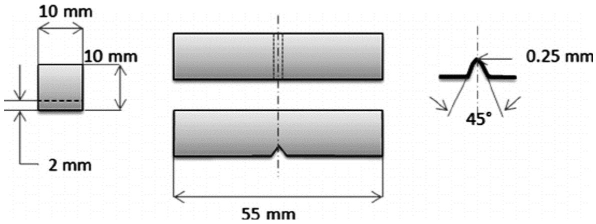


Fig. 1 Impact Specimen

The pre-treatment process can significantly affect the corrosion resistance of electroless Ni-P coatings. Many of the problems thought to be caused by improper electroless nickel plating are actually caused by failure to clean and pretreat surfaces adequately. To optimize the performance of the preplate line, proper temperature and concentration must be maintained. Filtration of the preplate chemicals will reduce the chance of drag-in of particulate matter.

3.3 Coating Setup

In the present experimental work electroless nickel phosphorus coating is done on the substrate by using the chemicals with respect to change in the percentage are Nickel chloride, Ammonium chloride, Sodium-hypophosphite, Hydrochloric acid, Sodium hydroxide, Sulphuric acid and Ammonium hydroxide. The composition of electroless nickel bath is depicted in the table 3 and the setup is as shown in the figure 2.

Table 3 Composition of Electroless Plating Bath and Plating Conditions

Bath Parameters	Value
Nickel chloride	30g/L
Sodium hypophosphite	10g/L
Ammonium chloride	50g/L
pH	8-10
Temperature	70-90^{o}c
Plating time	60 mins

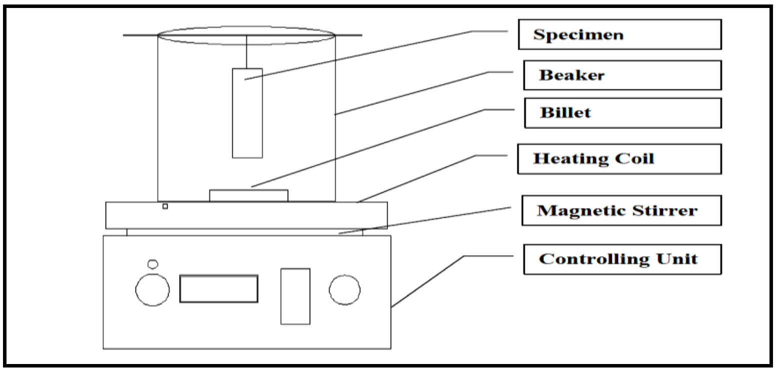


Fig.2 Schematic Diagram of Coating Setup

3.4 Experimental Setup

Mild Steel as the substrate material specimen were prepared according ASTM E23 standard and is shown in Fig 3.A corner notch is made at centre of the specimen with a depth of 2mm for the deposition of Ni-P films. The chemicals were weighed as per requirement and have been tabulated in the Table 4 and coating bath is prepared. These mixtures are kept on a heater to increase the bath temperature and its temperature is monitored, until it gets heated to the required temperature. Meanwhile, the samples are cleaned for any foreign particles and corrosion products prior to coating. Then the samples are cleaned with deionised water. The specimens after thorough cleaning are given a pickling treatment with dilute hydrochloric acid for one minute to remove any surface layer formed like rust. Finally they are cleaned with deionised water prior to coating. The cleaned samples were activated in sodium hydroxide solution.After all these operations, specimens were again rinsed in deionised water to clean the acid which adhered on the surface of the specimen, should not touch this area once cleaned.The specimen is placed in the bath for deposition duration of 1 hour. For each sample,the temperature of the plating solution and plating time were taken. The range of coating thickness was found between 10-14 microns. After deposition specimen is left to dry completely.

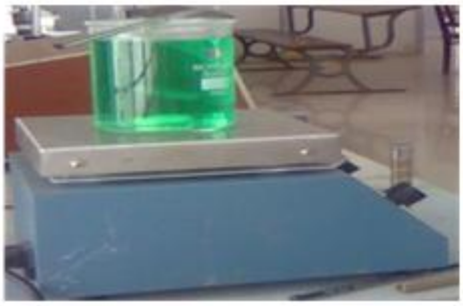


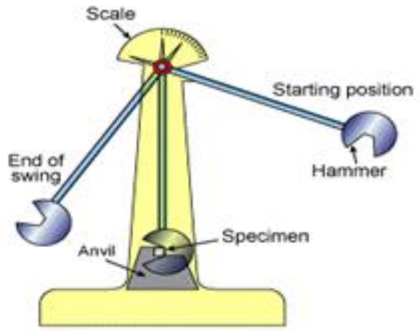
Fig.3 Coating Setup

3.5 Characterisation of coated specimen

Characterization of coating is done through impact test, which enables the influence of parametric variation on the coated specimen.

3.5.1 Impact Test

A low velocity pendulum type impact testing machine is used and it is illustrated in figure 6 & 7. The amount of energy absorbed in fracturing the test piece is measured and this gives an indication of the notch toughness of the test material.



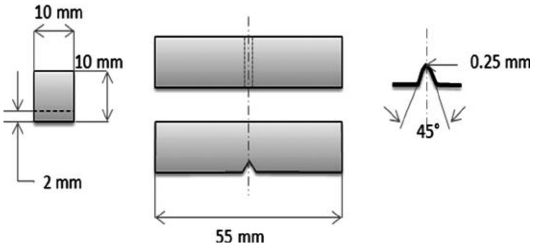


Fig.4 Impact Testing MachineFig. 5 Impact Specimen

In the present work impact strength is evaluated using a specimen with corner notch, which is more prone to failure rather than other verities of notches. A Slight modification is been made to carry out the test with corner notched specimen, and the dimensioned view of specimen used is shown in figure 3.5. The specimen prepared is placed in the impact testing machine in the space provided at an inclination of 45^0. The orientation of notch is placed in such a way that the loading plane is perpendicular to it.

3.6 Design of Experiments (DOE)

Design of Experiments (DOE) is based on the objective of desensitizing a product's performance characteristic(s) to variation in critical product and process design parameters. Through DOE, a series of tests are performed, where pre-planned changes are made to the controllable variables so that the reason for changes in the response can be observed and identified. The data collected from all the experiments in the set are analysed to determine the effect of various design parameters. The Impact energy as a result of Impact test was subjected to analysis of variance (ANOVA). The parameters chosen in the present work are given in the Table 3.1.

Table 3.1 Summary of Parameters Considered in DOE

Levels	pH	Temp.	Reducing Agent
1	6	70	10
2	8	80	20
3	9	90	30

In the present investigation an L_{27} orthogonal array is chosen. This has 27 rows and 13 columns as shown in the Table 3.2. The parameters chosen are pH, Temperature and Reducing Agent. The experiments consist of 27 tests (each row in the L_{27} orthogonal array) and were assigned with parameters. The first column in table was assigned to pH, second column was assigned to Temperature, fifth column was assigned to Reducing Agent and remaining columns were assigned to their interactions.

Table 3.2 L_{27} Standard Orthogonal Array

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$L_{27}(3^3)$	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2	2	2	2
3	1	1	1	1	3	3	3	3	3	3	3	3	3
4	1	2	2	2	1	1	1	2	2	2	3	3	3
5	1	2	2	2	2	2	2	3	3	3	1	1	1
6	1	2	2	2	3	3	3	1	1	1	2	2	2
7	1	3	3	3	1	1	1	3	3	3	2	2	2
8	1	3	3	3	2	2	2	1	1	1	3	3	3
9	1	3	3	3	3	3	3	2	2	2	1	1	1
10	2	1	2	3	1	2	3	1	2	3	1	2	3
11	2	1	2	3	2	3	1	2	3	1	2	3	1
12	2	1	2	3	3	1	2	3	1	2	3	1	2
13	2	2	3	1	1	2	3	2	3	1	3	1	2
14	2	2	3	1	2	3	1	3	1	2	1	2	3
15	2	2	3	1	3	1	2	1	2	3	2	3	1
16	2	3	1	2	1	2	3	3	2	1	2	3	1
17	2	3	1	2	2	3	1	1	2	3	3	1	2
18	2	3	1	2	3	1	2	2	3	1	1	2	3
19	3	1	3	2	1	3	2	1	3	2	1	3	2
20	3	1	3	2	2	1	3	2	1	3	2	1	3
21	3	1	3	2	3	2	1	3	2	1	3	2	1
22	3	2	1	3	1	3	2	2	1	3	3	2	1
23	3	2	1	3	2	1	3	3	2	1	1	3	2
24	3	2	1	3	3	2	1	1	3	2	2	1	3
25	3	3	2	1	1	3	2	3	2	1	2	1	3
26	3	3	2	1	2	1	3	1	3	2	3	2	1
27	3	3	2	1	3	2	1	2	1	3	1	3	2

IV. Results and Discussion

The experimental investigation on electroless nickel-phosphorus (Ni-P) coating, were made by using both acidic and alkaline hypophosphate reducer electroless plating. Nickel chloride was the source of nickel, where as sodium hypophosphite served as the reducing agent and the source of phosphate and the sodium hydroxide was used to vary the pH of the coating bath. The experimental study was made by varying the bath parameters which includes the percentage or concentration of phosphate, plating temperature and pH of the plating solution. The coated samples were tested for hardness and impact energy by conducting micro hardness test and impact test. The surface roughness of the coated samples was analysed using surface roughness tester.

4.1 Effect of coating bath parameter on the impact energy absorbed

The different types of standard notches are made in the specimens to analyse the material properties. There is a stable crack growth in all the cases except in corner notch, this is because of more cleavage triggering sites found in corner notched specimens. This cleavage triggering sites will cause unstable crack growth and hence lesser Fracture Toughness. From this it can be inferred that corner notched specimens are more prone to failure. Whereas cleavage triggering sites are crack initiating points.

4.1.1 Effect of Temperature on Impact Energy Absorbed

In this study, the influence of electroless nickel phosphorus plating bath temperature,impact energy absorbed by the specimens was analysed.Theimpact energy for different parameters conditions was plotted and the contribution of temperature on the electroless nickel plated specimens and impact energy absorbedwere analysed.

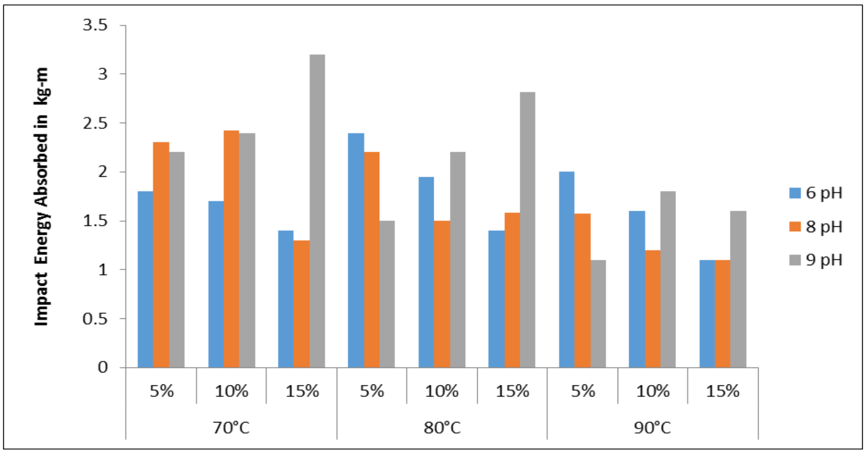

Fig. 4.1 Effect of Temperature on Impact Energy Absorbed

Figure 4.1 represents temperature effect on impact energy absorbed by the electroless Ni-P coated samples. The obtained impact energy absorbed from the impact test for all the combination of parameters was plotted and the contribution of temperature on the impact energy absorbed of the electroless nickel coated specimen was analysed. Figure 4.1 shows the dependence of impact energy absorbed on the coated samples with the change in temperature of an electroless nickel phosphorus bath. It was observed that, the impact energy absorbed increases with the increase in phosphate percentage at a temperature range of 70^{0}C. At 80^{0}C temperature, the impact energy absorbed for the 6pH and 8pH the impact energy is absorbed is more compared to 9pH. Similarly at 90^{0}C temperatureimpact energy absorbed for the 6pH and 8pH the impact energy absorbed seems to decrease.

Figure 4.2 represents pH effect on impact energy absorbed of the electroless Ni-P coated samples. The obtained impact energy absorbed from the impact test for all the combination of parameters was plotted and the contribution of pH on the hardness of the electroless nickel coated specimen is analysed.

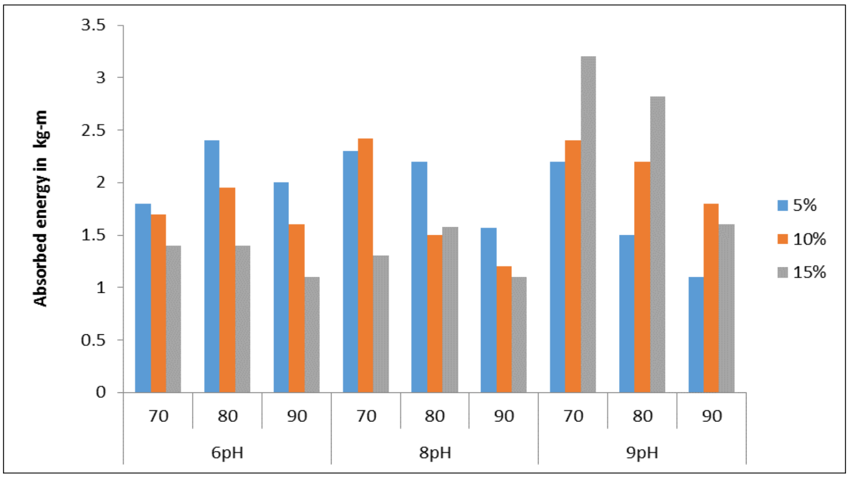

Fig. 4.2 Effect of pH on Impact Energy Absorbed

4.1.2 Effect of Phosphate on Impact Energy Absorbed

Figure 4.3 represents phosphate effect on impact energy absorbed of the electroless Ni-P coated samples. The obtained impact energy absorbed values from the Impact test for all the combination of parameters were plotted and the contribution of phosphate on the impact energy absorbed of the electroless nickel coated specimen was analysed.

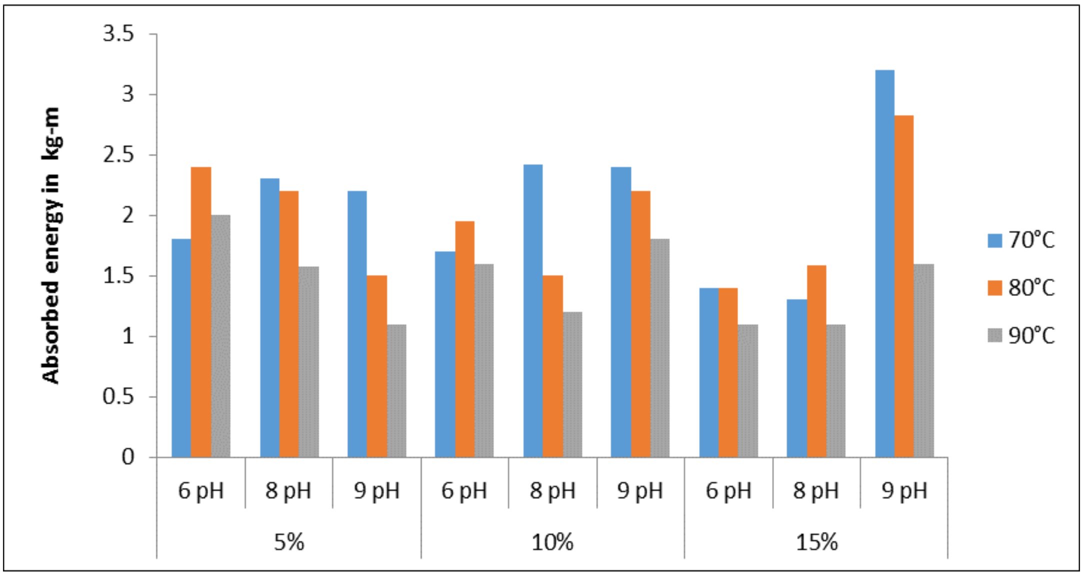

Fig. 4.3 Effect of Phosphate Content on Impact Energy Absorbed

4.2 Determination of percentage contribution of coating bath parameters by DOE

The experiments were conducted to plot the Process Parameters with their values at three levels is shown in the Table 4. The experimental values were transformed into S/N ratios for measuring the quality characteristics using MINITAB. The experimental results of impact test using L_{27} orthogonal array are depicted in Table 3.5.

Table 4. Process Parameters with Their Values at Three Levels

Levels	pH	Temp	Phosphate in grams
1	6	70^0c	05
2	8	80^0c	10
3	9	90^0c	15

4.2.1 DOE on Electroless Ni-P Coated Substrate

Electroless Ni-P coating experiment is carried-out with respect to DOE technique. In DOE Technique, the total number of experiments to be conducted is reduced to large extent with the help of an Array table. This table consists of permutation and combination of parameters under consideration. pH value, temperature and reducing agent (phosphate) were taken as the parameters under consideration and 3 Levels of parameters were chosen. An L_{27} Orthogonal Array is applied and Electroless Ni-P coating experiment is carried out according to combination of parameters given by the orthogonal array table and the adsorbed energy is recorded in each of the case. The parameters and levels chosen are given in Table 3.2 and the value of adsorbed energy for different parameters obtained is depicted in the Table 4.1.

Table 4.1Experimental Results of Impact Test Using L_{27} Orthogonal Array

Sl. No.	pH	Temp In ^{o}C	Reducing Agent in grams	Absorbed Energy in kg-m	Impact Energy in kg $m^{1/2}$
1	6	70	05	1.80	0.0197
2	6	70	10	1.70	0.0186
3	6	70	15	1.40	0.0153
4	6	80	05	2.40	0.0263
5	6	80	10	1.95	0.0213
6	6	80	15	1.40	0.0153
7	6	90	05	2.00	0.0219
8	6	90	10	1.60	0.0175
9	6	90	15	1.10	0.0120
10	8	70	05	2.30	0.0252
11	8	70	10	2.42	0.0265
12	8	70	15	1.30	0.0142

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Sl. No.	pH	Temp In °C	Reducing Agent in grams	Absorbed Energy in kg-m	Impact Energy in kg m$^{1/2}$
13	8	80	05	2.20	0.0241
14	8	80	10	1.50	0.0164
15	8	80	15	1.58	0.0173
16	8	90	05	1.57	0.0172
17	8	90	10	1.20	0.0131
18	8	90	15	1.10	0.0120
19	9	70	05	2.20	0.0241
Sl. No.	pH	Temp In °C	Reducing Agent in grams	Absorbed Energy in kg-m	Impact Energy in kg m$^{1/2}$
20	9	70	10	2.40	0.0263
21	9	70	15	3.20	0.0350
22	9	80	05	1.50	0.0164
23	9	80	10	2.20	0.0241
24	9	80	15	2.82	0.0309
25	9	90	05	1.1	0.0120
26	9	90	10	1.8	0.0197
27	9	90	15	1.6	0.0175

4.2.2 Time Series Plot for Impact Energy

Figure 4.4 reveals the time series plot of impact energy for the all the specimens which are coated under electroless Ni-P with different parameters. From the graph, it can be observed that, at the index value of 21 and 24, the specimen coated with 15 % phosphate gives higher impact energy. It is also observed that the specimen coated with 5 % phosphate gives average impact energy and index values of 3, 06, 09,12,17,18 and 25 shows the lowervalues of impact energy.

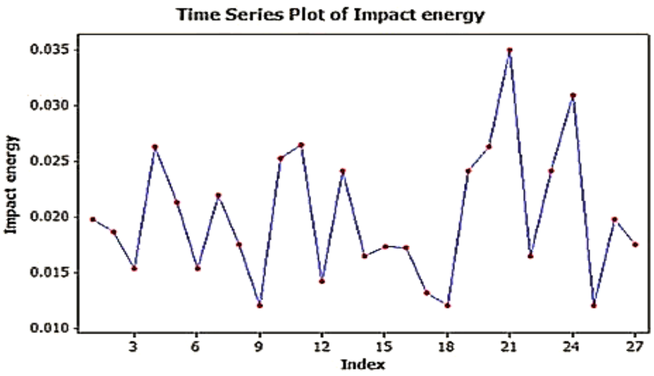

Fig4.4 Time Series Plot for Impact Energy

4.2.3 Main Effects Plot for Impact Energy

Figure 4.5 represents the influence of temperature, pH and reducing agent on the electroless Ni-P coated substrate. It can be observed that impact energy decreases as temperature increases. It is deduced that, as pH increases, impact energy also increases.

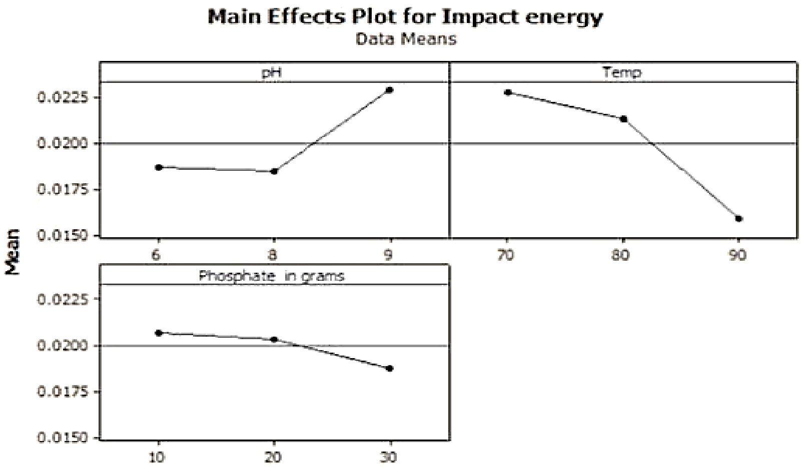

Fig. 4.5 Main Effects Plot for Impact Energy

4.2.4 Analysis of Variance (ANOVA)

The ANOVA results for electroless Ni-P coating is depicted in Table 4.2 It is seen that, concentration of pH has got the most significant influence on impact energy. The interaction(T*R) is found to have significant effect on the substrate characteristics of electroless Ni-P coating and interaction between bath temperature and concentration of (T * P) and concentration of phosphate (P ×R) shows negligible percent of contribution in coating.

Table 4.2 ANOVA Results for Impact Energy

FACTOR	SS	Dof	Mean Sq	F	P %
pH	1.98	2	0.99	4.304348	15.63786
Temp	0.94	2	0.47	2.043478	4.938272
Phosphate(R)	0.15	2	0.08	0.347826	---
(T*P)	0.52	2	0.26	1.130435	0.617284
(T*R)	1.46	2	0.73	3.173913	10.28807
(P*R)	0.09	2	0.04	0.173913	---
Error	4.58		0.23		75.5144
Total error	9.72	20			100

Note: Dof-Degrees of Freedom SS-Sum of Squares P-Percentage of Contribution

V. CONCLUSIONS

It is concluded that, the electroless Ni-P coating on Medium carbon steel shows vital role on the performance of the coated component when subjected to the change in coating bath temperature, pH value and percentage of phosphate.Electroless nickel coating done with parameters 9 pH, 70^{0}C temperature and 15 percentage of phosphate shows an increase in the impact energy of the specimen.Because of poor adhesion at the interface, the specimen coated with higher temperature has yielded low impact energy. Based on ANOVA, pH contribution is has shown maximum influence on the impact energy.Finally, it can be concluded that the bath parameters of the Ni-P coating has the influence on the strength of the specimen.

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