Abstract

Electro Galvanizing is widely used process to protect the surface of metal from getting corroded. Zinc layer is deposited on the surface of the metal. Zinc layer cuts off any contact with the environment and protects the substrate. Zinc coating have many factors on which quality of coating depends upon. Four of them are Current applied during coating, Time of deposition, Bath solution concentration and Temperature of the Bath. Samples were coated with different values of input variables. Response variables like Hardness of coating, Thickness of coating and surface roughness of coating were tested.

Using Taguchi's method and ANOVA analysis, optimum setting of Zinc coating were found. Each response variable has percentage of contributing input variable. Most visible among them were recorded for optimum operations.

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CHAPTER 1
Introduction

Electro-Galvanizing is a process widely used to cover the surface of the metal parts to protect them from corroding in an open environment. In Pakistan small and medium scaled parts are zinc coated in batch or rack process. In both of these processes most of the electroplaters in Pakistan, use hit and trial methods which have coating thickness that is unknown to most of them. Thickness of coating varies with many factors but the most dependent factors are four: Bath composition, current, temperature of the bath and time. Operating range of these four variables vary machine to machine on which electroplating has been carried on. Machine dimensions, size and shape all these factors can change the operating range variation of above mentioned four variable that has to be set to a single robust value. According to **ASTM B 633**, **Standard Specification for**
Electrodeposited Coatings of Zinc on Iron and Steel, thickness of coating are divided into four categories.

Thickness Classes for Coatings

Classification[A] Number and Conversion Coating Suffix	Service Condition[B,C]	Thickness, min µm
Fe/Zn 25	SC 4 (very severe)	25
Fe/Zn 12	SC 3 (severe)	12
Fe/Zn 8	SC 2 (moderate)	8
Fe/Zn 5	SC 1 (mild)	5

[A] Iron or steel with zinc electroplate. Numeral indicates thickness in micrometres.

Table 1 Standard Specification for Zinc Coating on Steel Substrate.

Our experiments will help to categories different set of perimeter values, on the bases of thickness, uniformity and adhesion with above mentioned table.

1.1 Electro-Galvanizing

Electro-galvanizing is a process in which metal parts/object are coated with zinc, onto the surface, to protect it from the attack of corrosion. In this process, solution bath is made from the salt of zinc e.g. zinc chloride. Anode is of pure zinc or graphite. Any other conductive material which do not dissolve during electrodeposition, other than zinc, can be made anode.

Part was hanged into the salt bath solution and made cathode. Electric current was applied and coating starts to deposit onto the surface of the part. At times agitation was required so ions flow in bath solution be as smooth as possible.

Zinc protects the surface of the metal by two means. First zinc coats all the surface of the metal which eliminates direct contact of bare metal with humid air. This blanket of zinc keep the metal protected from any attack of the environment.

Second, zinc is more electronegative than steel. When in contact with steel, zinc behave as negative end of electro-chemical cell and steel as anode. If a portion of coating get eroded from the surface of the steel part, exposing steel beneath it, negative zinc coating will attract any harmful ions which can start corrosion on the surface of the metal. Hence, even if coating get scratch away, steel under the coating is safe from the attack of harmful elements.

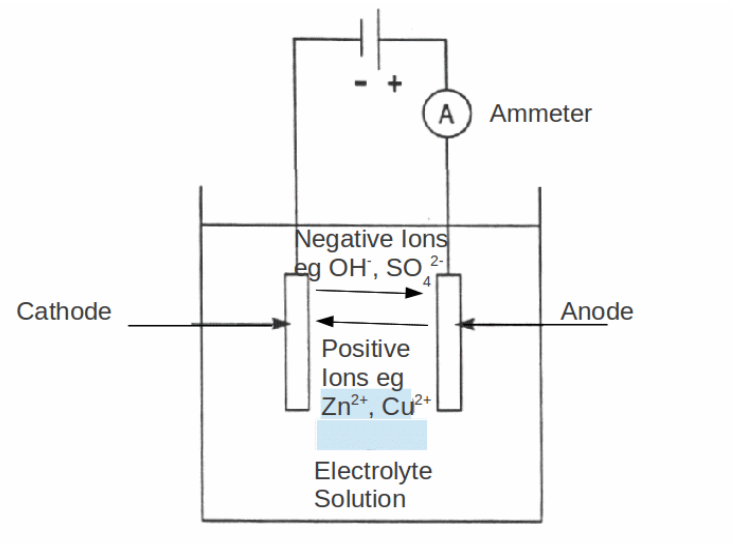


Figure 1: Symmetric illustration of Electro-Galvanizing process

The quality and thickness of coating is dependent upon many operating variables i.e. current that is applied to the part during electroplating, concentration of zinc ions present in water bath, total time provided to the part on a given current value and temperature of bath. These are four most basic variables to control the thickness and uniformity of coating. Operating range of above discussed variables are known but this range had to be narrowed down to a single value for each variable. In order to find a robust set of experiment perimeters several experiments needed to be performed. By changing one by one each value of these four variable, we will analyze the results and will be able to obtain single value for each perimeter through robust design of experimentation.

In NUST MRC a new galvanizing machine was installed. In order to find suitable operating range, set of initial trial experiments were performed. Experiments were important because main goal, to find the optimum value of each perimeter, will completely base on the values that will be obtain through these experiments. Part burning, blistering, non-uniform coating are among the defects that are very common in electrodeposition. These defects are the indication to further improve our values within the given range. Rolled steel samples were cut for this purpose and time, current, bath composition and temperature were change. Satisfactory results were noted and will be used in our main experiment. Values were obtained at the point where zinc coating starts to get uniform on the samples and end at the point just before blistering, burning occurs. These experiment resulted in the minimum and maximum values of above mentioned variables

CHAPTER 2
Literature Review

2.1 Solution Bath Composition:

There are four ways to form electroplating bath; acidic bath, cyanide, ammonia and non-ammonia bath. All these bath types are widely use and produce in Pakistan. Acidic bath has an advantage of electroplating many parts per unit volume. Rest are highly dangerous and very hard to dispose of. Fumes and pungent smell of all three baths are very hard to deal with.

Acidic baths are of two types' chloride and sulphate. Chloride baths are commonly use in Pakistan due to availability of materials, cheap, easy to handle and store. But the most important thing about chloride bath is that it can be store and reuse many months after it was prepared. With the addition of 2 brighteners 1111 and 2222 this bath reactivates and ready to produce electroplating parts. **(Winand 2011)**

The disadvantage acidic bath is that steel base materials are corrosive when in contact with this solution. So care should be taken during and at the end of electroplating. Different bath compositions that were taken out of research papers are

Chemicals	grams/liter	grams/Liter	grams/Liter	grams/Liter
Potassium chloride	185-225	187-239	188-210	200
Zinc chloride	22-38	67-90	45-75	50-60
Boric Acid	22-38	26-41	26-36	20-30
1111 Brightener	4% Vol	4% Vol	4% Vol	4% Vol
2222 Brightener	0.25% vol	0.25% vol	0.25% vol	0.25% vol

Table 2 Concentration of Acidic Salt bath solution ***(C.A Lotto and WInand, American society of Galvanizing)***

These concentrations are in research papers and books written by **Rene Winand, Herb Geduld, C.A lotto and Vana Chemicals Pakistan Limited respectively.**

During experiments only zinc concentration was changed. Zinc chloride is the basic salt for zinc electroplating. This salt produce zinc ions that will cover the surface area of samples.

Potassium chloride was also added in bath because this will form complex ions with zinc positive ions that will ease the movement of ions in bath solution. Potassium chloride can be referred as ion carrier salt. **(Fontana)**

Boric acid was added to enhance the movement of ions and throwing power of the bath. Which means ions can flow into the parts that have threads, holes, in depth geometry etc. Boric acid also act as the buffer for the solution. Because when current pass through the solution, hydrogen gas evolve from the water molecules, remaining hydroxide ions in the solution turn bath to base. **(Koleske)**This can ruin the zinc salt ions because of reaction with hydroxide ions. Boric acid neutralizes this reaction and help to maintain the PH. Operating PH range of all the solution concentrations are 4.5-5.5.

Specific gravity was kept in between 16-20. If it is below the range add potassium chloride or zinc chloride. Or if it is more then add water.

2.1 Current:

Current is very important factor that controls the deposition rate of zinc ions on the substrate i.e. mild steel. Electron flow is the reason ions are formed, so by increasing or decreasing the current will have an effect on zinc ion formation in the solution.

According to research too little current supply will result in hydrogen embrittlement of steel samples. Hydrogen evolve because of hydrolysis. Small current value will result in increasing the time to form a coating on the sample. **(C.A lotto)**This mean sample will be in hydrogen enriched environment for long enough to corrode the steel which is very harmful. But low current has the advantage of controlling the rate deposition of zinc coating and deposition morphology. **(Fonatana)** Low current will allow zinc ions to deposit on top of each other in layers. This will result in

Larger grains of zinc. Less grain boundaries will formed in layers of coating. This will slow the corrosion reactions to take place. Thus increasing the coating life. This is due to high energy zones i.e. grain boundaries are less. **(T.J Tuaweri)** Adhesion of coating of this current theory will be less.

High current values got advantage of less time span samples will be in acidic solution bath. This will cause less time for hydrogen and other oxides to damage the surface of the samples. Reaction will be fast hence coating will be done in less time. But the disadvantage of high current value is that this causes zinc grains to be small in size because zinc ions will be force to deposit where ever they got interaction with surface of the samples. **(Herb Geduld)**This will cause corrosion of samples to be fast than slow current value samples. Because high energy zones i.e. grain boundaries will be more. But according to research adhesion of the coating will be more. High current density can also cause darkness of samples that is called burning of samples. This can happen if care is not taken during coating. This blackness or burning is caused because reaction of oxides with zinc coating.**(Hiroaki NAKANO)** These oxides are formed when high current values are applied, not only zinc ions are formed at large pace but also hydrogen formation increase in the solution. Hydrogen is gas and evolve out of the solution. Hydroxide that are left behind in the solution causes blackness of the samples. Blistering can also happen. This can be control by proper agitation. **(Winand)**

Current range values that were used for experiments 2-5 $A/dm^{2.}$

Current is important parameter because the single optimum value that is set and working on one machine or tank can cause different results on different apparatus. **(Koleske)** Even the dimensions of tank can change the single parameter for optimum coating. For our convenience we are using units in $A/in^{2.}$

To determine the optimum values of current density within the range allowed, we have to perform test experiments before main experiment.

2.2 Time:

Time that is allowed to the samples in the solution bath when current is applied. Because too much and too less time can cause defects on the coating. **(T.J Tuaweri)** Time is a factor that can be increase or decrease in order to achieve desire results of coating regardless of what parameters are applied. (**Herb Geduld)** Time, like current, varies with machine to machine electroplating is being carried on. It is because of the dimensions and shape of the solution tank.

2.3 Temperature:

Solution bath composition is highly dependent upon the concentration of ions. Which directly effects the quality and nature of coating. **(Koleske)** Temperature of bath if increased will increase the energy of the ions to move around the bath. Thus theoretically it should enhance in the electrodeposition of zinc. **(Hyounso Park 1997)** Increase in temperature also help gas molecules that will evolve during operation to escape at fast rate. **(Winand)** Too little temperature will increase the resistance of the bath by slowing the movement of the ions. **(Fontana)**

Before main experiment, as describe earlier, bath composition, current and time will be check on trials samples so a narrowed down values within the range given in research papers, could be find out. **(Herb Geduld)**

CHAPTER 3
Design and trials of Experiments

Main purpose of our experimentation is to find optimized perimeters i.e. Current, Temperature, Time and bath composition. Therefor these four variables will be change and analysis of coating thickness, uniformity, adhesion will be done. All this will carried out with robust design of experiments.

Following design of experiments were formed using Taguchi's method.

3.1 Design of Experiments:

A. Temperature:

- A1: 30 C
- A2: 40 C
- A3: 50 C

B. Zinc concentration:

- B1: 60 g/l
- B2: 70 g/l
- B3: 80 g/l

C. Current:

- C1: 0.5 A/in^2
- C2: 1 A/in^2
- C3: 2 A/in^2

D. Time:

- D1: 60 sec
- D2: 100 sec
- D3: 140 sec

The L9 orthogonal array should be used. The filled in orthogonal array should look like this

Experiment Number	Temperature Celsius	Bath Composition g/L	Current A/in^2	Time Second
1.	30	60	0.5	60
2.	30	70	1	100
3.	30	80	2	140
4.	40	60	1	140
5.	40	70	2	60
6.	40	80	0.5	100
7.	50	60	2	100
8.	50	70	0.5	140
9.	50	80	1	60

Table 3 Design of experiments, L9 orthogonal array

This setup allows the testing of all four variables without having to run 81 [=3^4= (3 Temperatures) (3 Currents) (3 Zinc concentrations) (3 Time)] separate trials.

3.2 Sample preparation:

Samples for the main and trials experiments were taken from the same material "rolled Mild steel". Mild steel is the most common ferrous alloy that is used in industries and daily life. From ancient times to this day almost every industry is connected directly or indirectly with

This material. Mild steel has numerous properties that are varied accordingly for our use for example some mild steel parts are heat treated to become rail tracks and some mild steel parts are forged to become nuts and bolts. Only disadvantage this material has that it get corroded in open or even in humid indoor environment. This phenomena is also referred as rusting. Rusting cause material to deteriorate. Surface of mild steel part convert into ferrous oxide in humid environment. Ferrous oxide has dark orange, golden color which flakes out of the bulk material and erode from the surface exposing fresh metal surface underneath. This continues and thickness of part get smaller and smaller till the part under load or under stress breaks away. This is the main reason to protect mild steel from the environment. Electro Galvanization is one of many ways to protect the part. Dimensions of samples for the experimentations are: 3×3 inches of mild steel and thickness of parts were 3mm.

Small holes were also made in order to hang the parts with copper wire to complete the circuit.

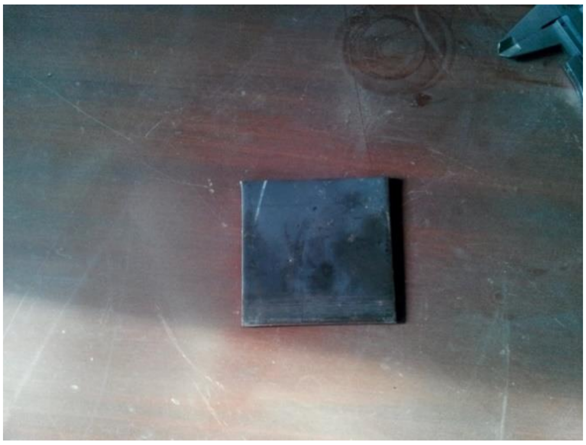


Figure 2: Rolled mild steel sample. Thickness 3 mm, Length and width 3 inches

3.3 Electroplating Tank:

Dimensions of our electroplating tank is as follows:

Length: 36 inches

Width: 25 inches

Height: 21 inches

Electroplating bath tub is made of steel. It is a general purpose electroplating machine designed for batch operations. This machine has automatic rectifier to control DC current. Rectifier itself adjust output current according to the number of parts it is carrying and salt solution resistivity.

Figure 3: Electroplating Machine in NUST MRC

In order to make above shown machine operational for rack or hanging electroplating process adjustments and modifications were made.

Since the tank of the electro deposition machine is made of steel, which is very reactive to acidic solutions, Poly Vinyl Chloride lining has to be done inside of the water tank walls and at base. PVC is non-reactive to most of the acids. This will protect the tank and will not contaminate the bath solution during the experiments. By default our electrodeposition machine has a rotating drum on top of water tank for bulk electroplating purpose. The drum was removed in order to electroplate one sample at a time. This removal allowed us to plug a

Copper strip that moves to and fro. Copper strip was made cathode and mild steel samples connected/hanged by copper wire. To and fro motion was carried in order to agitate the solution for removal of hydrogen and other gases trapped in the bath during operation. Else these gases will react with cathode to start embrittlement on the surface of mild steel samples.

Rectifier was modified and made adjustable by means of scaled (amperes) knobs in order to set the values of current. Rheostats and other electrical parts were connected and output ammeters were also plugged in the rectifier panel. To check the output current, hand held ammeter was also use to counter check the output current value. **(V.Thangaraj 2008)**

All these changes were tested for any leakages in PVC lining, output current values and movement of cathodes.

3.4 Trial Experimentation:

For general experiments 4 batches of solution were produce to check the working and concentrations of chemicals. Due to availability of commercial chemicals, concentrations of salts were taken high.

After preparations of salt baths, current and time were also tested and end results were noted.

$ZnCl_2$ g/L	KCl g/L	H_3BO_3 g/L	Current A/in^2	Time Minutes
80	200	50	0.5	10, 30, 50, 60
60	200	30	0.5	10,30, 50, 60
75	200	25	0.5	5,15, 30, 60
50	200	25	0.5	5,2 30 sec/ 60 sec

Table 4 all experiments were performed at room temperature

All these experiments were performed and analysed. Random samples of high current i.e. 2 A/in^2 were also taken at different time periods. Some observations that were made and referred by research was that whatever the bath composition was, within range limits, the only thing that bath concentration really affects is uniformity of zinc coating on substrate. Just at the start

Of burning effect samples should be taken out. Burning first occurs at the edges of the samples. So samples should be taken out with timed intervals and take considerations at what point experiment should be stop.

Good coating got a nice grey colour with no blackness or any other defects. Patches of coating i.e. having dark grey colour on one part of the same side of sample than other is also characterise as defect. These are some indications that values of our variables were not correct so values were altered to get a nice uniformed grey colour coating. **(Lotto, Milan Paunovic)**

Figure 4 These pictures are of high current and too much time applied. Blistering and burning occurred.

Figure 5 These pictures are of low current and high time values. Only burning occurred.

This is a sign that time should be low and current value is fine.

3.5 Outcome:

Time of experiments were too high. It was brought down to few minutes.

This Pre experimentation was important to check the salt concentration in the bath and set the bases for main experiment. Current and time are inversely proportional to one another if one is increase other should be decrease. Otherwise defects starts to form. These experiments give us following narrowed down and approved range of perimeters. In which we will perform our main experiments.

3.6 Findings:

These are the perimeter range values that will be use to perform and find the optimum single value for coating. Following respective variables;

Current: 0.5-2 A/in^2

Time: 60-240 seconds (start point to form a solid coat and end point where burning starts respectively)

Bath solution composition:

$ZnCl_2$ 60-80 g/L

KCl 200 g/L

H_3BO_3 50 g/L

These are the range values that will be use to perform and find the optimum single values for respective variables.

CHAPTER 4
Experiments

In order to optimize our electro galvanization process, findings from our trails were implemented in our main experiments.

Following preparation is in accordance with **ASTM B 183** (**Standard Practice for Preparation of Low-Carbon Steel for Electroplating**)

4.1 Sample preparation:

Samples were prepared following way:

1. Surface of samples were wire grinded to remove all the rust.
2. Samples were washed with degreasing solution.
3. One by one samples were Pickled. In 3:1 solution of Water and Hydrochloric acid for 2-3 minutes. This removes any impurity that might affect the quality of coating.
4. Samples are then removed and wash under tap water. Vim or any other soap was used to remove the acid.
5. Hang the samples with the help of copper wire to the copper strip that will be made cathode.

Figure 6 Rectifier and electroplating tank

4.2 Experiments:

The experiment that was conducted:

1. Samples were hanged with the help of copper wire into the salt bath.
2. Machine was checked and set at the given values given in table.

3. After coating was done in respective time, samples were taken out and washed with water.
4. Air dry the samples and nicely packed in air-tight plastic bags.

Experiment No.	Temperature Celsius	Bath Composition g/L	Current A/in^2	Time Second
1	30	60	0.5	60
2	30	70	1	100
3	30	80	2	140
4	40	60	1	140
5	40	70	2	60
6	40	80	0.5	100
7	50	60	2	100
8	50	70	0.5	140
9	50	80	1	60

Table 5 Final values for main experiments

A total of 3 sets of 9 samples were prepared. All of these samples will be analyzed for surface roughness, Coating thickness and Hardness.

Chapter 5
Results and Discussion

5.1 Surface Roughness test

Surface roughness of 3 sets of samples, each coated with 9 different settings of 4 variables, and were conducted on surface profilometer. Profilometer uses laser pointer to map 2D topography of sample surface. Profilometer has least count of 0.1 um and a resolution of 13nm. Samples are placed one by one on a moving plate, this plate allow operator to scan the area to be observe under laser pointer of profilometer.

Area of sample was scanned 3cm from the centre. Each set samples were scanned and recorded for surface roughness reading.

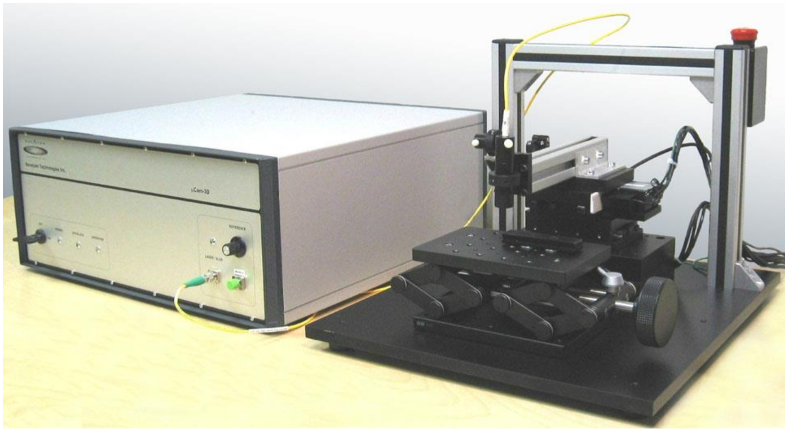


Figure 7. Common Noncontact Profilometer in SCME

A total of 81 readings were taken. Care must be taken on every reading, sample must not touch probe which can damage laser pointer and receiving sensor. Surface must be smooth and not be tilted which can cause altered readings. **(Philip J. Ross)**

L9 Taguchi orthogonal array was use to design the experiment. Below table shows the parameters, Levels and Response variable (Surface roughness).

Experiment No.	Temperature Celsius	Bath Composition g/L	Current A/in^2	Time Second	Surface Roughness Set 1	Surface Roughness Set 2	Surface Roughness Set 3	Average Roughness
1	30	60	0.5	60	1.79433	1.456333	1.985333	1.745333
2	30	70	1	100	1.685	1.837667	1.742333	1.755
3	30	80	2	140	3.68733	1.807	2.562	2.685444
4	40	60	1	140	1.37466	1.67	2.379667	1.808111
5	40	70	2	60	2.027	1.204667	1.903667	1.711778
6	40	80	0.5	100	2.181	1.664	1.615	1.82
7	50	60	2	100	2.15533	1.625333	1.545	1.775222
8	50	70	0.5	140	2.35366	1.692	2.084667	2.043444
9	50	80	1	60	2.15729	2.707333	2.136667	2.333764

Table 6 Surface roughness of each set of samples and average roughness.

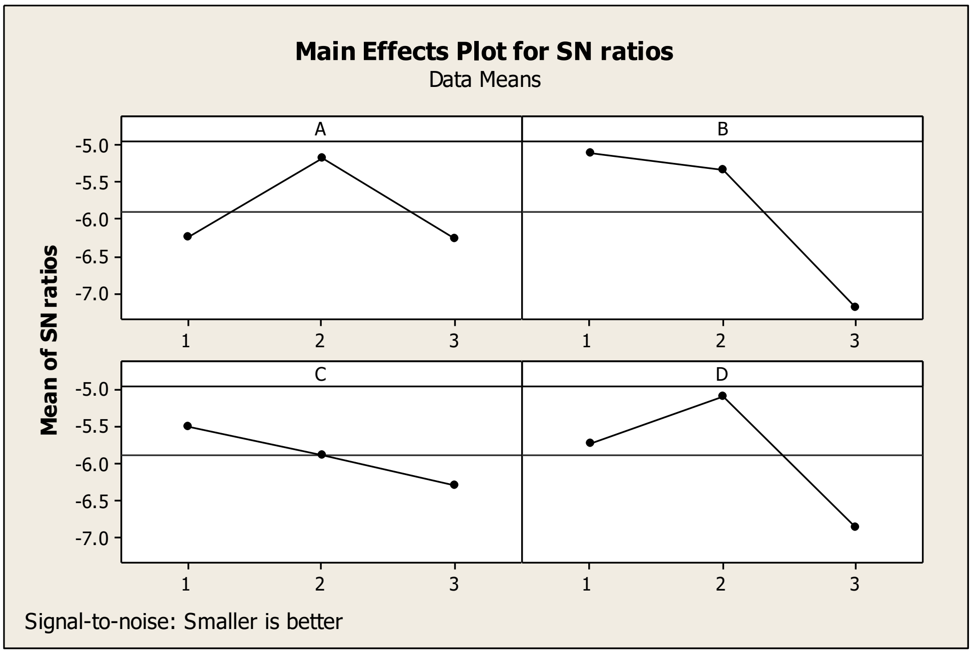
Using Minitab V 16, a statistical data analysis software, Signal-to-Noise ratio was find out. With the help of this data graph were plotted for each variable i.e. Temperature of solution bath, Time taken for coating, Bath composition and Current density. **(Philip J. Ross).** These graphs were use to correct the variance of response variables.

Taguchi analysis of S/N ratio and Means of surface roughness.

The Taguchi analysis of 3 repeat values of surface roughness were conducted for S/N ratio and Means of surface roughness following are the results that were find out.

Level	A	B	C	D
1	-6.241	-5.122	-5.492	-5.727
2	-5.173	-5.345	-5.894	-5.088
3	-6.262	-7.210	-6.290	-6.861
Delta	1.088	2.088	0.798	1.774
Rank	3	1	4	2

Table 7 Response Table for Signal to Noise Ratios for coating surface roughness
Smaller is better

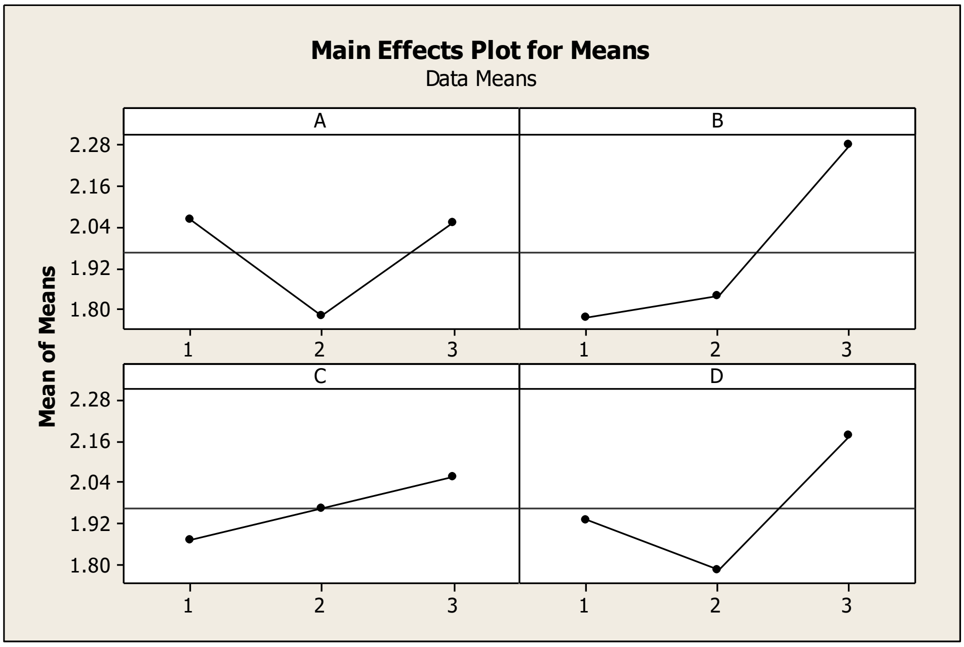


Graph 1 Main effects of SN ratio for Surface Thickness

Signal to Noise ratio or S/N ratio is a value that is use to reduce the variance of output signal. Signal is an anticipated output value and Noise is the loss of output value that can occur due to many factors. Noise can occur due to controlled or uncontrolled factors. There are three values of S/N ratio. Smaller is better, Normal is good and Larger is better. Three of these settings are use to check whether what we want from the output values and what we can get if input is varied. Larger the S/N ratio value greater will be noise free signal we get.

Level	**A**	**B**	**C**	**D**
1	2.063	-1.776	1.890	1.930
2	1.780	1.837	1.966	1.783
3	2.051	2.280	2.057	2.179
Delta	0.282	0.504	0.188	0.396
Rank	3	1	4	2

Table 8 Response Table for Means of Coating Surface Roughness



Graph 2 Main effect of means of surface roughness

Above graphs can be use to predict settings for our input variables to minimize the variance of zinc coating surface roughness on mild steel. According to above results mean value factor B has the rank of 1. Which means bath composition has the largest effect on surface roughness following are time, temperature and current.

In order to minimize the variance in surface roughness we have to look at graph 1 and graph 2. In graph 2 each variable settings are predicted by observing the centre line. For our desired results surface roughness should be as low as possible. In each variable graph it can be observe that minimum value of each variable has the maximum S/N ratio (graph 1). This way we can minimize the variance of surface roughness and predict the optimum settings. **(Joseph)**

Following factors value will have maximum S/N ratios that can be verified using S/N ratio graph 2.

Temperature: 40˚C

Bath Composition: 60 g/L

Current: 0.5 A

Time: 100s

Analysis of Variance or ANOVA was also applied to above experiment. Acceptance criteria was taken 10%. Following were the results of ANOVA:

Analysis of Variance for SR, using Sequential SS for Tests

Source	DF	Seq SS	Adj SS	Seq MS	F	P	Percentage contribution
A	2	0.4590	0.4590	0.2295	1.11	0.351	7.15%
B	2	1.3603	1.3603	0.6802	3.29	0.061	21.19%
C	2	0.1589	0.1589	0.0794	0.38	0.686	2.47%
D	2	0.7198	0.7198	0.3599	1.74	0.204	11.21%
Error	18	3.7207	3.7207	0.2067			
Total	26	6.4186					

S = 0.454649   R-Sq = 42.03%   R-Sq (adj) = 16.27%

With above results we can see the only variable that can be accepted using 10% acceptance is variable B i.e. Bath composition. This test strengthens Taguchi's analysis. In order to find percentage contribution of bath composition on overall result we will use following formula **(Philip J. Ross)**

$$P\% = [SS_B / SS_T] \times 100$$

Percentage contribution of bath composition on surface roughness is 21.19%. Using this one can optimize and control the surface roughness of zinc coating.

A surface coated with Zinc requires a smooth surface in order to not let water droplets to form or stay long enough to start corroding/damaging the coated surface. With the results of above given experiments and analysis Zinc coating roughness is most dependent upon zinc concentration in solution bath. Lower bond value of bath composition is lowest value within our range that was set throughout our experiments. Lower the concentration of Zinc will result in smooth surface of coating, reason behind this is lower zinc ions present in bath solution will attracted towards negative end of terminal i.e. Part being electroplated.. This will allow a limited amount of Zinc ions to get deposited on the surface of the part. These limited Zinc ions will be arrange epitaxial to the surface of the substrate. **(Hiroaki NAKANO)**. Small grains of

Zinc will result in close packing of these epitaxial layers which will produce smooth surface. High concentration of Zinc ions cause a large concentration of ions to be attract towards the surface of part. This will cause large ions deposition on very little area or this can said that per unit volume availability of ions are too large. This availability of ions will cause sudden deposition of Zinc resulting in large grains formation on the surface of the substrate. These large grain formation will cause an uneven structure on the surface of substrate hence uneven or rough coating will form. **(S R Rajkumar)**

5.2 Coating Thickness Test

One of the most important factor that defines the quality of coating is thickness of coating on the substrate. In this test thickness of Zinc coating was measured using profilometer. Profilometer has least count of 0.1um and a resolution of 13nm.

Thickness of Zinc coating was measured by creating a step between the coating and substrate. Since coating was already done on samples, it was remove using HNO_3. A very fine cotton swab was use. Dipping swab into HNO_3 and applying on one edge of the sample. Zinc was removed by reacting with HNO_3. Afterwards another water soaked cotton swab was use to clear any residual mess.

9 different samples were made using 9 different set of experiments, as mentioned in table 2. One by one each sample was placed and with care readings were taken.
At the step of substrate and coating laser detects a peak which was recorded. The peak was thickness of coating. Laser started from edge of sample where coating was removed and substrate was bare and continued till the coating came under the laser pointer.

Given below is the table containing thickness readings for each experiment.

Experiment No.	Temperature Celsius	Bath Composition g/L	Current A/in^2	Time Second	Thickness of coating Microns	Thickness of coating Microns
1	30	60	0.5	60	1.292	1.361
2	30	70	1	100	8.88	8.532
3	30	80	2	140	7.57	8.15
4	40	60	1	140	1.168	1.31
5	40	70	2	60	5.75	5.512
6	40	80	0.5	100	2.32	2.184
7	50	60	2	100	8.20	8.12
8	50	70	0.5	140	3.41	3.23
9	50	80	1	60	2.83	2.76

Table 9 Coating thickness of 2 sets of samples.

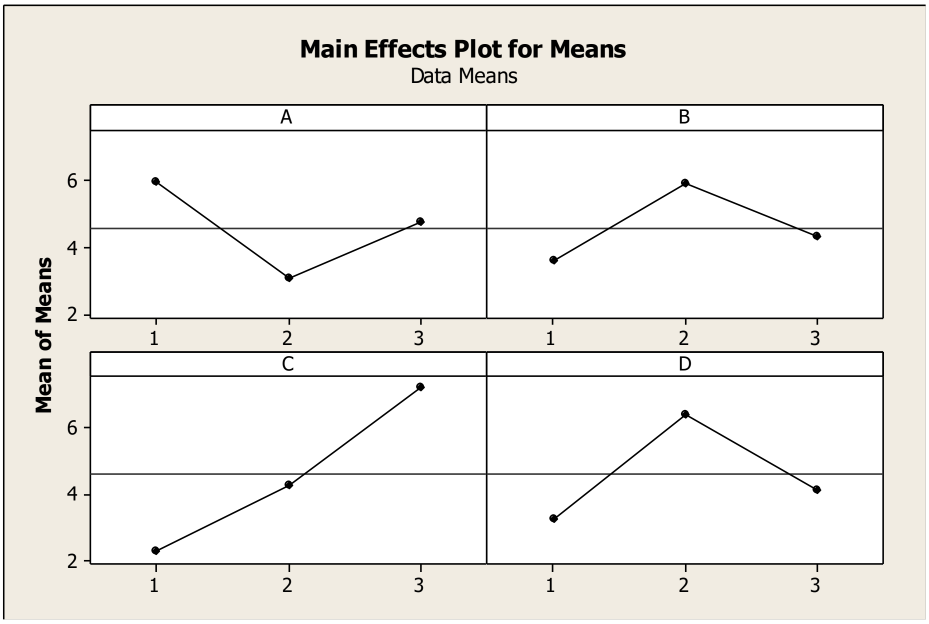
Using Minitab V 16, a statistical data analysis software, Signal-to-Noise ratio was find out. With the help of this data graph were plotted for each variable i.e. Temperature of solution bath, Time taken for coating, Bath composition and Current density. Below are the graphs for each variable for response variable coating thickness.

Taguchi analysis of S/N ratio and Means of Coating thickness.

The Taguchi analysis of 2 repeat values of coating thickness were conducted for S/N ratio and Means of coating thickness following are the results that were find out.

Level	**A**	**B**	**C**	**D**
1	5.964	3.575	2.300	3.251
2	3.041	5.886	4.247	6.373
3	4.758	4.302	7.217	4.140
Delta	2.923	2.310	4.917	3.122
Rank	3	4	1	2

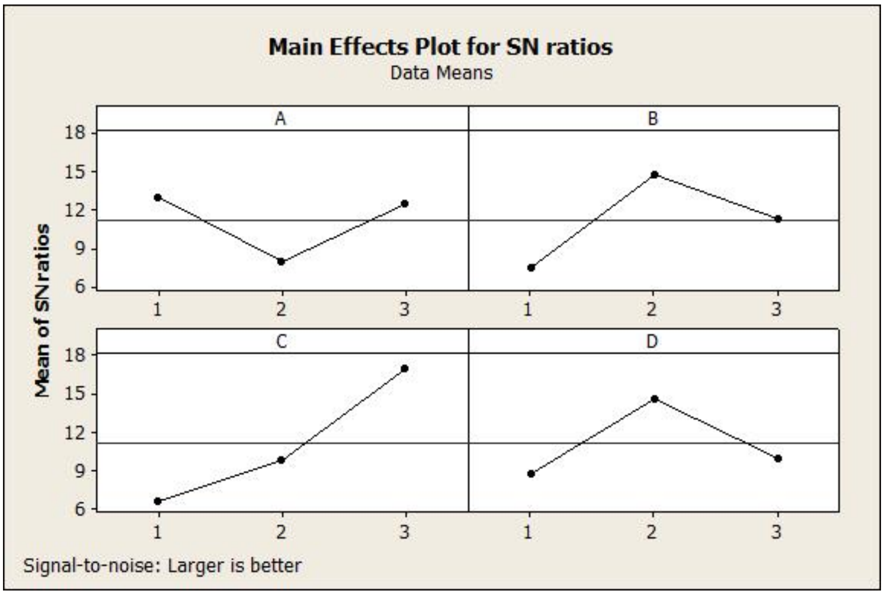
Table 10 Response Table for Means of coating thickness



Graph 3 Main effect of means of coating thickness

Level	A	B	C	D
1	13.042	7.499	6.633	8.792
2	7.955	14.737	9.845	14.688
3	12.524	11.285	17.043	10.041
Delta	5.088	7.238	10.411	5.896
Rank	4	2	1	3

Table 11 Response Table for Signal to Noise Ratios of Coating thickness
Larger is better



Graph 4 Main effect of SN ratios of thickness

Signal to Noise ratio or S/N ratio is a value that is use to reduce the variance of output signal. Signal is an anticipated output value and Noise is the loss of output value that can occur due to many factors. Noise can occur due to controlled or uncontrolled factors. There are three values of S/N ratio. Smaller is better, Normal is good and Larger is better. Three of these settings are use to check whether what we want from the output values and what we can get if input is varied. Larger the S/N ratio value greater will be noise free signal.

Above graphs can be use to predict settings for our input variables to minimize the variance of zinc coating thickness on mild steel. According to above results mean value factor C has the rank of 1. Which means current has the largest effect on coating thickness following are time, temperature and bath composition.

In order to minimize the variance in coating thickness we have to look at graph 3 and graph 4. In graph 3 each variable settings are predicted by observing the centre line. For our desired results coating thickness should be as high as possible. In each variable graph it can be observe that maximum value of each variable has the maximum S/N ratio (graph 4). This way we can minimize the variance of coating thickness and predict the optimum settings. **(Joseph)**

Following factors value will have maximum S/N ratios that can be verified using S/N ratio graph 4.

Temperature: 30˚C

Bath Composition: 70 g/L

Current: 2 A

Time: 100s

Analysis of Variance or ANOVA was also applied to above experiment. Acceptance criteria was taken 10%. Following were the results of ANOVA:

Source	DF	Seq SS	Adj SS	Adj MS	F	P	Percentage contribution
A	2	25.903	25.903	12.951	387.72	0.000	49.86%
B	2	16.748	16.748	8.374	250.69	0.000	17.55%
C	2	73.592	73.592	36.796	1101.55	0.000	11.34%
D	2	31.044	31.044	15.522	464.68	0.000	21.08%
Error	9	0.301	0.301	0.033			
Total	17	147.588					

S = 0.182767   R-Sq = 99.80%   R-Sq(adj) = 99.62%

Above results tell us that all four variables are significant and are in the acceptance range. This test strengthens Taguchi's analysis. Most significant of variable among all is current. In order to find percentage contribution of current on overall result we will use following formula

$$P\% = [SS_c / SS_T] \times 100$$

Percentage contribution of current on coating thickness is 49.86%. Using this one can optimize and control the coating thickness of zinc coating. For other 3 variables percentage contribution can also be find out.

Temperature 17.55%

Bath composition 11.34%

Time 21.08%

Coating thickness is dependent upon Current applied to the part that is being electroplated. With above experiments and analysis we can conclude that higher the current value thicker the coating will be. This is because more electrons are induce into the electroplating process which will cause more production of Zinc ions. These positive Zinc ions will attract towards negative terminal i.e. part being electroplated. With more ions being deposited on the surface of substrate thicker will be the coating. **(Hyounso Park)** Care should be taken because higher current values can cause uneven coating on substrate, burning of coating, cracks can appear on coating and even hydrogen embrittlement can cause defects on coating. **(T.J Tuaweri)** Hydrogen evolves due to acidic nature of solution bath. The hydrogen and other unwanted elements can cause defects in coating. Post heat treatment of part can prevent these defects and one can easily apply large currents to electroplating process. **(S R Rajkumar)**

Greater the thickness of coating greater the protection of substrate against corrosion attack and greater will be the life span of coating.

On these values mild steel substrate will have the maximum coating thickness of Zinc. This is the highest in given commercially available data. With thickness close to 9um, it can withstand mild-severe conditions. Allowing parts to perform without any damage due to corrosion in the harsh environment.

5.3 Coating Hardness Test

Hardness of coating is define as the ability of coating to withstand indentation, scratching, cutting and penetration. Micro hardness Vicker test was conducted on Zinc coating. Vicker test uses Pyramidal diamond shape indenter on the surface of zinc coating to penetrate the surface of the coating in microns. A force in Kg_f is applied for the certain period of time. After indent is made on the surface of the coating diamond shape indent is measured using scaled microscope to measure the area of indent that is formed on the surface. Using this area and force that was applied for the certain time, we can calculate the hardness of the coating. Greater the depth of indent, softer will be the material. In our case softer will be the coating.

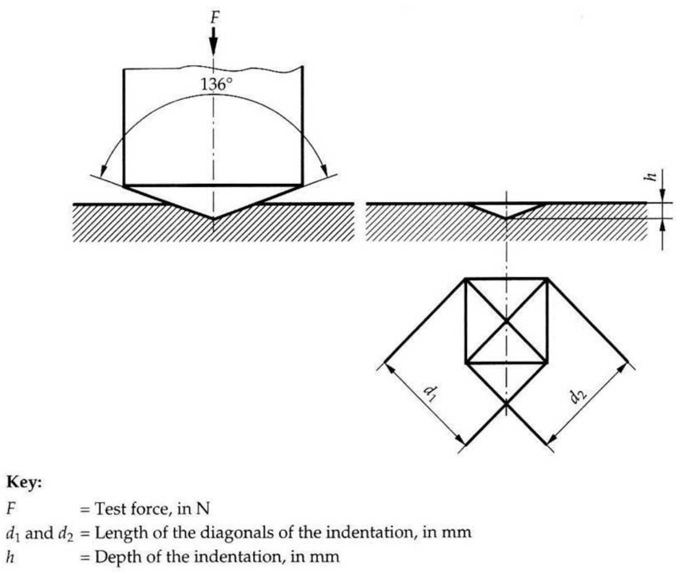


Figure 8 detailed illustration and demonstration of Pyramidal Diamond Indenter

In our test the following were the settings:

- Force applied (mN): 9800
- Dwell time: 10(s)

Using settings mentioned above, one set of 9 samples were tested for Vickers hardness.

Experi ment No.	Temperature Celsius	Bath Composition g/L	Current A/in^2	Time Second	Hardness of coating in HV	Hardness of coating in HV
1	30	60	0.5	60	469.7	480.9
2	30	70	1	100	297.7	260.1
3	30	80	2	140	246.2	295.3
4	40	60	1	140	273.2	355.2
5	40	70	2	60	264.0	289
6	40	80	0.5	100	246.1	284.3
7	50	60	2	100	261.3	302.0
8	50	70	0.5	140	390.1	314.2
9	50	80	1	60	449.6	348.2

Table 12 Vickers Hardness of coating in HV

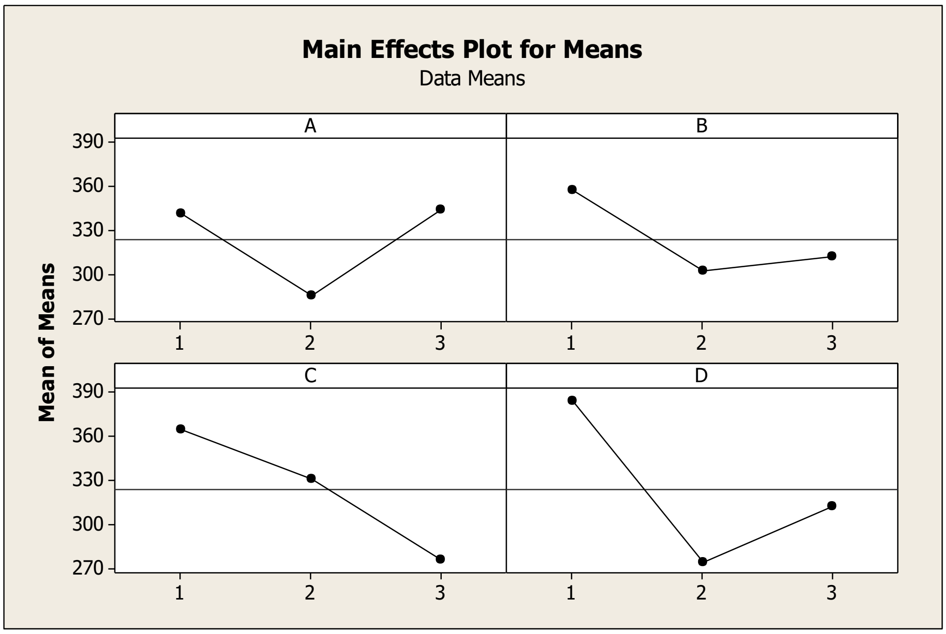
Using Minitab V 16, a statistical data analysis software, Signal-to-Noise ratio was find out. With the help of this data graph were plotted for each variable i.e. Temperature of solution bath, Time taken for coating, Bath composition and Current density. Below are the graphs for each variable for response variable coating thickness.

Taguchi analysis of S/N ratio and Means of Coating Hardness.

The Taguchi analysis of 2 repeat values of Coating hardness were conducted for S/N ratio and Means of coating thickness following are the results that were find out.

Level	**A**	**B**	**C**	**D**
1	341.6	357.1	364.2	383.6
2	285.3	302.5	330.7	275.2
3	344.2	311.6	276.3	312.4
Delta	58.9	54.5	87.9	108.3
Rank	3	4	2	1

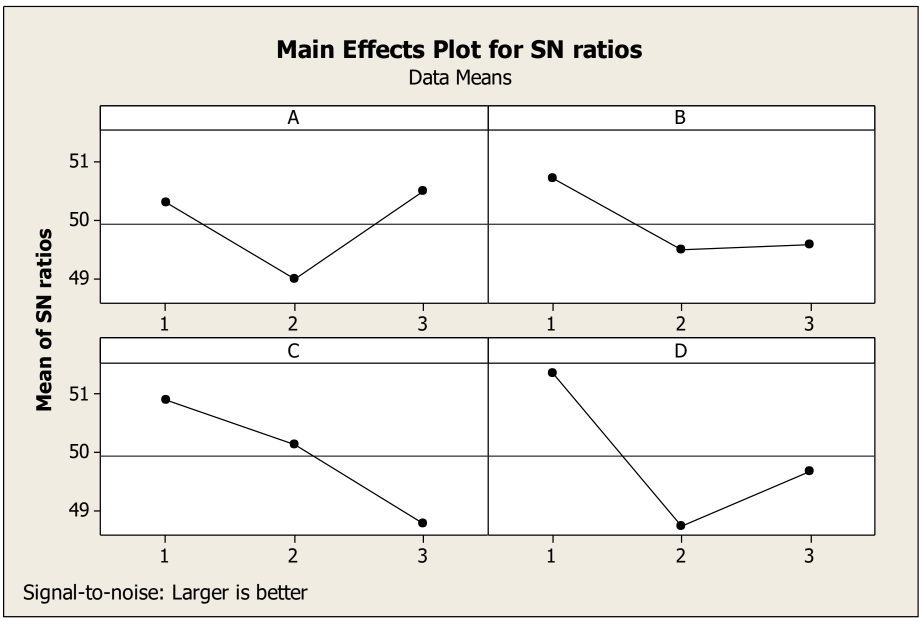
Table 13 Response Table for Means of Hardness values



Graph 5 Main effect of Coating Hardness

Level	A	B	C	D
1	50.31	50.73	50.91	51.38
2	48.98	49.48	50.13	48.73
3	50.51	49.58	48.76	49.68
Delta	1.58	1.25	2.15	2.66
Rank	3	4	2	1

Table 14 Response Table for Signal to Noise Ratios of Hardness Values Larger is better



Graph 6 S/N ratio of Coating Hardness

Signal to Noise ratio or S/N ratio is a value that is use to reduce the variance of output signal. Signal is an anticipated output value and Noise is the loss of output value that can occur due to many factors. Noise can occur due to controlled or uncontrolled factors. There are three values of S/N ratio. Smaller is better, Normal is good and Larger is better. Three of these settings are use to check whether what we want from the output values and what we can get if input is varied. Larger the S/N ratio value greater will be noise free signal we get.

Above graphs can be use to predict settings for our input variables to minimize the variance of zinc coating hardness on mild steel. According to above results mean value factor D has the rank of 1. Which means time has the largest effect on coating thickness following are current, bath composition and temperature.

In order to minimize the variance in coating hardness we have to look at graph 5 and graph 6. In graph 5 each variable settings are predicted by observing the centre line. For our desired results coating hardness should be as high as possible. In each variable graph it can be observe that maximum value of each variable has the maximum S/N ratio (graph 6). This way we can minimize the variance of coating hardness and predict the optimum settings.

Following factors value will have maximum S/N ratios that can be verified using S/N ratio graph 6.

Temperature: 50˚C

Bath Composition: 60 g/L

Current: 0.5 A

Time: 60s

Analysis of Variance or ANOVA was also applied to above experiment. Acceptance criteria was taken 10%. Following were the results of ANOVA:

Source	DF	Seq SS	Adj SS	Adj MS	F	P	Percentage Contribution
A	2	13310	13310	6655	3.93	0.059	13.47%
B	2	10242	10242	5121	3.03	0.099	10.37%
C	2	23621	23621	11811	6.98	0.015	23.91%
D	2	36359	36359	18180	10.74	0.004	36.81%
Error	9	15229	15229	1692			
Total	17	98761					

S = 41.1349   R-Sq = 84.58%   R-Sq(adj) = 70.87%

Above results tell us that all four variables are significant and are in the acceptance range. This test strengthens Taguchi's analysis. Most significant of variable among all is Time. In order to find percentage contribution of Time on overall result we will use following formula

$$P\% = [SS_D / SS_T] \times 100$$

Percentage contribution of Time on coating hardness is 36.81%. Using this one can optimize and control the hardness of zinc coating. For other 3 variables percentage contribution can also be find out.

Temperature 13.47%

Bath composition 10.37%

Current 23.91%

Using above results one can optimize the hardness of coating. Greater will be the hardness, greater will be the scratch resistance of coating. This property will prolong the serviceability of zinc coating even in those environment in which movable parts be use. Hard coating will protect the inner mild steel part and no crevice or any other defect will cause the harm from the environment.

5.2.1 SEM images of cross section analysis of Coating Hardness

Scanning Electron Microscopy was use to observe the zinc coating that deposited on the surface of mild steel sample. This analysis will help us to learn more and in detail about zinc and mild steel sample surface-coating interaction. EAS will allow us to observe the penetration of zinc coating particles into the substrate and to what depth. This study will connect the hardness characteristics of coating with diffusion of zinc into the mild steel substrate. **(ASTM B-487)**

In order to prepare our samples for SEM analysis following preparations were made.

- ✓ Steel sample was cut into smaller pieces.
- ✓ 1.5cm×1.5cm small piece was made at one corner of steel sample using metacut.
- ✓ Precaution should be taken as to not use any type of lubricant that will corrode the sample during cut, or to damage coating by penetrating into the zinc-substrate interface.
- ✓ With slow feed rate on metacut samples were neatly cut.
- ✓ Small samples were embedded into the Bakelite mould in order to expose the zinc-substrate interface at the open face of mould.

- ✓ This moulded sample was place in SEM machine to get the images of interface.

Zinc particles diffuse into the substrate during electrodeposition. This diffusion occurs due to attractive forces also known as Van der valls forces between Zinc and iron particles. Zinc and Iron are metallic in nature so in between them metallic bond exists. This bonding is the basis of increase in hardness values at Zinc- substrate interaction level.

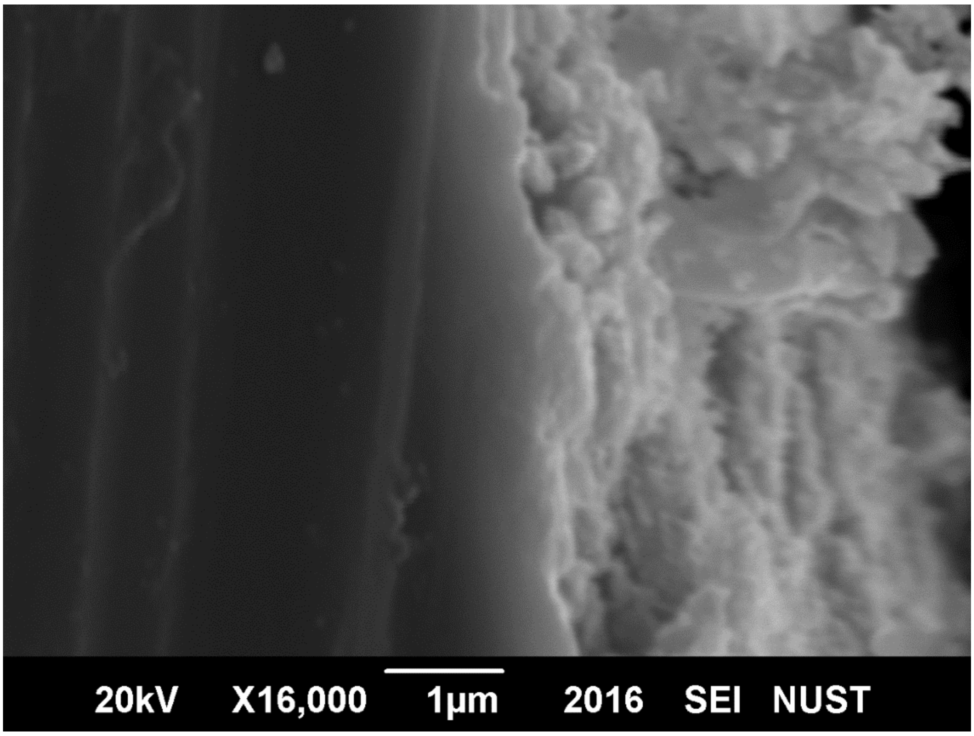


Figure 9 SEM image of Cross section of zinc and substrate intersection

What happens on interaction zone is that zinc particles sit in between iron particles, this further packs the iron particles that were before tightly packed due to carbon alloying. This phenomena increases the hardness of surface of substrate. This can also be seen in EAS result.

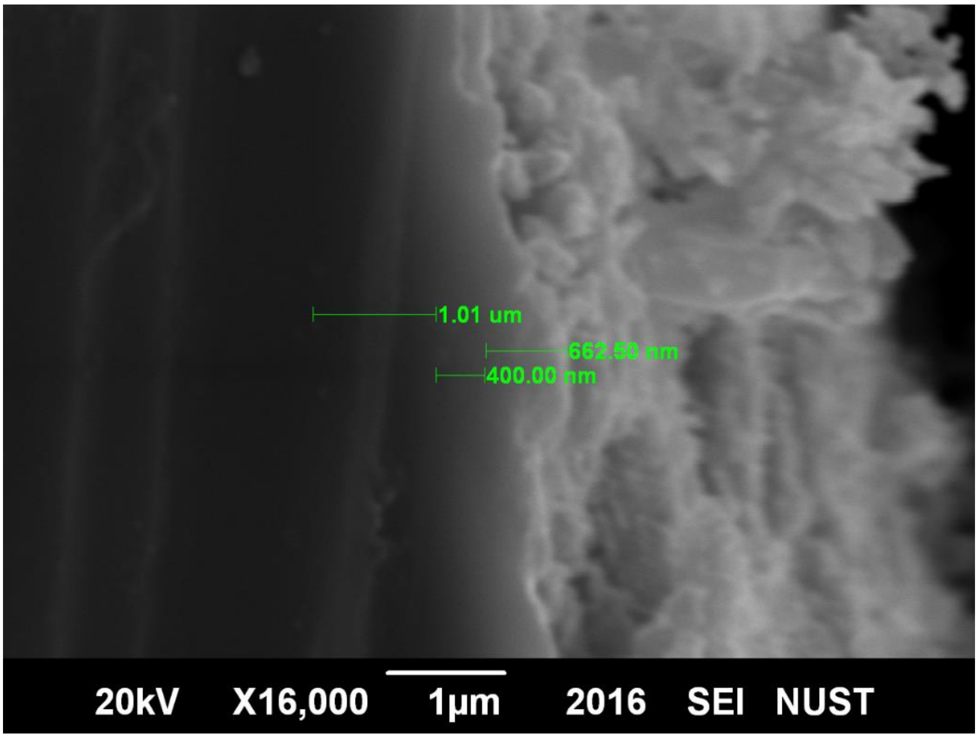


Figure 10 SEM image of zinc-substrate boundary and diffusion measurement

Image above shows the cross section of zinc-substrate. At right side of image Bakelite exist, this is Bakelite moulding use to hold the metallic sample mentioned before. Then in the centre the interaction zone exist. And at the right side of this interaction zone mild steel sample can be seen. Numbering line shows the three points taken by operator for analysis. These lines show us the depth to which zinc has penetrated into the steel sample, almost 2 µm.

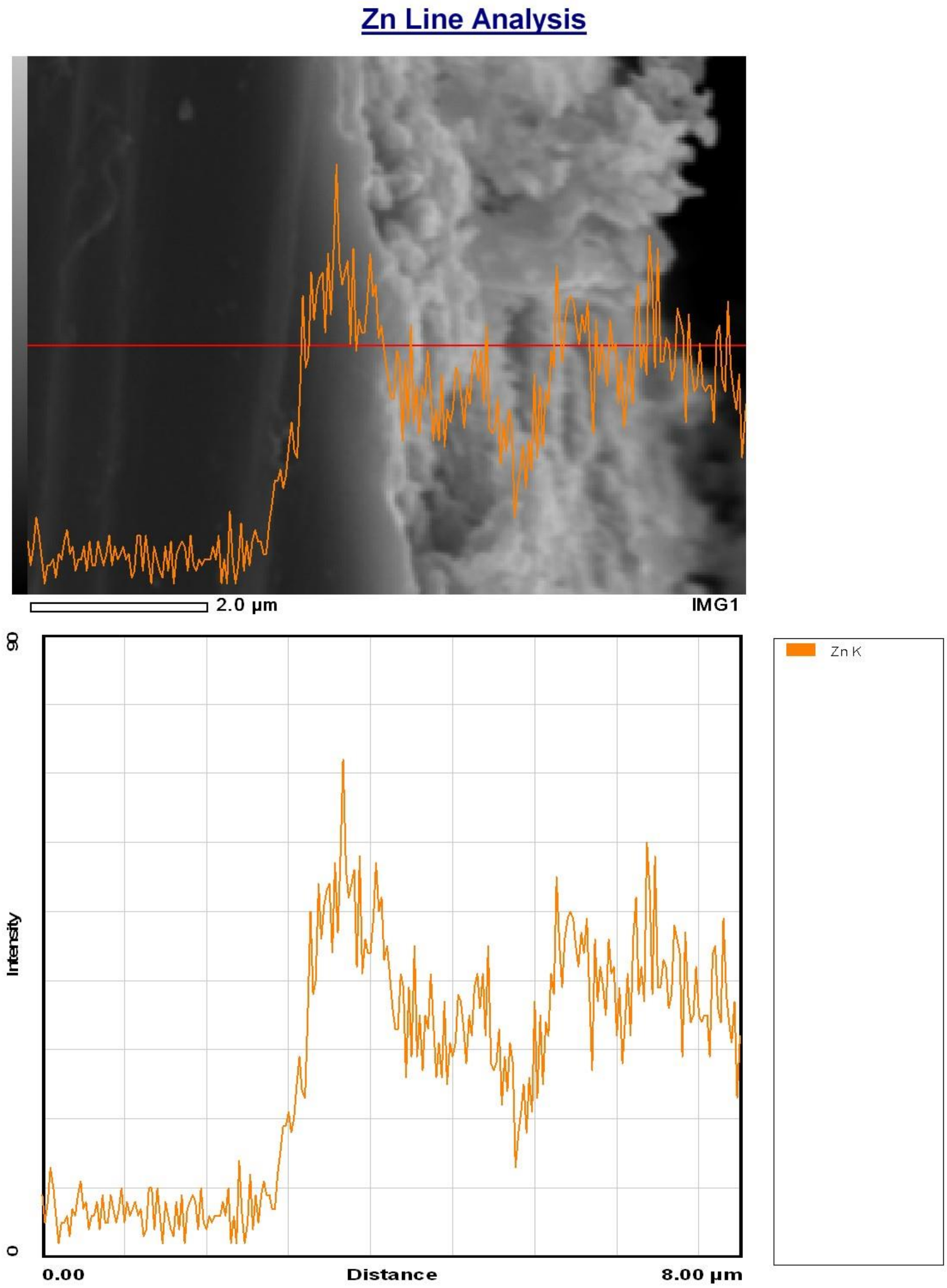


Figure 11 Elemental analysis of zinc in metallic substrate

Image above tell us the EAS analysis of cross section of our steel sample. This can be seen that Zinc element analysis line peak strikes top right at the interaction zone within the metallic sample. This strengthens the diffusion argument. With this data we can say that zinc particles has diffused into the metallic substrate up to 2µm. This increases the hardness of metallic substrate surface. Thus hardness of coating is the sum of coating and interaction zone hardness values.

Coating of any kind is useless, until that coating adhere to substrate properly. Adhesion is describe as bond between (physical or chemical) two adjacent materials and is related to force to completely separate these materials or to penetrate it. **(Joseph V. Koleski)**. For scratch resistance, cracking and to find how much coating has resistance to daily life physical abuse hardness was checked. Adhesion can be categories into four categories. Interfacial adhesion, Interdiffusion adhesion, Intermediate layer adhesion and mechanical interlocking. In this study interdiffusion adhesion was considered. Interdiffusion adhesion is describe as the film and substrate diffuse into one another on to a wider interfacial region. In order to check this interdiffusion adhesion micro hardness test was done. For our consideration, area of indent which was studied was the boundary at which coating and substrate were connecting. In our study thicker the coating, less will be the hardness value due to indenter not reaching the interfacial diffusion zone i.e. substrate-coating boundary.

Hardness is dependent upon Time given for a part during electrodeposition process. With above mentioned experiments and analysis we can conclude that Time given for electrodeposition should be less. But one should keep in mind that hardness of coating is calculated for coatings that are very thin <5 µm. This is due to the fact that thicker coatings have hardness values that are less than the thinner ones because micro hardness indenter do not reach substrate-coating boundary. **(M.Arif Butt)**. Diffusion is the main factor behind all this.

EAS and SEM images has revealed that up to 2 µm into the substrate surface, Zinc ions have diffused. This increases the hardness of substrate surface by tightly diffusing into the M.S structure. This is the layer that causes an increase in hardness of substrate. Thick coatings do not need Hardness test because of amount of Zinc it is containing that scratch do not or very less penetrates to reach the surface of substrate. The boundary of substrate and coating is the area that is considered as the adhesion zone. Common practice that should be done is during electrodeposition dummy parts should be withdrawn from the bath and hardness test be conducted. This will give electroplater a qualitative idea of adhesion strength that coating has adhere to substrate and to what extent.

Summary

Electrodeposition is very common and daily used process in industries to save the metallic part from getting rusted in an open environment. This process is dependent upon many factors that effects the quality of zinc coating. In order to minimize the variation of zinc coating quality, four factors were tracked down that have the most effect on quality of zinc coating and these factors analyzed to find what percent these factors affect the coating. Four factors were Time of electrodeposition process, Concentration of Zinc salt in Zinc bath, Current applied to the electrodeposition process and the Temperature of salt bath.

In order to check the variation of zinc coating quality on mild steel, steel samples were electro galvanized by changing the values of our input variables. Design of experiments were mapped out using Taguchi's orthogonal array. In order to record and observe the quality of coating three response variables were taken. Coating thickness as it is one of the most important factor in coating technology. Thicker the coating more protection it will provide to substrate. Surface roughness, this allows water or other fluids to slide off easily to protect coating itself. Surface roughness should be low as possible. And last was hardness of coating, this characteristics don't allow any scratch or damage to happen on the coating. Hardness should be maximum in order to protect the coating from any harm.

After galvanizing steel samples, testing and analysis of our response variables were conducted using Taguchi's method and ANOVA. Results observed from Profilometer and Vickers hardness method were carefully analyzed and found out that on each response variables a separate input variable is contributing the most on the result. For Surface roughness Bath composition is the contributing factor, for Hardness the most contributing factor to control hardness is Time and for coating Thickness Current is the most contributing factor. These contributing factors are the key to control the quality of zinc coating. With this analysis an optimum settings for each response variables were find and recorded. By controlling the contributing factors one can have a smooth, hard and thick coating.

With this study electroplaters will have in-depth knowledge about the zinc coating. This data will help to minimize quality defects and to save the resources that will otherwise get wasted.

Future Work Recommendation

Zinc coating techniques have evolved very much with time. Controlling electro deposition, zinc layer can be formed with very little defects. Throughout the world research has been carried out for controlling the grain size of zinc layer. By controlling the grain growth of zinc, corrosion can be prevented to the maximum level. Electrodeposition techniques have ability to control this grain growth structure of zinc. The area of study is vast and can be helpful for industries worldwide.

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