# ELECTRODEPOSITION OF ZINC-NICKEL ALLOY IN THE PRESENCE OF LAWSONE ISOLATED FROM LAWSONIA INERMIS LINN LEAF

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## Abstract

*The electro deposition of zinc-nickel alloy was carried out in the presence of Lawsone (2-hydroxy1,4-napthoquinone) isolated from Lawsonia inermis Linn leaf. The bath constituents were optimized through Hull cell experiments. Operating parameters such as pH, temperature and current density were also optimized. The current efficiency and throwing power are measured at different current densities.SEM photomicrographs revealed fine-grained structure of the deposit from the optimum bath. IR spectrum of the scratched deposit showed inclusion of addition agent. XRD and EDAX studies revealed the inclusion of lawsone.*

*Keywords: Lawsone, 2-Hydroxy1,4-Napthoquinone, Corrosion Resistance, Hull Cell, SEM, XRD*

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## 1. INTRODUCTION

Electrodeposition of Zn-Ni alloy is one of the well known examples of the anomalous co deposition, in which less noble metal deposits preferentially. This alloy coating provides better corrosion protection to steel than electrogalvanised or hot dipped Zinc coatings. As the electrode potential of Zinc is more negative than iron, Zinc coating is expected to provide electrochemical protection to steel parts against corrosion under ordinary atmospheric conditions[1-5].

The Zn-Ni alloy obtained by electrodeposition process with nickel varying between 8% and 14% by weight give corrosion protection five to six times superior to that obtained with Zinc deposits [6]. Brighter deposits are obtained by addition of certain compounds in the bath solution. It is evident from the literature that the single addition agent generally does not produce good deposit over a wide current density range. In order to get good deposit, two or more addition agents are required[7]. The presence of more addition agents poses problems in determining their consumption during plating. Also some of the addition agent cause pollution problem and health hazard[8-10]. In the present work, efforts have been made to develop sulphate bath containing non toxic and eco friendly Lawsone isolated from Lawsonia inermis linn leaf extract. Lawsonia inermis Linn. Most commonly known as 'Henna' invites attention of the investigators worldwide for its pharmacological profile ranging from anti inflammatory to anti cancer activities[11].The principal colouring substance of henna is a red orange coloured molecule (lawsone, 2-hydroxy1,4,napthoquinoine) having molecular formula, $C_{10}H_6O_3$ and M.P- 190$^O$, Present in dried leaves in a concentration of 1-1.4%w/w[12-14]. Upadhyay et al in 2010 confirmed that the quantitative estimation of leaves of L. Inermis collected in different seasons showed variations in the active ingredient (Lawsone)[15].

## 2. EXPERIMENT

The chemicals used were of AR grade and easily soluble in water. For the preparation of solutions, distilled water was used. The standard Hull cell of 267mL capacity was used to optimize the bath constituents. The Hull cell experiments with bath solution (table 1) were carried out without agitation. The pH of the bath solution was adjusted with 10%hydrochloric acid or sodium carbonate solution. Zinc plate of 99.99% purity was added as anode. The anode was activated each time by immersing in 10% HCl followed by water wash. Mild steel plates (AISI-1079) of standard Hull cell size were mechanically polished to obtain a smooth surface. The scales and dust on the steel plates were removed by dipping in 10% HCl and were subjected to electrocleaning process. These steel plates were washed with water and used for the experiments as such. After plating experiment, the plates were subjected to bright dip in 1% nitric acid for 2 s followed by water washes. The nature and appearance of zinc plating was carefully studied and recorded through Hull cell codes.

All the experiments were conducted at room temperature. A known amount of lawsone was added to the bath solution. The bath solution was stirred for 30 min and then used for the Hull cell experiments. The deposits were obtained at a constant current density from the optimized solution taken in a rectangular methacrylate cell of 2.5 L capacity. Polished, degreased and electro cleaned cathodes of 3 X 4 cm$^2$ were used for plating. Experiments were done in triplicate. Standard experimental procedures (Parthasarathy 1989) were adopted for measurement of properties of the deposit such as ductility, adherence etc. In all the above studies the average thickness of the deposit was 20μm. Current Efficiency and throwing power were determined. Haring and Blum cell was used to measure throwing power and the current distribution ratio between anode and cathode

was 1:5. IR spectra of the scrapped deposit were taken to know the inclusion of addition agent. SEM photomicrographs were taken to know the nature of deposit in the presence of addition agents. XRD and EDAX analysis were also taken to find out the inclusion of addition agent.

**Table 1:** Basic bath composition and operating condiitons

| Bath composition | Conc(gl$^{-1}$) | Operating conditions |
|---|---|---|
| $ZnSO_4 .7H_2O$ <br> $NiSO_4.6H_2O$ <br> $Na_2SO_4$ <br> $H_3BO_3$ | 130 g/l <br> 15 g/l <br> 40 g/l <br> 15 g/l | Temperature: Room temperature <br> Anode: Zinc metal (99.99% pure) <br> Cathode: mild steel |

## 3. RESULTS AND DISCUSSION

To get bright deposit certain compounds are being used in the bath solution. It is evident from the literature that the single addition agent generally did not produce good deposit over a wide current density range. In order to get good deposit, two or more addition agents were required. The presence of more addition agents posses problems in determining their consumption during plating. Also some of the addition agents caused pollution problem and health hazard. In the present work, efforts had been made to develop sulphate bath containing non toxic and eco friendly Lawsone, (2-hydroxy-1,4 Naphthoquinone) isolated from Lawsonia inermis Linn Leaf.
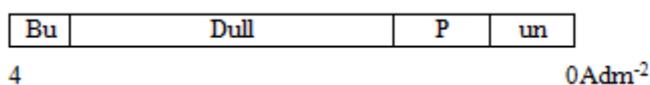
### 3.1 Hull Cell Studies

### 3.1.1 Effect of Lawsone

Table 1. Basic bath solution gave dull deposit between the current density range of 1 and 4 Adm$^{-2}$ at 1A cell current (Figure 1). In order to improve the nature of deposit, Lawsone was added in to the bath solution. At a concentration of 45ml of Lawsone, the hull cell panels were bright between the current density range of 0.5 and 3.5 Adm$^{-2}$. With further increase in the concentration of Lawsone, the nature of deposit became burnt at higher current density region. Therefore, on the basis of the above observations, the concentration of Lawsone was kept at 45ml/L as optimum. The Hull cell pattern for 45ml/l was shown in Figure1 A.

### 3.1.2 Key

Br- Bright, Bu- Burnt, D- Dull, SB –Semi Bright, St- Streaky, P- Powder



**Fig- 1:** Hull Cell Diagram – Basic Bath At 1a Current
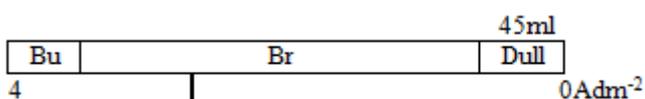


**Fig- 1A:** Hull Cell Diagram – Effect of L.Inermis Extract

### 3.1.3 Effect of Zinc Sulphate

The effect of Zinc ion was studied by varying the concentration of Zinc Sulphate from 25-200gL$^{-1}$ keeping Lawsone at 45mlL$^{-1}$. At lower concentrations, bright and streaky deposits were observed in the current density region of 2-4Adm$^{-2}$. At low current density region, dull deposits and at high current density range, burnt deposit was obtained. It was observed that the increase in the concentration of Zinc Sulphate, the brightness range was extended to higher and lower current density. As given in the literature, concentration of Zinc sulphate increases the brightness also increases. At a concentration of 91g/L, a satisfactory bright deposit was obtained. Above this concentration of Zinc Sulphate, there was no improvement in the nature of deposit. The concentration of Zinc Sulphate was fixed at 91g/L as optimum.
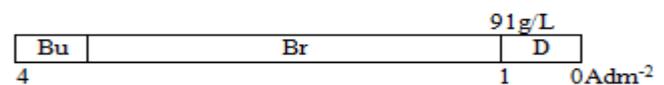


**Fig-1B:** Hull Cell Diagram: Effect of Zinc Sulphate

### 3.1.4 Effect of Nickel Sulphate

Roev et al showed that 3g/L of Ni gave fine grained deposit in alkaline Zn-Ni alloy plating bath. Further increase in the concentration produce black powdered deposit. So it was necessary to optimize the concentration of Ni in the bath solution. The concentration of Nickel Sulphate was varied from 2-26g/L. At a very low concentration the Hull cell panels were shown burnt deposit at high current density region and dull deposit at low current density region. The burnt and dull deposit regions were found to be reduced and at 20g/L, the deposit was bright over the current density range of 1-4Adm$^{-2}$. Further increase in the concentration did not show any improvement in the bright current density region.
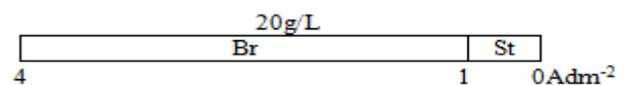


**Fig- 1C:** Hull Cell Diagram: Effect of Nickel Sulphate

### 3.1.5 Effect of Sodium Sulphate

Sodium Sulphate was added to increase the conductance of the bath solution. The concentration of Sodium Sulphate was varied from 2-50g/L. At lower concentrations, Hull cell panels had semi bright deposit at low current density region and burnt at high current density region. The semi bright and burnt regions were found to be reduced. With increase in the concentration of sodium sulphate and at 16g/L, the deposit was bright over a current density range of 0.3-3.5Adm$^{-2}$. Further increase in the concentration (>16g/L) did not introduced any effect on the nature of deposit and the conductance also. So, the concentration of Sodium sulphate was fixed at 16g/L in the bath solution.
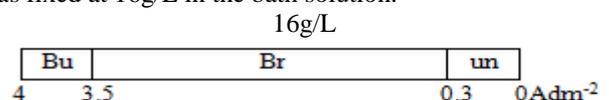


**Fig- 1D:** Hull Cell Diagram- Effect of Sodium Sulphate

### 3.1.6 Effect of Boric Acid

The presence of boric acid increased the current efficiency of deposition process, amount of Zinc in the deposited alloy, and nucleation density of the deposit. These effects have been attributed to the adsorptive interactions of boric acid at the electrode surface. Also, boric acid acts as a buffer to maintain the $P^H$ of the electrolyte bath. Similar effects of boric acid were observed in the present work during Zn-Ni deposition from suggested sulphate bath. The concentration of boric acid was varied from 10-30g/L. At lower concentrations, the Hull cell panels had shown semi bright deposit at low current density region and burnt at high current density region. The semi bright and burnt regions were found to be reduced with increase in the concentration of boric acid and at 8g/L, the deposit was bright over a current density range of 0.3-3.5Adm$^{-2}$.Further increase in the concentration (>8g/L) did not introduced any effect on the nature of deposit and the conductance also. So, the concentration of boric acid was fixed at 8g/L in the bath solution.
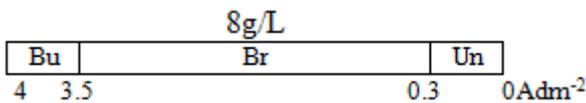
**Fig- 1E:** Hull Cell Diagram- Effect of Boric Acid

### 3.1.7 Effect of pH

To know the effect of pH, the pH of the bath solution was varied from 2-5. At higher pH the Hull cell panels had shown burnt deposit at high current density region. At pH 3.5, satisfactory deposit was obtained. At lower pH (<3.5), the specimens had dull deposit at low current density region. From the above observations, the pH of the bath solution was kept at 3.5 as optimum.

**Fig- 1F:** Hull Cell Diagram- Effect of pH

### 3.1.8 Effect of Temperature

To study the effect of temperature on Hull cell experiments, the plating experiments were carried out in a thermostat, The temperature of the thermostat was varied from 293-323K. At room temperatures (303K), the deposition was bright in the current density range 1-4Adm$^{-2}$ at 1Acell current. Above 303K, the deposit was dull in the low current density region. Therefore the optimum operating temperature was 303K.

**Fig- 1G:** Hull Cell Diagram- Effect of Temperature 303K

### 3.1.9 Effect of Current

The Hull cell experiments were carried out at different cell currents (1-3A) for 10 min using optimum bath solution. It was found that at a cell current of 1A deposit was bright in the current density range 1-5Adm-2. At a cell current of 2A, the deposit was semi bright in the current density range of 1.5-3Adm$^{-2}$ . At a cell current of 3A the deposit was semi bright over the current density range between 2 and 3Adm$^{-2.}$ At cell currents of 3A and 4A, the Hull cell panels showed burnt deposit on the side of High cathode current density. This increased the anode polarization and led to large decrease of deposition speed of Zn-Ni. This observation revealed bath gave bright deposit in the current density range of 1-4Adm$^{-2}$ at a cell current of1A
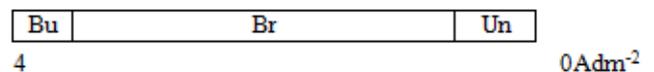
**Fig- 1H: Hull Cell Diagram- Effect of Cell Current 1A**

### 3.1.10 Optimized Bath

By varying the components in the basic bath in the above manner, led to an optimized. This optimized bath contained 45ml/L of Lawsone. The bath composition and operating conditions were shown in table 1.

**Table 1:** Optimum Bath Composition And Operating Conditions For Zinc- Nickel Alloy Electrodeposition

| Bath composition | Concentration gL$^{-1}$ | Operating conditions |
|---|---|---|
| Zinc sulphate Nickel sulphate Sodium sulphate Boric acid pH Lawsone | 91gL$^{-1}$ 20gL$^{-1}$ 16gL$^{-1}$ 8gL$^{-1}$ 3.5-4 0.45gL$^{-1}$( 45 ml= 0.45g in 45ml of ethanol) | Anode: Zinc metal(99.99% pure) Cathode: Mild steel Temperature:303K pH:3.5 |

### 3.2 .Effect of Current Density On Current Efficiency

Current efficiency of Zn-Ni alloy electrodeposited carbon steel obtained from Basic bath and Optimized bath were measured at various current densities. At lower current density (1Adm$^{-2}$), the current efficiency of Zn-Ni electrodeposited carbon steel obtained from Basic Bath and Optimized were found to be 40% and 70% respectively. At a current density range of 1-5Adm$^{-2}$ , the efficiency was found to be increased and reached high at 4Adm$^{-2}$. The Efficiency obtained were 75% and 90% respectively. Further increase in current density was found to decrease the efficiency. This showed the absence of hydrogen evolution at a current density range of 1-5Adm$^{-2}$ , after this hydrogen evolution was started.

**Table 2:** Effect of Current Density On Current Efficiency During Zinc-Nickel Alloy Electrodeposition

| Current Density ($Adm^{-2}$) | Current Efficiency (%) | |
| --- | --- | --- |
| | Basic Bath | Optimized Bath +Lawsone |
| 1 | 40 | 70 |
| 2 | 52 | 82 |
| 3 | 64 | 85 |
| 4 | 70 | 88 |
| 5 | 75 | 90 |
| 6 | 80 | 87 |

### 3.3 Determination of Throwing Power

Throwing power for basic bath, optimized bath and optimized bath with Lawsone for Zn-Ni alloy electrodeposition was measured by using Haring Blum Cell at different current densities. At lower current density, throwing power for basic bath and optimized bath were found to be 14..4 % and 29.5% respectively. Further increase in current density, increased the Throwing Power and attained the maximum of 26.5% and 42.5% respectively at $5Adm^{-2}$. (Table 3). Thorough literature survey revealed the presence of additive increased the throwing power on Zinc-Nickel alloy electrodeposition. The values obtained for the optimized bath with Lawsone proved the effect of additive on throwing power during Zinc-Nickel alloy electrodeposition.

**Table 3:** Effect of Current Density On Throwing Power

| Current Density (A/dm2) | Throwing Power (%) | |
| --- | --- | --- |
| | Basic Bath | Optimzed Bath +Lawsone |
| 1 | 14.4 | 29.6 |
| 2 | 17.5 | 30.5 |
| 3 | 20. 6 | 31.9 |
| 4 | 22.4 | 36.4 |
| 5 | 26.5 | 42.5 |
| 6 | 23.5 | 36.5 |

### 3.4 SEM Analysis of Metal Surface

The SEM Micrograph of Zinc-Nickel electro deposited Carbon steel surface from basic bath (Figure.4A ) had different and slightly larger crystal size. It was found that the crystal size was not uniform. It was observed a very rough surface with a cauliflower structure indicating that the electrodeposit has a larger surface area. The SEM Micrograph of Zinc-Nickel electro deposited Carbon steel surface from Optimized bath (Figure.4B showed Cluster of hexagonal plates were deposited with an average diameter of 0.5–1 μm and hence gave a bright deposit. This showed the effect of Lawsone on electro deposition of Zinc-Nickel alloy on carbon steel surface.
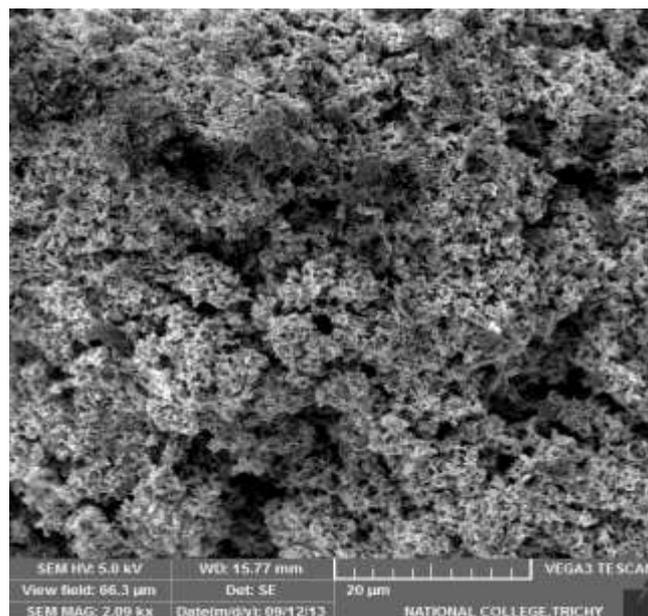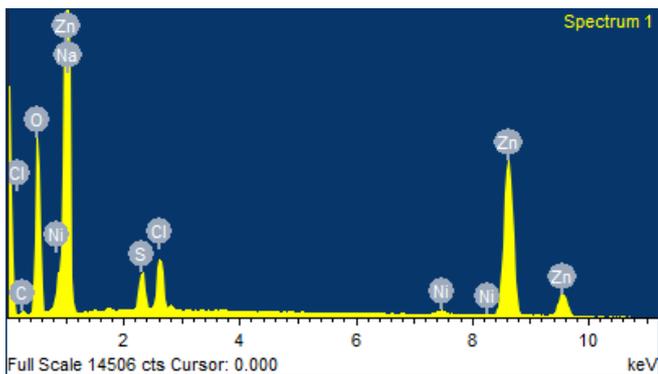


**Fig- 4a:** Sem Photo Micrographs Obtained For Zinc-Nickel Alloy Electrodeposition From Basic Bath
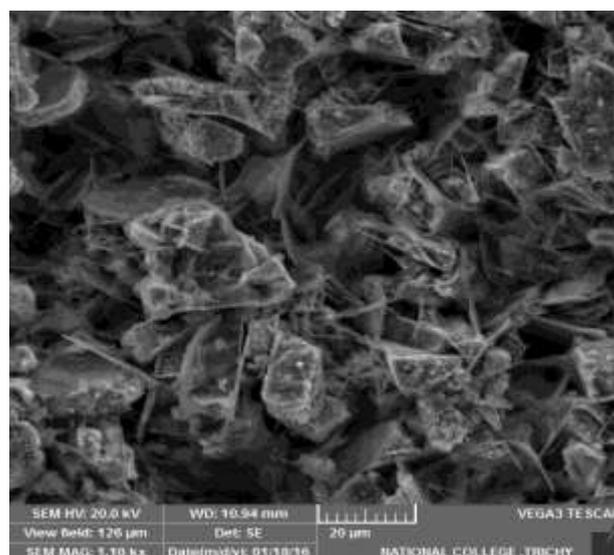


**Fig. 4b:** SEM Photo Micrographs Obtained For Zinc-Nickel Alloy Electrodeposition From Optimized Bath

### 3.5. EDAX Analysis

EDAX photographs of Zinc electrodeposited carbon steel from Basic bath and optimized bath showed the presence of Zinc, carbon and oxygen on the metal surface. The weight percentages of Zinc, Nickel, Carbon and Oxygen in Zinc-Nickel electrodeposited carbon steel from Basic bath were found to be 73%, 8.56%, 2.6 % and15.84% respectively. (Figure 5A)But in the Zinc-Nickel electrodeposited carbon steel from Optimized bath had only 60.54% of Zinc. This showed that the some of the active sites of Zinc were occupied by Lawsone. The weight percentage of Nickel, Oxygen and carbon in the Zinc-Nickel electrodeposited carbon steel from optimized bath was found to be increased. (Ni-8.75%, Oxygen-18.35% and carbon- 1.59%). (Figure 5B). This confirmed the inclusion of the Lawsone during Zinc-Nickel electrodeposition.
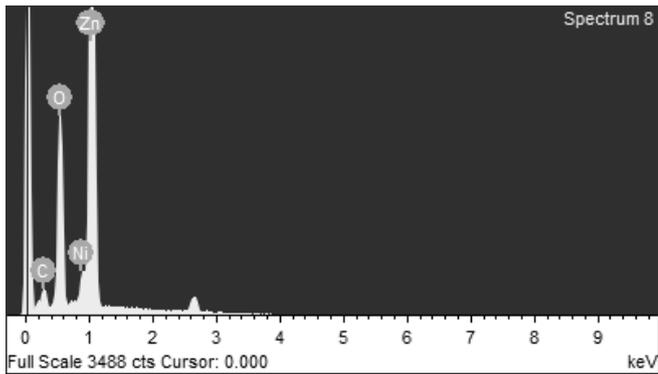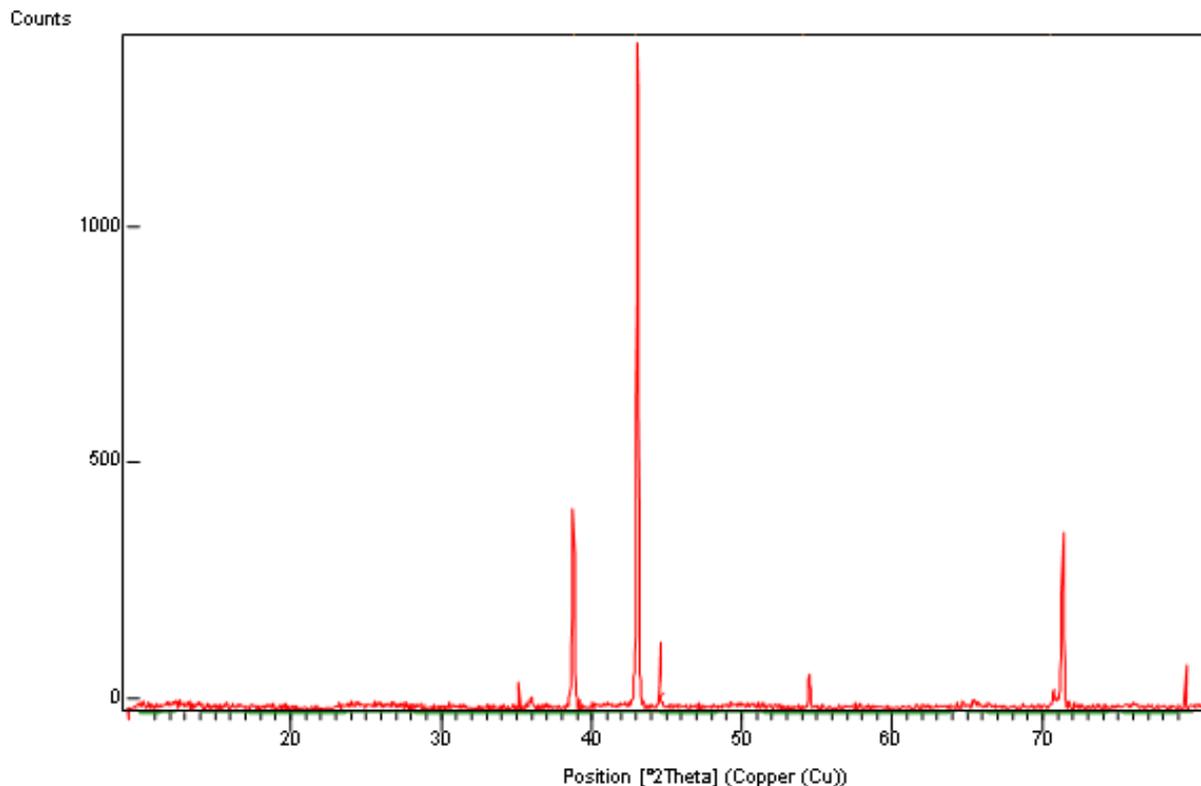
**Fig-5a:** EDAX Photograph Obtained For Zinc- Nickel Alloy Electrodeposition From Basic Bath
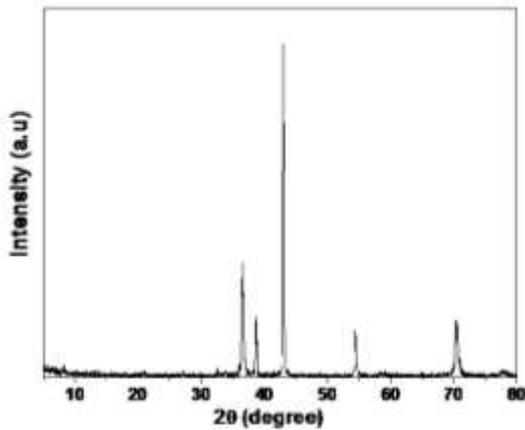


**Fig- 5b:** EDAX Photograph Obtained For Zinc- Nickel Alloy Electrodeposition From Optimized Bath

### 3.6. X- Ray Diffraction Studies

X- ray diffraction analysis carried out on the thin film of Zinc-Nickel alloy electroplated carbon steel obtained from basic bath and optimized bath were shown in Figure 6A and 6B. Intensity of peaks of Zinc- Nickel alloy electrodeposited carbon steel from optimized bath was lower and the peak width was broader than that of Zinc electrodeposited carbon steel obtained from Basic bath. The average crystal size was found to be 0.70nm against 1.65nm of Zinc- Nickel alloy electrodeposited carbon steel obtained from Basic bath. The incorporation of Lawsone influenced the growth of Zinc-Nickel alloy crystal such that it brought about a reduction in the crystal size. . Zinc nickel alloys with 8-17% nickel usually have a single γ-phase in electrodeposited coatings. The peaks obtained were in good agreement with the standard pattern of Zn-Ni alloy electrodeposition. The sharp and prominent peak at 2θ of 43.2° indicates that γ-$Zn_3Ni$ alloy is the dominant phase in the alloy composition.



**Fig- 6a:** XRD Photograph Obtained For Zinc-Nickel Alloy Electrodeposition From Basic Bath

**Fig- 6b:** XRD Photograph Obtained For Zinc-Nickel Alloy Electrodeposition From Optimized Bath

## 3.7. FT-IR Spectroscopy

The FT- IR Spectrum of the scrapped deposit obtained from optimized bath was given in Figure 8. This spectrum was used to determine the inclusion of Lawsone in the deposit. It was observed that OH stretching frequency in the free state had shifted from 3250- 3389 cm$^{-1}$. The C=C aromatic stretching had shifted from 1598-1700 cm$^{-1}$. The CO stretching frequency had shifted from 1150- 1295 cm$^{-1}$. These observations indicated the inclusion of major component, Lawsone in L.inermis extract into the metal surface. These observations showed that the major component had co ordinate with Zinc and Nickel alloy through oxygen atom of Lawsone and also through the $\pi$ electrons of Naphthalene ring resulting in the formation of Zn- Ni alloy - Lawsone complex formed on the anodic sites of the metal surface. The peak at 1398cm$^{-1}$ was due to Zinc hydroxide formed on the cathodic sites of the metal surface.
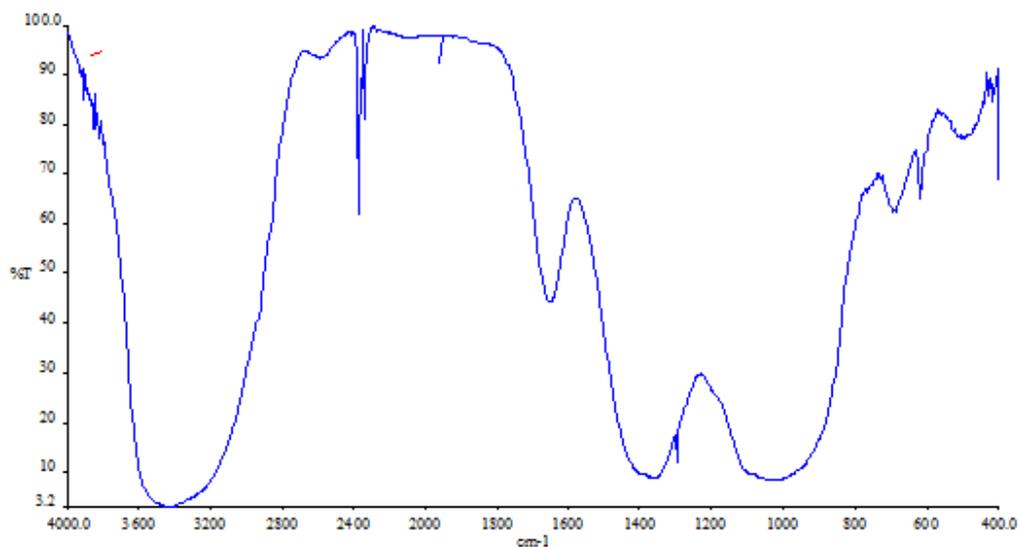


**Fig 7:** FTIR Spectrum Of Scrapped Zinc-Nickel Deposit Obtained From Optimized Bath

## 4. CONCLUSION

Optimised bath composition for Zinc-Nickel alloy electrodeposition in the presence of Lawsone is given in the Table 6. 1

**Table 6.1:** Optimized Bath Composition And Operating Conditions For Zinc- Nickel Alloy Electrodeposition

| Bath composition | Conc.( gL$^{-1}$) | Operating conditions |
|---|---|---|
| ZnSO$_4$ .7H$_2$O<br>NiSO$_4$.6H$_2$O<br>Na$_2$SO$_4$<br>H$_3$BO$_3$<br>Lawsone | 91 gL$^{-1}$<br>20 gL$^{-1}$<br>16 gL$^{-1}$<br>8gL$^{-1}$<br>0.45mg/L | Anode: Zinc metal(99.99%pure)<br>Cathode: mild steel<br>Temperature:303K<br>PH: 3.5<br>Plating time:30 minutes<br>Bright current density range: 0.3-3.5 Adm$^{-2}$<br>Cell constant in Ampere:1A |

The Zinc-Nickel alloy deposits on carbon steel obtained from this optimized bath had shown better characteristic properties than the Zinc-Nickel alloy deposits obtained from Basic Bath. This confirmed the influence of Lawsone on electrodeposition of Zinc-Nickel alloy.

The Current efficiency and the throwing Power of Zinc-Nickel alloy Electrodeposited carbon steel from optimized bath was found to be increased than in the case of Zinc-Nickel alloy deposits on carbon steel from basic bath. The fine grained deposits on Zinc-Nickel alloy electroplated carbon steel from optimized bath revealed the inclusion of addition agent on Zinc-Nickel alloy electrodeposition. XRD spectra revealed the reduction in the particle size of Zinc-Nickel deposits on carbon steel obtained from optimized bath. EDAX analysis confirmed the inclusion of Lawsone on Zinc-Nickel alloy electroplated carbon steel from optimized bath and it revealed that Nickel percentage in this deposition is 8.75%. FT-IR Spectroscopy confirmed the inclusion of Lawsone on Zinc-Nickel alloy electroplated carbon steel from optimized bath.

## ACKNOWLEDGEMENT

## REFERENCES

[1]. Kim H, Popov BA, and Chem KS, Journal of Electrochemical society, 150, C81, 2003.

[2]. Shears A.P, Journal of Electrochemical Society, 133 6711989.

[3]. Angelopoulos M, IBM J. Res & Dev., 45, 57 , 2001.

[4]. Brooks I. and Erb U., Ser. Mater., 44,853 2001.

[5]. Muller C., Sarret M. and Benballa M., Journal of Electroanalytical Chemistry, 519, 2002, 85.

[6]. Anicai L., Siteavu M., and Grunwald E., Corrosion Prevention Control, 39, 89, 1992.

[7]. Abou- Krisha M.M., Zaky A.M. and Toghan A.A., Journal of Corrosion Science and Engineering, 7, 1, 2005.

[8]. Arthoba Naik Y. and Venkatesha T.V., Indian Journal of Chemical Technology, 10, 2003, 318.

[9]. Arthoba Naik Y. and Venkatesha T.V, Bulletin of Material Science, 28, 2005, 495.

[10]. Arthoba Naik Y., Venkatesha T.V. and Vasudeva Nayak P., Bulletin of Electrochemistry, 16, 2000, 481.

[11]. Kamal M. Jawad T., Pharmocological activites of Lawsonia inermis Linn : a review.IJBR,1, 2, 2012,37-43.

[12]. JainVC, Shah DP,Sonani NG, Dhakara S, Patel NM. Pharmacognostical and preliminary phytochemical investigation of Lawsonia inermis L. leaf. Rom J Biol-Plant Biol, 55, 2, 2012, 127-133.

[13]. Chaudhary G. Goyal S, Poonia P. Lawsonia inermis Linnaeus: a phytopharmacological review. IJPSDR, 2,2,2010, 91-98.

[14]. Available :http://prr.hec.gov.pk/chapters/2135-3.pdf

[15]. Upadhyay B Dhaker AK, Singh KP, Kumar A.Phytochemical analysis and influence of edaphic factors on lawsone content of Lawsonia inermis L. J Phytol ,2 ,6,2010, 47-54.

## BIOGRAPHY



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