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A Study on the effect of Lawsonia Inermis Linn. (Henna) Leaf Extract on Zinc-Nickel Alloy electrodeposition on mild steel from acid Sulphate bath

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Abstract

The effect of Lawsonia inermis Linn. Leaf extract on electrodeposition of zinc-nickel on mild steel was Studied in acidic sulphate solutions. The effect of bath constitutients, pH, current density and temperature on nature of deposits were studied through Hull Cell Experiments. The bath constituents and operating conditions were optimized. Deposit Properties and corrosion resistance were discussed. Throwing Power, Current Efficiency and Polarisation Studies were carried out. SEM photographs obtained from optimum bath revealed fine grained deposit of the alloy in the presence of extract and hence modified the morphology of zinc deposit. IR Spectrum of the scrapped deposit showed inclusion of the addition agent.

Key Words: Mild steel; Lawsonia inermis Linn leaf extract; Hull Cell Test; Corrosion resistance; throwing Power.

1. Introduction

Electroplated Zinc coatings are considered as one of the many ways of corrosion protection of steel. Recently, interest in Zn-Ni alloy coating has increased owing to its better mechanical and corrosion properties compared with pure Zinc Coatings since the Zinc deposit has the disadvantage of rapid dissolution[1-5]. Among the various Zinc alloys, Zn-Ni shows the best corrosion resistance[6] it is a good inhibitor of hydrogen permeation on metallic substrate[7, 8] and adheres well to the substrate[9]. The Zn-Ni alloy has also replaced highly toxic cadmium deposits [10, 11]. 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[12]. 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 does not produce good deposit over a wide current density range. In order to get good deposit, two or more addition agents are required[13]. 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[14-16]. In the present work, efforts have been made to develop sulphate bath containing non toxic and eco friendly henna extract. The use of local plant, Lawsonia inermis Linn (henna) leaf extract, as addition agent in zinc electrodeposition from acid based solution, in this work, makes this study significant. 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[17].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'[18-20]. 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) [21]. Aqueous extract of Henna is also used in corrosion and it is best inhibitor for iron in HCl acid and in aqueous solution containing 60 ppm of Cl^- ion[22].Thus, it is expected to exhibit electrochemical activity of enhanced quality zinc electrodeposition on mild steel. It is also very environment friendly and its successful use as an additive, in the improved deposition of zinc on mild steel, will be technologically and economically beneficial.

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%

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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.

Table 1. Basic bath composition and operating conditions

Bath composition	Concentration gL^{-1}	Operating conditions
Zinc Sulphate Nickel Sulphate Sodium Sulphate Boric acid (H_3BO_3) pH	130 gL^{-1} 15 gL^{-1} 40 gL^{-1} 15 gL^{-1} 3.5-4.5	Temperature: $30^o \pm 2^o$ C Anode: Zinc metal (99.99% pure) Cathode: Carbon steel

All the experiments were conducted at room temperature. A known amount of Henna Extract 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. Polarization studies were carried out by using a three-compartment cell. The area of zinc anode was 2 cm^2.Mild steel was used as cathode with an exposed area of 2 cm^2.The cathode potential was recorded galvanostatically with respect to standard calomel electrode at different current densities. 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. The corrosion behavior of zinc coated samples with and without additive were studied by weight loss method at room temperature. The exposed area of the specimen was 5 x 2.5 cm^2. The thickness of the coating was 15µm. For weight loss method, the corrosive medium was 3.5% NaCl. The coated samples were immersed in NaCl solution and the plates were weighed accurately and periodically for every 5 days till 30 days. The loss in weight so obtained was used to determine in corrosion velocity. Polarisation and AC impedence studies were also carried out to fnd out the corrosion resistance property of the sample with additive.

The porous nature of the deposit of the specimens was examined by adopting porosity test. The steel samples of 5x2.5 cm^2 were taken for this study. The specimens after plating were subjected to bright dip in 1% nitric acid followed by water wash. The porosity of the deposit was assessed by ferroxyl test[23]. This test indicated the porous free nature of the deposit. Further, the salt spray test as per ASTM B 117 was carried out in a salt spray chamber. The deposited plates were subjected to a continuous spray of 5% sodium chloride vapours.

3. Results and discussion:

3.1Hull cell studies

Effect of Lawsonia inermis extract

Table 1. 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, Henna Extract was added to the bath solution. Addition of Henna Extract will improve the nature of deposition and at a concentration of 100ml of Henna Extract, the Hull cell panels were bright between the current density range of 0.3 and 3.5Adm^{-2}.With further increase in the concentration of Henna Extract, the nature of the deposit became burnt at higher current density region. Therefore, on the basis of the above observations, the concentration of Henna Extract was kept at 100 ml/l as optimum. The Hull cell patterns are shown in Figure 3.1A.

Table 2.Basic Bath Composition And Operating Conditions For Zinc-Nickel Alloy Electrodeposition

Key

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

Fig.3.1 Hull Cell Diagram – Basic Bath At 1A Current

Bu	D	P	un

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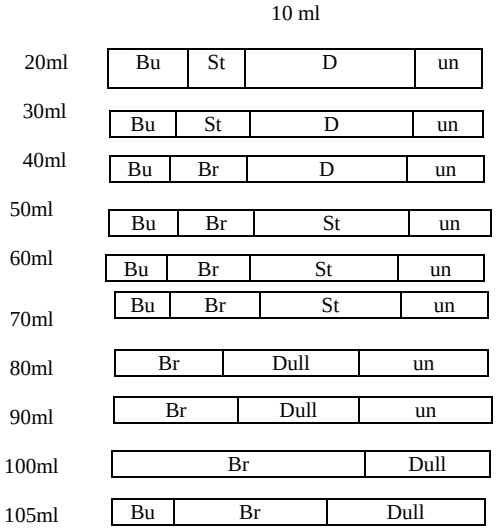
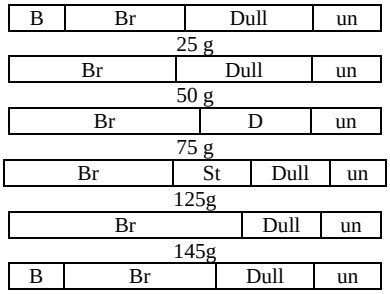
Fig. 3.1A Hull Cell Diagram – Effect of L.Inermis Extract

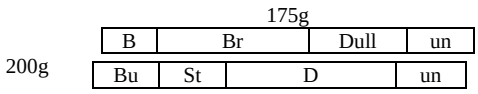


Effect of Zinc Sulphate

There was a close relation between the concentration of Zinc Sulphate and appearance of plating layer in cell experiment. Veeraraghavan et al[24] reported that in order to get high corrosion resistance a bright Zinc deposit, it was essential to strike a balance between amounts of Zinc content in bath solution.To find out the effect of Zinc ion, the Zinc sulphate concentration was varied from 25-200gL^{-1} keeping Henna Extract at 100 mlL^{-1}. At lower Concentrations, bright deposit was observed in the current density region of 1-4Adm^{-2}. At low current density region, dull deposits and at high current density range, burnt deposits were obtained (Figure 3.1B).With increase in the concentration of Zinc Sulphate; the brightness range was extended to higher and lower current density regions. At a concentration of 145gL^{-1}, a satisfactory bright deposit was obtained. Above this concentration of Zinc Sulphate, no improvement in the nature of deposit was observed. The concentration of Zinc Sulphate was fixed at 145g L^{-1} as optimum.

Fig.3.1B
Hull Cell Diagram: Effect of Zinc Sulphate

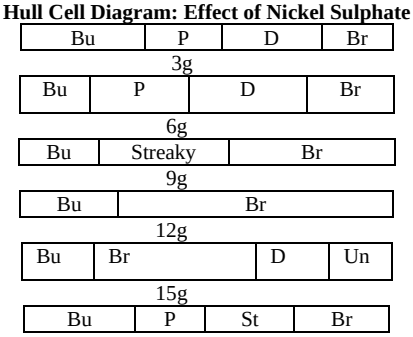




Effect of Nickel Sulphate

At particular concentration of Nickel ions in the solution, anode was properly beneficial to dissolution and cathode polarization increased. So a fine crystalline layer was obtained. Roev et al[25] showed that 3gL^{-1} of Ni gave fine grained deposit in alkaline Zn-Ni alloy plating bath. Further increase in the concentration produce black powdered deposit. So it is necessary to optimize the concentration of Ni in the bath solution. The Concentration of nickel Sulphate was varied from 2-20gL^{-1}. At a very low concentration, the Hull cell panels have 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 12gL^{-1}, the deposit was bright over the current density range of 0.3-4$Adm^{-2.}$ Further increase in the concentration, did not show any improvement in the bright current density region. The Hull Cell patterns showing the effect of nickel sulphate are shown in Fig. 3

Fig.3. 1C
Hull Cell Diagram: Effect of Nickel Sulphate



Effect of Sodium Sulphate

Sodium sulphate was added to increase the conductance of the bath solution. The concentration of Sodium sulphate was varied from 15-75gL^{-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 Sodium sulphate and at 55g L^{-1}, the deposit was bright over a current density range of 0.3-3.5Adm^{-2}. Further increase in the concentration (>55gL^{-1}) did not introduced any effect on the nature of deposit and on the conductance also. So, the concentration of Sodium sulphate was fixed at 55gL^{-1} in the bath solution. The Hull cell patterns showing the effect of sodium sulphate are given in Figure 3.1D.

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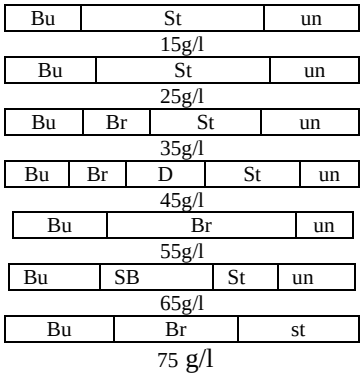
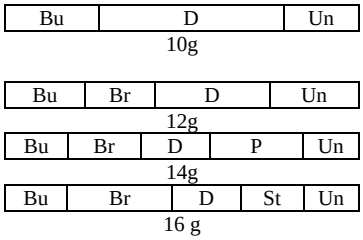
Fig.3.1.D.
HULL CELL DIAGRAM- EFFECT OF SODIUM SULPHATE

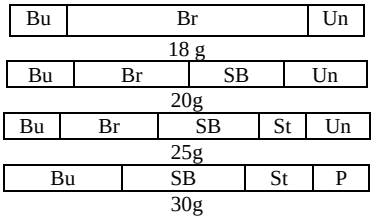


Effect of Boric Acid:

The role of boric acid has been great interest in the electrodeposition of Ni[26 &27] and Zn-Ni alloy[28].It is now believed that boric acid either complexes with Ni^{2+}, acting as a homogenous catalyst, or adsorbs on the electrode surface and has a significant role in morphology and composition characteristics. The presence of boric acid results in an increase of current efficiency of deposition process, amount of zinc in the deposited alloy, nucleation density of the deposit[28]. 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 pH of the electrolyte bath[29,30]. 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 10-30gL^{-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 boric acid and at 18gL^{-1}, the deposit was bright over a current density range of 0.3-3.5Adm^2.Further increase in the concentration (>18gL^{-1}) did not introduced any effect on the nature of deposit and on the conductance also. So, the concentration of boric acid was fixed at 18gL^{-1} in the bath solution. The Hull cell patterns showing the effect of boric acid are given in Figure 3.1E.

Fig. 3.1.E
Hull Cell Diagram- Effect of Boric Acid

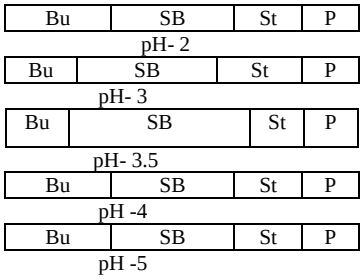




Effect of pH And Temperature

To know the effect of pH, the pH of the bath solution was varied from 2-5.At higher pH, the Hull cell panels showed 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. The Hull cell patterns are as shown in Figure 3.1F.

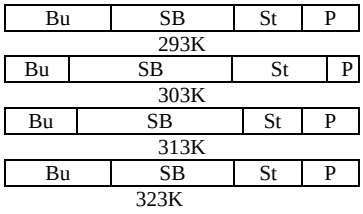
Fig. 3.1.F.
Hull Cell Diagram- Effect of pH



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 1-4Adm^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 showing the effect of temperature are shown in Figure 3.1G.

Fig. 3.1.G.
Hull Cell Diagram- Effect of Temperature.



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 the deposit was bright in the current density range 0.3-5 Adm^{-2}. At a cell current of 2A, the deposit was semi bright in the current density range of 1-3Adm^{-2}. At a cell current of 3A the deposit was semi bright over the

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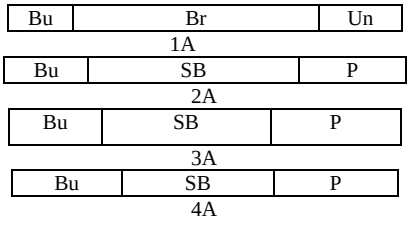
current density range between 2 and 3 Adm^{-2}. At cell current s of 3 A and 4A, the Hull Cell panels showed burnt deposit on the side of High cathode current density. This increases the anode polarization and led to large decrease of deposition speed of Zn-Ni[31]. This observation revealed bath gave bright deposit in the current density range of 0.3-3.5Adm^{-2}. The Hull cell patterns are as shown in Figure 3.1H.

Fig. 3.1H.
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 100mlL^{-1} of L. inermis Extract. The bath composition and operating conditions were shown in Table 2

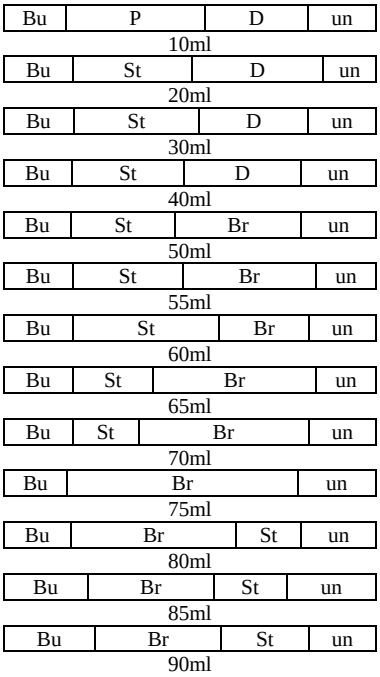
TABLE .2
Optimum Bath Composition and Operating Conditions For Zinc- Nickel Alloy Electrodeposition

Bath composition	Conc.(gL^{-1})	Operating conditions
$ZnSO_4.7H_2O$ $NiSO_4.6H_2O$ Na_2SO_4 H_3BO_3 Henna Extract	145 gL^{-1} 12 gL^{-1} 55 gL^{-1} 18 gL^{-1} 100 mlL^{-1}	Anode: Zinc metal(99.99%pure) Cathode: mild steel Temperature:303K PH: 3.5 Plating time:30 minutes Bright current density range: 0.3-3.5 Adm^{-2} Cell constant in Ampere:1A

Effect of Lawsone on Zinc- Nickel Alloy Electrodeposition:

Lawsone, the Principal Colouring agent in L. inermis extract, found by Qualitative analysis was dissolved in ethanol. In order to find out the effect of Lawsone on Zinc-Nickel alloy electrodeposition, Lawsone was added in optimized bath solution taken in the Hull cell in place of L. inermis extract. The amount of other components was not changed. The amount of Lawsone was varied from 5-90mlL^{-1} and it was found at 75mlL^{-1} of Lawsone, the deposit was bright at the current density range of 0.5-3.5 Adm^{-2}. At lower concentration, the Hull cell panels produced dull deposit at low current density region. The dull and burnt regions were found to be reduced with increase in the concentration and it showed maximum brightness at 75mlL^{-1} of Lawsone. Further increase in the concentration did not produce any effect on the nature of the deposit. The Hull cell patterns were given in the Figure 3.1I.

Fig. 3.1i.
Hull Cell Diagram- Effect of Lawsone



3.2. Effect of Current Density on Current Efficiency During Zinc-Nickel Alloy Electrodeposition

Current efficiency of Zinc-Nickel alloy electrodeposited carbon steel obtained from Basic Bath, Optimized bath and from Optimized bath with Lawsone were measured at various current densities. At lower current density (1Adm^{-2}), the current efficiency of Zinc-Nickel alloy electrodeposited carbon steel obtained from Basic Bath, Optimized bath and from Optimized bath with Lawsone were found to be 45 %, 75% and 72% respectively. At a current density range of 1-5Adm^{-2}, the efficiency was found to be increased and reached high at 5Adm^{-2}. The Efficiency obtained were 79%, 96%and 90% respectively. Further increase in the current density was found to decrease the efficiency (Table 3). This showed the absence of hydrogen evolution at a current density range of 1-5Adm^{-2}, after this hydrogen evolution was started. The same pattern was found in optimized bath with Lawsone. This showed Lawsone present in the Henna extract played major role on deposit. The current efficiency at 5 Adm^{-2} for optimized bath with Lawsone proved the effect of

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Lawsone on the deposits. There was no major difference in the current efficiency of deposits obtained from optimized bath and optimized bath with Lawsone (Figure 3.2) This proved the major effect on deposit was produced by Lawsone present in the Henna extract.

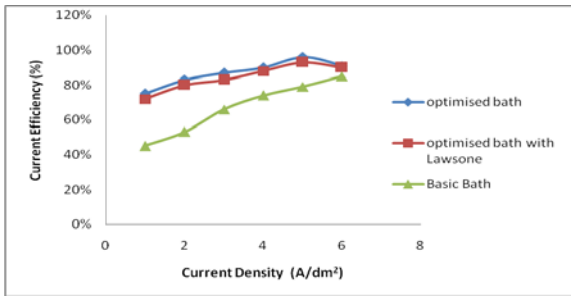
3.3. Determination of Throwing Power

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. Figure.3.3. showed the throwing power for basic bath, optimized bath and optimized bath with Lawsone at different current densities. It was found that the optimized bath had shown greater throwing power than Basic bath. At lower current density, throwing power for basic bath, optimized bath and optimized bath with Lawsone were found to be 15.4 %, 30.3 % and 28.2% respectively.

TABLE 3
Effect of Current Density on Current Efficiency During Zinc-Nickel Alloy Electrodeposition From Various Baths

CURRENT DENSITY (Adm^{-2})	CURRENT EFFICIENCY (%)		
	BASIC BATH	OPTMIZED BATH	OPTIMZED BATH + LAWSONE
1	45	75	72
2	53	83	80
3	66	87	83
4	74	90	88
5	79	96	93
6	85	91	90

Fig. 3.2.
Effect Of Current Density On Current Efficiency On Zinc- Nickel Alloy Electrodeposition

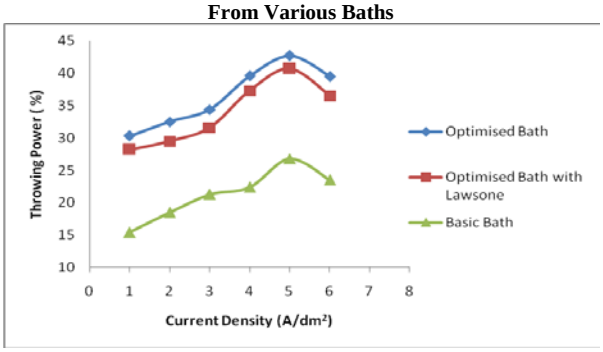


Further increase in current density, increased the Throwing Power and attained the maximum of 26.8%, 42.7% and 40.7% respectively at $5Adm^{-2}$. (Table 3.3.) Thorough literature survey revealed the presence of additive increased the throwing power on Zinc-Nickel alloy electrodeposition. The values obtained for optimized bath and the optimized bath with Lawsone were proven the effect of additive on throwing power during Zinc-Nickel alloy electrodeposition.

TABLE 4
Effect of Current Density on Throwing Power of Different Zinc- Nickel Alloy Baths

CURRENT DENSITY (A/dm2)	THROWING POWER (%)		
	BASIC BATH	OPTMIZED BATH	OPTIMZED BATH + LAWSONE
1	15.4	30.3	28.2
2	18.5	32.5	29.5
3	21.3	34.4	31.6
4	22.4	39.6	37.3
5	26.8	42.7	40.7
6	23.5	39.5	36.5

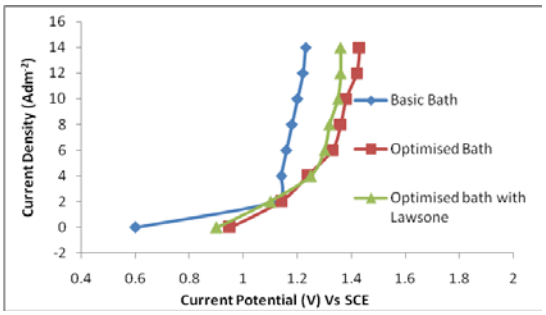
Fig. 3.3.
Effect Of Current Density On Throwing Power During Zinc-Nickel Alloy Electrodeposition At Various Current Densities From Various Baths



3.4. POLARIZATION STUDIES

The potential of carbon steel cathode was measured galvanostatically with respect to saturated calomel electrode at different current densities. The variation of potential in Basic bath, optimized bath and optimized bath with Lawsone on Zinc-Nickel alloy electrodeposition were shown in Figure 3.4. The shift in cathode potential towards negative direction was observed for Zinc-Nickel alloy electrodeposited carbon steel obtained from Basic bath, Optimized bath and Optimized bath with Lawsone. This showed the effect of additive on the deposits.

Figure.3.4.
Effect of Additive on Cathodic Polarization During Zinc-Nickel Alloy Electrodeposition



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3.5. SEM ANALYSIS OF METAL SURFACE

The SEM image of Carbon Steel Specimen electroplated with Zinc in the absence and presence of Henna extract were shown in Figure.3.5a and 3.5b respectively. The SEM Micrograph of Zinc-Nickel electro deposited Carbon steel surface from basic bath (Figure. 3.5A) had different and slightly larger crystal size. It was found that the crystal size was not uniform.The SEM Micrograph of Zinc-Nickel electro deposited Carbon steel surface from Optimized bath (Figure.3.5B) showed uniform arrangement of crystals, refinement in the crystal size and hence gave a bright deposit. This showed the effect of L.inermis extract on electro deposition of Zinc-Nickel alloy on carbon steel surface.

Figure.3.5a
Sem Photo Micrographs Obtained For Zinc-Nickel Alloy Electrodeposition From Basic Bath

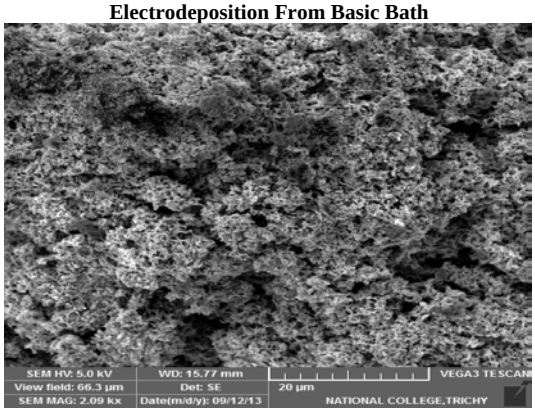
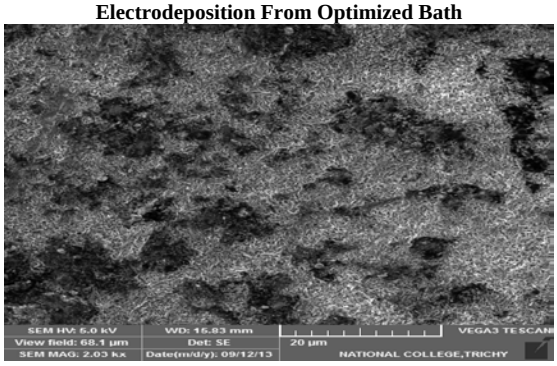


Figure.3.5b.
Sem Photo Micrographs Obtained For Zinc- Nickel Alloy Electrodeposition From Optimized Bath



3.6.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 3.6a). But in the Zinc-Nickel electrodeposited carbon steel from Optimized bath had only 65.54% of Zinc. This showed that the some of the active sites of Zinc were occupied by Lawsonia inermis Linn extract. 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-22.35% and carbon- 3.36%). (Figure 3.6b)This confirmed the inclusion of the L. inermis extract during Zinc-Nickel electrodeposition in the presence of extract.

3.7. 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 3**.7**a and **3.7**b. 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 L.inermis extract 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 peakat 2θ of 43.2° indicates that γ-Zn_3Ni alloy is the dominant phase in the alloy composition[32].

Fig. 3.6a.
Edax Photograph Obtained For For Zinc- Nickel Alloy Electrodeposition From Basic Bath

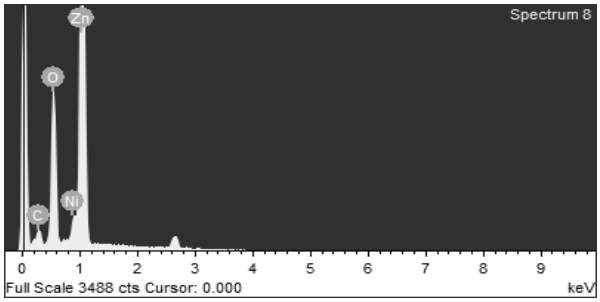
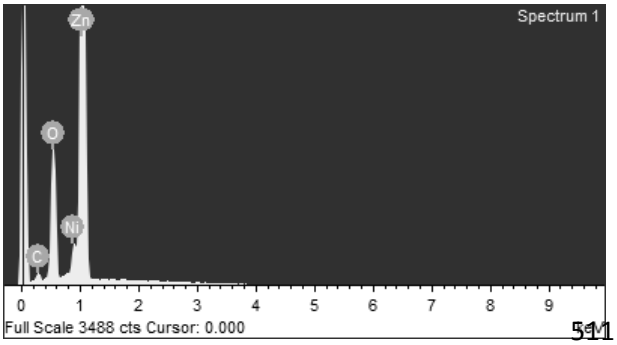


Fig. 3.6b.
EDAX Photograph Obtained For Zinc- Nickel Alloy Electrodeposition From Optimized Bath



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3.8.FT-IR Spectroscopy

The FT- IR Spectrum of the scrapped deposit obtained from optimized bath was given in Figure 3.8. This spectrum was used to determine the inclusion of L. inermis extract 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 π 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.

Figure. 3.7a
Xrd Photograph Obtained For Zinc-Nickel Alloy Electrodeposition From Basic Bath

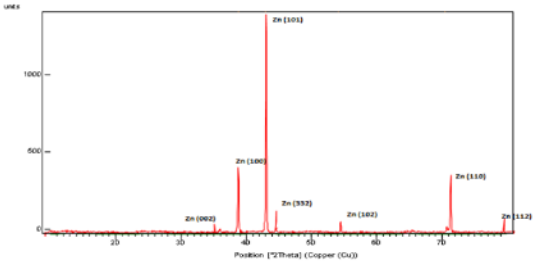


Fig. 3.7b
Xrd Photograph Obtained For Zinc-Nickel Alloy Electrodeposition From Optimized Bath

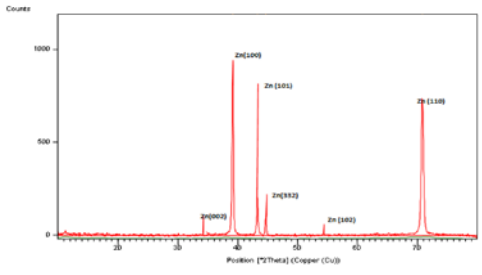
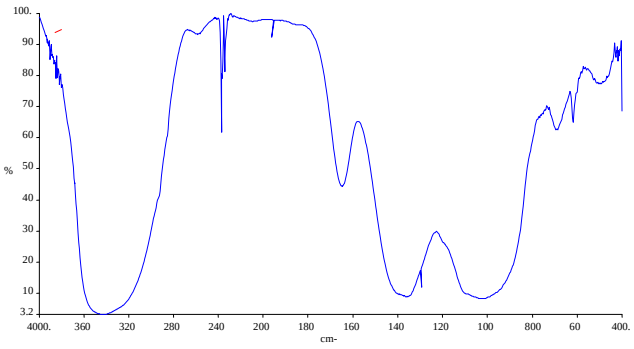


Figure. 3.8.
FT-IR Spectrum of Scrapped Zinc-Nickel Deposit Obtained From Optimized Bath



3.9.Hardness

Hardness of the deposit obtained from basic bath and optimized bath on Zinc-Nickel alloy electrodeposition on carbon steel at different current density was given in table. 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. This showed the influence of L.inermis extract on the deposit.

TABLE.5
Hardness of Zinc-Nickel Alloy Electrodeposited Carbon Steel At Various Current Densities

CURRENT DENSITY(Adm^{-2})	BASIC BATH H_v (50g Load)	OPTIMIZED BATH H_v (50g Load)
1	200.3	272.1
2	220.9	342.3
3	335.4	397.5
4	400.8	455.4
5	332.7	414.7

3.10. Corrosion Behaviour Zinc-Nickel Electroplated Carbon Steel Obtained From Basic Bath And Optimized Bath.

For Corrosion resistance study carbon steel cathodes were deposited to the thickness of 15µm. The specimens after plating were subjected to bright dip in 1% nitric acid.

3.10.1.Ferroxyl Test

The porosity of the deposit was tested with potassium ferric cyanide paper. The soaked paper with potassium ferric cyanide was placed on the Zinc-Nickel alloy electrodeposited carbon steel obtained from Basic bath and Optimized bath and no blue spots were observed. This test indicated pore free nature of the deposit.

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3.10.2. Salt Spray Test

Corrosion resistance test was carried out in a salt spray chamber. The Zinc- Nickel alloy electrodeposited carbon steel from Basic bath and Optimized bath were subjected to continuous spray of 5% sodium chloride solution. The Zinc- Nickel alloy electrodeposited carbon steel from Basic bath showed white rust within 120 hours. But the Zinc electrodeposited carbon steel from Optimized bath showed white rust at the end of 360 hours. (Table3.5).This behavior was mainly due to the formation of zinc chloride with 5% sodium chloride which was a stable by product in the corrosive environment. The basic $ZnCl_2$ that was produced at the corrosion site acts as a barrier film, however it had high electrical resistance and reduced the dissolution rate. This study showed the good corrosion resistance of the deposit.

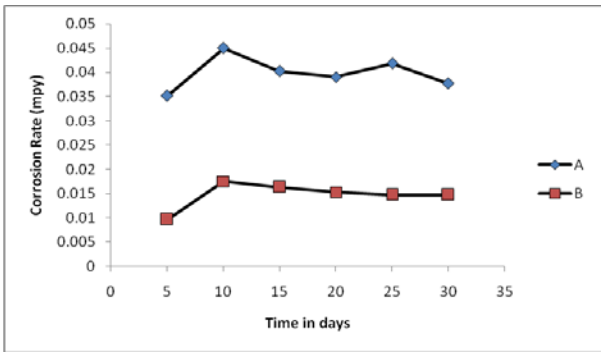
Table.6
Salt Spray Test Conducted At Different Time Intervals

PLATING BATH COMPOSITION	TREATMENT (HOURS)	OBSERVATION
BASIC BATH	24	No Rust
	48	No Rust
	96	No Rust
	120	White Rust
OPTIMIZED BATH	24	No Rust
	48	No Rust
	72	No Rust
	96	No Rust
	120	No Rust
	240	No Rust
	360	White Rust

3.10.3. WEIGHT LOSS METHOD

Figure.3.10.1 showed corrosion rate of Zinc-Nickel electrodeposited carbon steel from Basic bath and Optimized bath in 3.5 % NaCl solution. In both the cases the corrosion rate slightly increased in the beginning and then it decreased. The corrosion rate was higher for Zinc-Nickel electrodeposited carbon steel from Basic bath when compared that with Optimized bath. Thus it may be inferred that additive improved the corrosion resistant property of the deposit

Fig.3.10.1
Corrosion Rate Of Zinc- Nickel Electrodeposited Carbon Steel From Basic Bath And Optimized Bath In 3.5 % NaCl Solution



A. BASIC BATH **B. OPTIMIZED BATH**

3.10.4.Potentiodynamic Polarisation Studies

Figure 3.10.2a and 3.10.2b showed the effect of additive on corrosion behavior of Zinc-Nickel alloy deposits (Basic and Optimized Bath) in 3.5% NaCl Solution. The values were given in Table.7. The corrosion current (I_{corr}) for basic bath was 2.46 $x10^{-3}$ A/cm^2. It was decreased to 0.17 x 10^{-3} for optimized bath. The current of iron dissolution was decreased significantly, indicated that the surface was protected by the layer which was formed in the presence of additive, L.inermis leaf extract. The significant reduction in the corrosion current showed the adsorption of additive on the surface of carbon steel. It was also indicated that the protective film was formed on the metal surface. This gave protection from corrosion. Thus this protective layer by the additive controlled both the anodic and cathodic processes. Hence, the deposit obtained in the presence of additive, L.inermis extract showed maximum corrosion resistance.

3.10.5. AC IMPEDANCE SPECTRA

The AC impedance spectra of zinc plated carbon steel from Basic bath and optimized bath were shown in Figure 3.10.3a and 3.10.3b.

Table.7
Corrosion Parameter Of Zinc-Nickel Alloy Electrodeposited Carbon Steel By Potentiodynamic Polarisation Method

System	Ecorr mV vs SCE	bc mV/ decade	ba mV/ decade	LPR Ω cm^2	Icorr A/cm^2
Basic Bath	-1.12	23.8	4.48	8.56 x 10^{-3}	2.46 x 10^{-6}
Optimised Bath	-573.4	345.9	62.63	3.07 x 10^{-3}	0.17 x 10^{-6}

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Figure. 3.10.2a.
Potentiodynamic Polarisation Curve For Zinc-Nickel Alloy Electrodeposited Carbon Steel From Basic Bath

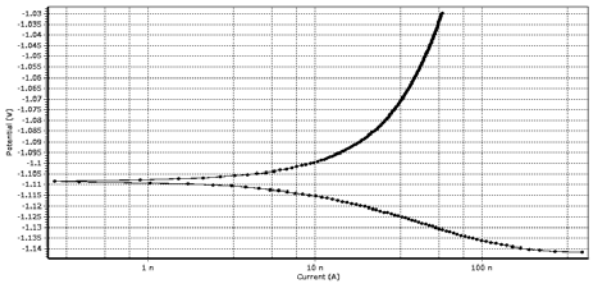
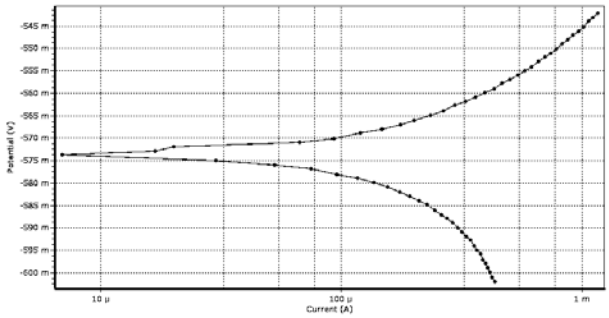


Figure. 3.10.2b.
Potentiodynamic Polarisation Curve For Zinc-Nickel Alloy Electrodeposited Carbon Steel From Optimized Bath



The AC impedance parameters, namely the charge transfer resistance (R_t) and double layer capacitance (C_{dl}) were given in the Table.8 For Basic bath, Rt value was found to be 42.5 Ω cm^2 and the C_{dl} value was 3.96 x 10^{-5}F/cm^2. But for optimized bath R_t value had increased tremendously from 4.246 Ω cm^2 to 975.4 Ω cm^2 and the C_{dl} value had decreased to 1.67x 10^{-9} F/cm^2. The increased in the R_t value and decreased in the C_{dl} value obtained from Ac impedance studies had shown the presence of protective layer in the presence of additive, Henna extract. This particular study justified the good Corrosion resistance of the layer which was formed on the Carbon steel surface in the presence of Henna extract. The increased corrosion resistance of the deposit may be also due to fine grained structure of the deposit.

Table.8
Corrosion Behaviour Of Zinc –Nickel Electrodeposited Mild Steel By Ac Impedence Study

System	Rt Ω cm^2	Cdl µF/cm^2
Basic Bath	42.5	3.96 x 10^{-5}
Optimized Bath	975.4	1.67x 10^{-9}

Figure.3.10.3.A
Ac Impedence Spectrum For Zinc-Nickel Alloy Electrodeposited Carbon Steel From Basic Bath

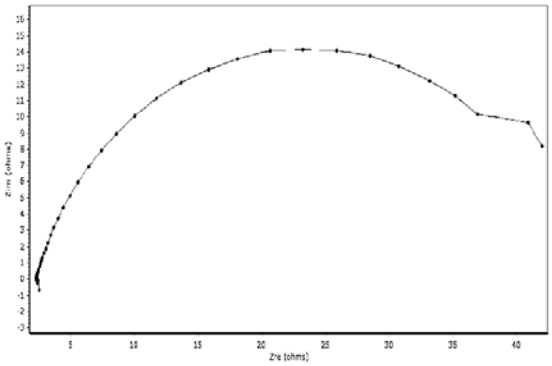
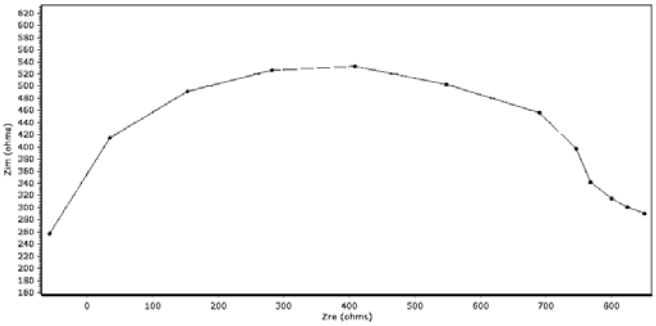


Figure.3.10.3b
Ac Impedence Spectra For Zinc-Nickel Alloy Electrodeposited Carbon Steel From Optimized Bath



3.10.6.SEM ANALYSIS

The SEM image of Zinc-Nickel alloy electrodeposited Carbon steel specimens of Basic bath and optimized bath in 3.5 % NaCl were shown in Figure 3.10.4A and 3.10.4B.The SEM micrographs of Zinc-nickel alloy electrodeposited Carbon steel in the absence of L.inermis extract (Basic bath) in 3.5% NaCl solution in Figure 3.10.4a showed the roughness on the metal surface which indicated that the Corrosion was possible in Zn-Ni alloy electrodeposited Carbon steel without L.inermis extract though the protective Zinc oxide layer was formed on the surface.The SEM micrographs of Zn- Nickel alloy plated Carbon steel in the presence of L.inermis extract (Optimized bath) in 3.5% NaCl solution in Figure 3.10.4b indicated that in the presence of Henna extract, the surface coverage increased which in turn resulted in the formation of insoluble Complex, on the surface of the metal (Henna-Zn^{2+} complex) and the surface was covered by a thin layer of Zn- Henna complex which effectively controlled the dissolution of carbon steel. The higher corrosion resistance was seen in Zn-Ni alloy electrodeposition from optimized bath with smaller grain size, higher uniformity or grain distribution . This was due to the protective properties of oxide layers

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formed on the surface of Zn-Ni alloy electrodeposited carbon steel along with L.inermis extract during corrosion.

Fig.3.10.4a
SEM Photograph of Zinc-Nickel Alloy Deposit Obtained From Basic Bath on Corrosion Study In 3.5% NaCl

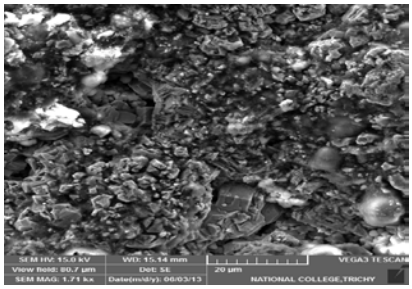
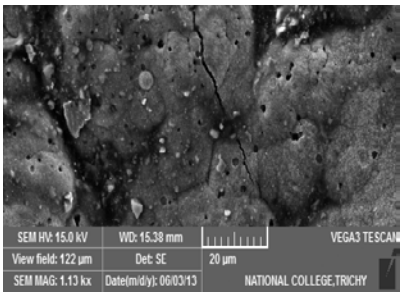


Figure.3.10.4b
SEM Photograph Of Zinc-Nickel Alloy Deposit Obtained From Basic Bath On Corrosion Study in 3.5% NaCl



Conclusion

The Zinc-Nickel alloy deposits on carbon steel obtained from this optimized bath has shown better characteristic properties than the Zinc-Nickel alloy deposits obtained from Basic Bath. This confirms the influence of L.inermis extract on electrodeposition of Zinc-Nickel alloy. The Current efficiency and the throwing Power of Zinc-Nickel alloy Electrodeposited carbon steel from optimized bath is found to be increased than in the case of Zinc-Nickel alloy deposits on carbon steel from basic bath. The shift in cathodic potential towards negative direction is observed for Zinc-Nickel alloy electrodeposited carbon steel from optimized bath on Polarization study confirms the effect of additive on electrodeposition. The fine grained deposits on Zinc-Nickel alloy electroplated carbon steel from optimized bath reveal the inclusion of addition agent on Zinc-Nickel alloy electrodeposition. XRD spectra reveals the reduction in the particle size of Zinc-Nickel deposits on carbon steel obtained from optimized bath. EDAX analysis confirm s the inclusion of L.inermis Extract on Zinc-Nickel alloy electroplated carbon steel from optimized bath and it reveals that Nickel percentage in this deposition is 8.75%. FT-IR Spectroscopy confirms the inclusion of L.inermis Extract on Zinc-Nickel alloy electroplated carbon steel from optimized bath. Hardness value is also increased for zinc electroplated carbon steel from optimized bath.The results obtained from weight loss method show that the Zinc-Nickel alloy electrodeposited carbon steel obtained from optimized bath controls corrosion to the greater extent than the Zinc-Nickel alloy electrodeposited carbon steel obtained from basic bath. Ferroxyl test confirms the absence of pore free nature of the deposits obtained from optimized bath. Salt spray test confirms the greater corrosion resistance property of the deposits from optimized bath. Polarization study reveals that the Zinc-Nickel alloy deposits obtained from optimized baht on carbon steel function as mixed inhibitor controlling both anodic and cathodic processes. From AC impedance spectra it is clear that a protective film is formed on the metal surface. SEM micrographs confirm the protective layer on the carbon steel surface. From these corrosion studies the Zinc-Nickel alloy electrodeposited carbon steel from optimized bath (in the presence of L.inermis extract) has greater corrosion resistant property. Ferroxyl test reveals the presence of pore free nature of deposits in both the cases. Salt spray test confirms the corrosion resistance power of Zinc-Nickel alloy electrodeposited carbon steel from optimized bath and cadmium electrodeposited carbon steel are equal. The results obtained from weight loss method confirms the corrosion rate of Zinc-Nickel alloy electrodeposited carbon steel from optimized bath and cadmium electrodeposited carbon steel are same. Potentiodynamic Polarisation study reveals the action of Zinc-Nickel alloy electrodeposited carbon steel from optimized bath towards corrosion is similar to cadmium electrodeposited carbon steel. Ac impedence Spectra confirms the protective layer formed on the surface of the Zinc-Nickel alloy electrodeposited carbon steel from optimized bath has produced similar effect towards corrosion when compared with cadmium electrodeposited carbon steel. Thus this Zinc-Nickel alloy electrodeposited carbon steel from optimized bath can replace cadmium.Thus Lawsonia inermis Linn leaf extract acts as a Green addition agent and also it can satisfy the properties of the good addition agent. It is ecofriendly, nonhazardous addition agent and it has many medicinal properties.

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