A Study on the Effect of Lawsone (2-Hydroxy 1, 4-Napthoquinone) Isolated from *Lawsonia Inermis Linn*. Leaf on Nickel Electrodeposition from Waats Bath

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Abstract: Nickel electrodeposition is carried out in the presence of Lawsone (2-hydroxy1,4-napthoquinone) isolated from Lawsonia inermis Linn leaf. The bath constituents are optimized through Hull cell experiments. Operating parameters such as pH, temperature and current density are also optimized. The current efficiency and throwing power are measured at different current densities. The surface of the plated steel is examined using scanning electron microscopy (SEM); and Energy Dispersive Spectroscopy (EDS) for the surface elemental composition analysis. The crystal structure is studied by X-ray diffraction study. The inclusion of addition agent in the deposit is confirmed by FT-IR . SEM photomicrographs reveals fine-grained structure of the deposit from the optimum bath. IR spectrum of the scratched deposit shows inclusion of addition agent. XRD and EDAX studies reveals the inclusion of lawsone.

Key Words: Waats Bath, Nickel, current Efficiency, Throwing Power, SEM, XRD

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1 INTRODUCTION

Nickel electroplating is a commercially important and versatile surface finishing process. Its commercial importance may be judged from the amount of nickel in the form of metal and salts consumed annually for electroplating roughly 100,000 metric tons worldwide as well as its versatility from its many current applications[1-3]. Professor Oliver P. Watts at the University of Wisconsin, aware of most of these developments, formulated an electrolyte in 1916 that combined nickel sulphate, nickel chloride, and boric acid and optimized the composition of nickel electroplating solution[4].

Today the Watt's solution is widely applied and its impact on the development of modern nickel electroplating technology cannot be overstated. Nickel deposits from well known watts nickel bath are white and matt. The watts solution is the basis for most decorative nickel plating solutions and it could be used successfully at lower temperatures[5].

It is known that organic additives are added in traces to electroplating baths to modify the structure, morphology and properties of the metal deposits. For nickel plating from Watts bath additives unsaturated groups such as >C= O, >N-C=S, -C=N etc are recognized as brighteners[6]. Thus in this present study, Lawsone isolated from Lawsonia inermis Linn leaf is used as an additive with the functional group >C= O.

2. EXPERIMENTAL METHODS

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 3.1A) were carried out without agitation. The pH of the bath solution was adjusted with 10%hydrochloric acid or sodium carbonate solution. Nickel 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 Hullcell 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 Nickel plating was carefully studied and recorded through Hull cell codes.

All the experiments were conducted at room temperature. Lawsone was isolated by Tommassi[7] Procedure from Lawsonia inermis Linn leaf. 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. The surface of the plated steel is examined using scanning electron microscopy (SEM); and Energy Dispersive Spectroscopy (EDS) for the surface elemental composition analysis. The crystal structure is studied by X-ray diffraction study. The inclusion of addition agent in the deposit is confirmed by FT-IR and hardness study.

3. RESULTS AND DISCUSSION

3.1 HULL CELL STUDIES:

EFFECT OF LAWSONE

Basic bath composition was given in Table 3.1A. Basic bath solution gave coarse dull deposit between the current density range of 1 and 4Adm^{-2} at 1A cell current (Figure.3.1).To improve the nature of deposit, Lawsone isolated from Lawsonia inermis linn leaf was added to the bath solution. 1g of Lawsone is dissolved in 100ml of ethanol and then it is used for electrodeposition process. With increase in the concentration, the nature of deposition was improved and became bright. At a concentration of 120ml of Henna Extract, the Hull cell panels were bright between the current density ranges of 1 and 3.5 Adm^{-2}.With further increase in the concentration of Lawsone, the nature of the deposit became burnt at higher current density region. Therefore, on the basis of the above observations, the concentration of Lawsone was kept at120mlL^{-1} as optimum. Further experiments were carried out by keeping the amount of Lawsone at 120mlL^{-1}.

EFFECT OF NICKEL SULPHATE:

To find out the effect of nickel ion, the Nickel sulphate concentration was varied from 15-300 gL^{-1} keeping Lawsone at 120mlL^{-1}. At low current density region, dull and streaky deposits and at high current density range, burnt deposits were obtained (Figure3.1B).

TABLE 3.1A
BASIC BATH COMPOSITION AND OPERATING CONDITIONS FOR NICKEL ELECTRODEPOSITION

Bath composition	Concentration gL^{-1}	Operating conditions
Nickel Sulphate Nickel Chloride Boric Acid pH	300 gL^{-1} 60 gL^{-1} 40 gL^{-1} 4-4.5	Temperature: 30^{o}C Anode : Nickel metal (99.99% pure) Cathode: Carbon steel

Key
Br- Bright, Bu- Burnt, D- Dull, SB –Semi Bright, St- Streaky, Un- Uncoated, P- Powdery

FIGURE – 3.1
HULL CELL DIAGRAM BASIC BATH FOR NICKEL ELECTRODEPSOITION AT 1A CURRENT

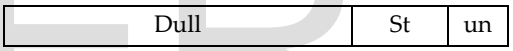
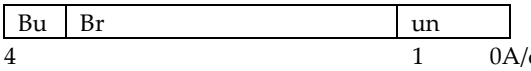
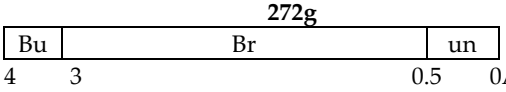


FIGURE- 3.1A
HULL CELL DIAGRAM – EFFECT OF LAWSONE
120ml



With increase in the concentration of Nickel sulphate, the brightness range was extended to higher and lower current density regions. At a concentration of 272gL^{-1}, a satisfactory bright deposit was obtained over a current density range of 0.5-3Adm^{-2} was obtained. Above this concentration of Nickel sulphate, no improvement in the nature of deposit was observed. The concentration of Nickel sulphate was fixed at 272gL^{-1} as optimum.

FIGURE- 3.1B
HULL CELL DIAGRAM- EFFECT OF NICKEL SULPHATE
272g

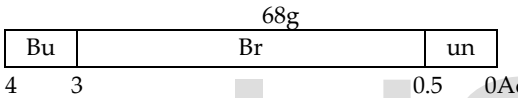


EFFECT OF NICKEL CHLORIDE:

Nickel Chloride was added to increase the anode dissolution and the conductance of the bath solution. The concentration of Nickel Chloride was varied from 2-70 gL^{-1}. At lower concentrations, the Hull cell panels showed 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 Nickel Chloride and at 68 gL^{-1}, the deposit was bright over a current density range of 0.5-3Adm^{-2}.Further increase in the concentration (>68gL^{-1}) did not introduced any effect on the nature of deposit and on the conductance also. So, the concentration of Nickel Chloride was fixed at 68 gL^{-1} in the bath solution. The Hull cell patterns showing the effect of Nickel Chloride are given in Figure 3.1C

FIGURE- 3.1C
HULL CELL DIAGRAM- EFFECT OF NICKEL CHLORIDE

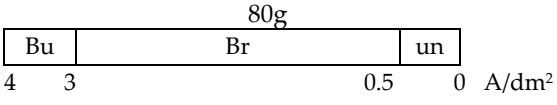


EFFECT OF BORIC ACID:

Boric acid was added to Produce smoother, more ductile deposits and increase the current density range of the bath solution. Boric acid acts as a buffer to maintain the pH of the bath. The concentration of Boric acid was varied from 2-100 gL^{-1}. At lower concentrations, the Hull cell panels showed dull deposit at low current density region and burnt at high current density region.

The dull and burnt regions were found to be reduced with increase in the concentration of Boric acid and at 80 gL^{-1}, the deposit was bright over a current density range of 0.5-3Adm^{-2}.Further increase in the concentration(>80 gL^{-1}) did not introduce any effect on the nature of deposit and on the conductance also. So, the concentration of boric acid was fixed at 80 gL^{-1} in the bath solution. The Hull cell pattern for the effect of boric acid was given in Figure 3.1D

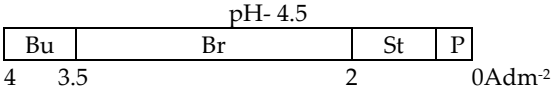
FIGURE- 3.1D
HULL CELL DIAGRAM- EFFECT OF BORIC ACID



EFFECT OF pH

To know the effect of pH, the pH of the bath solution was varied from 2-6. At pH 6, the Hull cell panels has shown burnt deposit at high current density region. Satisfactory deposit was obtained at pH of 4.5.. 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 4.5 as optimum. The Hull cell pattern was given in Figure 3.1E

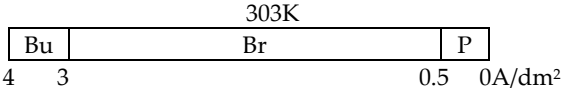
FIGURE- 3.1E
HULL CELL DIAGRAM- EFFECT OF pH



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 (<303 K), the deposition was bright in the current density range 0.5-3Adm^{-2} at 1A cell current. Above 303K, the deposit was dull in the low current density region. Therefore, the optimum operating temperature range was 303K.The Hull cell panels for the effect of temperature was given in Figure 3.1F

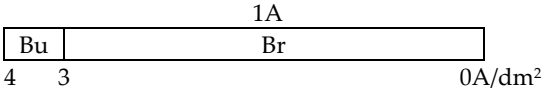
FIGURE V.1F
HULL CELL DIAGRAM- EFFECT OF TEMPERATURE



EFFECT OF CURRENT:

The Hull cell experiments were carried out at different cell currents (1-3A) for 10 minutes using optimum bath solution. It was found that at a cell current of 1A the deposit was bright in the current density range 0-3 Adm^{-2}.At a cell current of 2A, the deposit was bright in the current density range of 3-4 Adm^{-2}.At a cell current of 3A the deposit was bright over the current density range between 1.5 and 2.8 Adm^{-2}.The Hull cell pattern was given in Figure 3.1G

FIGURE- 3.1G
HULL CELL DIAGRAM- EFFECT OF CELL CURRENT



OPTIMIZED BATH:

By Varying the components in the Basic bath in the above manner made an optimized bath. This optimized bath contained 120ml of Lawsone. The bath composition and operating conditions were shown in Table 3.1B

TABLE 3.1B
OPTIMIZED BATH COMPOSITION AND OPERATING CONDITIONS FOR NICKEL ELECTRODEPOSITION

Bath composition	Concentration (gL^{-1})	Operating conditions
Nickel sulphate Nickel Chloride Boric acid Lawsone	272 gL^{-1} 68 gL^{-1} 80 gL^{-1} 120mlL^{-1}	Anode: Nickel metal (99.99%pure) Cathode: Carbon steel Temperature :303K, PH: 4.5 Plating time:10minutes Bright current density range: 0-3Adm^{-2} Cell constant in Ampere:1A

3.2. EFFECT OF CURRENT DENSITY ON CURRENT EFFICIENCY DURING NICKEL ELECTRODEPOSITION ON CARBON STEEL

Current efficiency of Nickel electrodeposited Carbon steel obtained from Basic Bath and from Optimized bath with Lawsone were measured at various Current densities. At lower current density (1Adm^{-2}), the current efficiency of Nickel electrodeposited Carbon steel obtained from Basic bath and optimized bath with Lawsone were found to be 65% and 92% respectively.

The current density ranges from 1-4 Adm^{-2}, the efficiency was found to be increased and reached high at 4Adm^{-2}. The efficiency obtained were 75% and 99% respectively. Further increase in the current density, decreased the current efficiency (Table 3.2). This showed the absence of Hydrogen evolution at a current density range of 1-4 Adm^{-2}. Above this current density, hydrogen evolution was started but not to greater extent as in the case of basic Waats bath. This confirms that the additive Lawsone isolated from Lawsonia inermis linn leaf reduce the hydrogen evolution

3.3 DETERMINATION OF THROWING POWER:

Throwing power of Nickel electrodeposition obtained for Basic bath and optimized bath with Lawsone at different Current densities were given in Table 3.3. It was found that the optimized bath had shown greater throwing power than Basic bath. This showed the effect of Lawsone on deposition.

TABLE 3.2
EFFECT OF CURRENT DENSITY ON CURRENT EFFICIENCY DURING NICKEL ELECTRODEPOSITION ON CARBON STEEL

CURRENT DENSITY (A/dm2)	CURRENT EFFICIENCY (%)	
	BASIC BATH	OPTIMIZED BATH + LAWSONE
1	65	92
2	69	94
3	73	96
4	75	99
5	68	97

At lower current density, throwing power for Basic bath and optimized bath with Lawsone were found to be 14.99%, and 24.26% respectively. Above 1 Adm^{-2}, the throwing power of Nickel electrodeposition obtained from Basic bath and Optimized bath with Lawsone was found to be increased. Comparing the values with Watt's bath i.e. basic bath, the values obtained for optimized bath with Lawsone was high. This confirmed the effect of an additive, Lawsone

TABLE 3.3.
EFFECT OF CURRENT DENSITY ON THROWING POWER

CURRENT DENSITY (A/dm2)	THROWING POWER (%)	
	BASIC BATH	OPTIMZED BATH + LAWSONE
1	14.99	24.26
2	11.13	23.15
3	10.47	20.23
4	10.12	17.58
5	9.25	16.47

3.4 POLARIZATION STUDIES:

The potential of Carbon steel Cathode was measured galvanostatically with respect to saturated Calomel electrode. The variation of potential in Basic bath and optimized with Lawsone was shown in the Figure 3.4 The shift in Cathode potential towards negative direction was observed for Nickel electrodeposited Carbon steel

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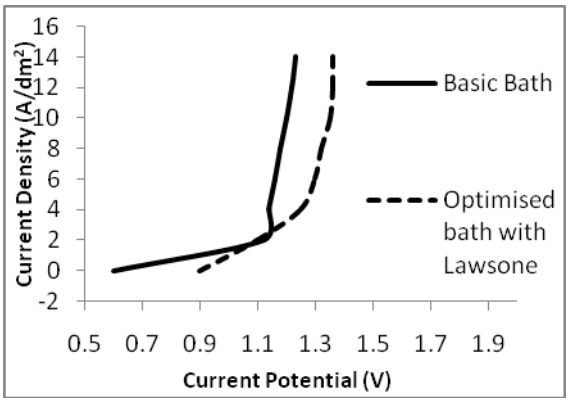
obtained from Basic bath and optimized with Lawsone. This showed the effect of Lawsone on Nickel electrodeposition.

FIGURE V.4
EFFECT OF ADDITIVE ON CATHODIC POLARISATION DURING NICKEL ELECTRODEPOSITION



3.5. SEM ANALYSIS ANALYSIS ON METAL SURFACE

The SEM images of Carbon steel specimen electroplated with Nickel in the presence and the absence of Lawsone were shown in Fig 3.5A and 3.5B.

The SEM image of Nickel electrodeposited Carbon steel obtained from Basic bath (i.e) in the absence of Lawsone had produced deposits, with irregular shape and larger crystal size. The crystal size and metal surface were not uniform. (Fig.3.5A) for the Basic bath.

Thus, the metal surface was very rough in the absence of Lawsone. The SEM image of Nickel electrodeposited Carbon steel surface obtained from optimized bath with Lawsone (Fig. 3.5B) showed uniform crystal size and their arrangements were also uniform. Hence, gave a bright deposit. This was due to the effect of Lawsone. It was incorporated into the metal surface, and made the surface smooth.

3.6. EDAX ANALYSIS

EDAX spectrum of Nickel electrodeposited carbon steel from Basic bath showed the presence of Nickel, Iron, Oxygen and Carbon on the metal surface. The weight percentages of Nickel, ,Iron, Oxygen and Carbon. in Nickel electrodeposited carbon steel from Basic bath were found to be 80.01%, 3.97% , 3.14%, and 12.88% respectively.(Figure 3.6A)

But in the Nickel electrodeposited carbon steel from Optimized bath had 95.91% of Nickel and 4.09% of Oxygen. There was no Fe on the metal surface .This showed that in the presence of additive, there were no pores. This led to the conclusion that the deposition was uniform on the metal surface in the presence of additive. The inclusion of additive was also confirmed by the presence of Oxygen with 4.09% which was greater than in the case of Oxygen in Basic bath (Fig.3.6B)

FIGURE.3.5A
SEM PHOTOMICROGRAPH OBTAINED FOR NICKEL ELECTRODEPOSITION FROM BASIC BATH

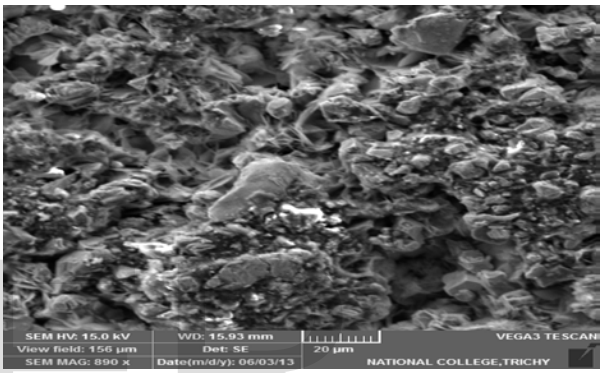
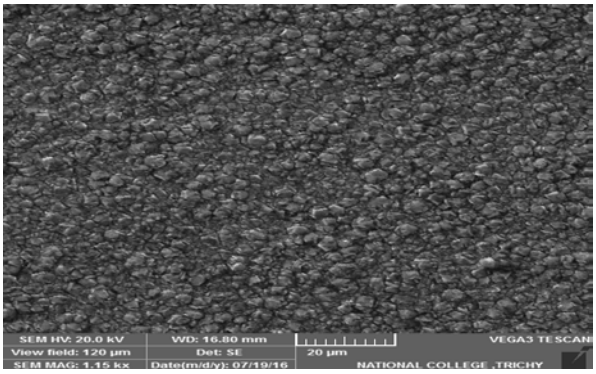


FIGURE 3.5B
SEM PHOTOMICROGRAPH OBTAINED FOR NICKEL ELECTRODEPSOITION FROM OPTIMIZED BATH



3.7. X- RAY DIFFRACTION STUDIES:

X- ray diffraction analysis carried out on the thin film of nickel electroplated carbon steel obtained from basic bath and optimized bath were shown in Figure 3.7A and 3.7B. Intensity of peaks of Nickel electrodeposited carbon steel from optimized bath was lower and the peak width was broader than that of Nickel electrodeposited

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carbon steel obtained from Basic bath. The average crystal size was found to be 8.95nm against 36nm of Nickel electrodeposited carbon steel obtained from Basic bath. The incorporation of Lawsone influences the growth of Nickel crystal such that it brought about a reduction in the crystal size. The Lawsone included in the deposit acted as protrusions in a metal electrolyte interface resulting in a higher current density which increased the rate of nucleation and inhibited the growth of Nickel crystal and finally gave fine grained deposits.

The Preferred orientation Ni (111) for Nickel deposition obtained from basic and optimized bath showed higher activity towards Hydrogen and Oxygen evolution due to the presence of large amount of active sites of Nickel . The peaks observed at 2θ of 44.5^0, 51.8^0 and 76.4^0 are characteristic peaks of fcc nickel phase.

FIGURE 3.6A
EDAX PHOTOGRAPH OBTAINED FOR NICKEL ELECTRODEPOSITION FROM BASIC BATH

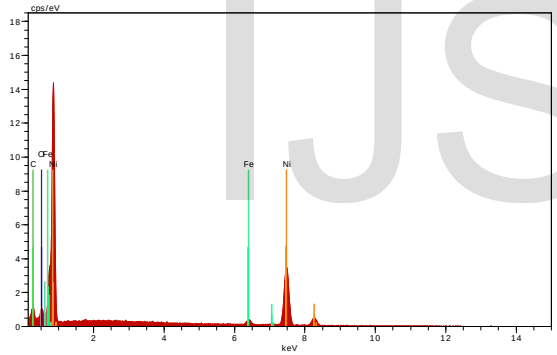
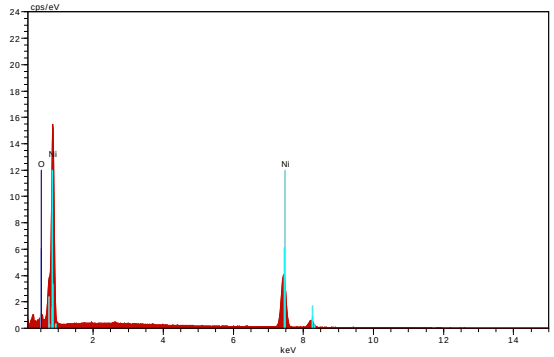


FIGURE 3.6B
EDAX PHOTOGRAPH OBTAINED FOR NICKEL ELECTRODEPOSITION FROM OPTIMISED BATH



3.8. FT- IR SPECTRAL ANALYSIS

The FT- IR Spectrum of Pure Lawsone and the scrapped deposit obtained from optimized bath was given in Figure V.8A and V.8B. 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 3159-3506 cm^{-1}. The C=C aromatic stretching had shifted from 1573-1635 cm^{-1}. The CO stretching frequency had shifted from 1116- 1259 cm^{-1}. The weak bands between 365-605 cm^{-1} was due to metal-oxygen bond

These observations indicated that the inclusion of principal colouring agent Lawsone in L.inermis extract into the metal surface. These observations showed that the major component had coordinated with Ni^{2+} through oxygen atom of Lawsone and also through the π electrons of Naphthalene ring resulting in the formation of Ni^{2+}- Lawsone complex formed on the anodic sites of the metal surface.

FIGURE 3.7A.
XRD PHOTOGRAPH OBTAINED FOR NICKEL ELECTRODEPOSITION FROM BASIC BATH

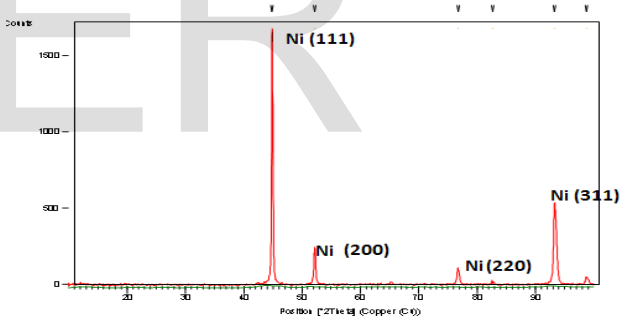


FIGURE 3.7B.
XRD PHOTOGRAPH OBTAINED FOR NICKEL ELECTRODEPOSITION FROM OPTIMISED BATH

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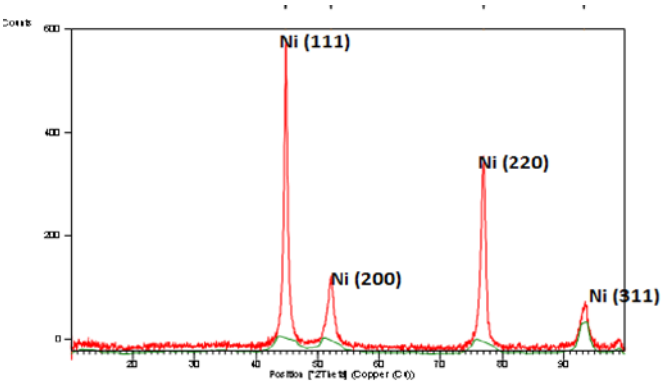


FIGURE 3.8A.
FT-IR SPECTRUM OF SCRAPPED NICKELDEPOSIT OBTAINED FROM PURE LAWSONE

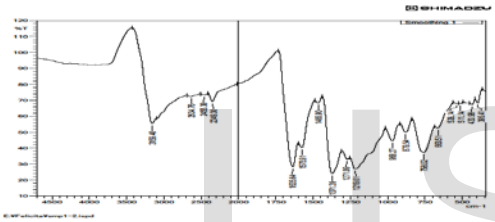
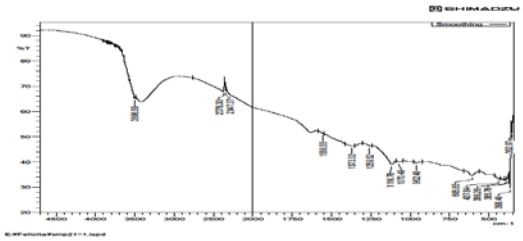


FIGURE 3.8B.
FT-IR SPECTRUM OF SCRAPPED NICKEL DEPOSIT OBTAINED FROM OPTIMIZED BATH



3.9.HARDNESS OF NICKEL ELECTRODEPOSITED CARBON STEEL

Hardness of the deposit obtained from basic bath and optimized bath at different current density was given in Table 3.4 The hardness value of basic bath was increased with respect to current density range of 1-4Adm^{-2} and at 5Adm^{-2} it was suddenly decreased. This trend was also the same in deposits obtained from optimized bath.

But the hardness value for deposits obtained from optimized bath was greater compared to value which was obtained for the deposit obtained from basic bath. The increase in hardness may be due to the fine grained structure of the deposits obtained in the presence of Lawsone. This showed the influence of Lawsone on the deposit.

TABLE.3.4.
HARDNESS OF NICKEL ELECTRODEPOSITED CARBON STEEL AT VARIOUS CURRENT DENSITIES

CURRENT DENSITY A/DM²	BASIC BATH Hv (50g LOAD)	OPTIMIZED BATH Hv (50g LOAD)
1	325.3	434.6
2	340.2	572.1
3	364.3	646.8
4	437.6	706.3
5	372.8	241.5

4. CONCLUSION

The Nickel deposits on carbon steel obtained from this optimized bath has shown better characteristic properties than the Nickel deposits obtained from Basic Bath. This confirms the influence of L.inermis extract on electrodeposition of Nickel. The Current efficiency and the throwing Power of Nickel Electrodeposited carbon steel from optimized bath is found to be increased than in the case of Nickel deposits on carbon steel from basic bath.

The shift in cathodic potential towards negative direction is observed for Nickel electrodeposited carbon steel from optimized bath on Polarization study confirms the effect of additive on electrodeposition. The fine grained deposits on Nickel electroplated carbon steel from optimized bath reveal the inclusion of addition agent on zinc electrodeposition. XRD spectra reveals the reduction in the particle size of Nickel deposits on carbon steel obtained from optimized bath. EDAX and FT-IR Spectroscopy confirm the inclusion of Lawsone on Nickel electroplated carbon steel from optimized bath. Hardness value

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is also increased for Nickel electrodeposited carbon steel from optimized bath.

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