Optimisation of Zinc Electrodeposition in the Presence of Aqueous Lawsonia Inermis Linn Leaf Extract

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Abstract— In the zinc electrodeposition acid zinc based baths have become popular. These baths use the toxic chemical cyanide. The costly effluent treatment method to remove cyanide and the stringent environmental regulations necessitates the need to develop environmental friendly, non-toxic additive for the acid-sulphate bath. In the present work the effect of addition of green and non-toxic additive aqueous Lawsonia inermis Linn leaf extract on zinc electrodeposition has been investigated. It is carried out to optimize the zinc electrodeposition in the presence of aqueous Lawsonia inermis Linn leaf extract by varying the bath constituents, pH, temperature, and current density through Hull cell experiments. The current efficiency and throwing power are measured at different current densities. The optimized plating bath composition is Zinc sulphate -70g/l, Aluminium Sulphate - 18g/l, Sodium acetate -14g/l, Aqueous Lawsonia inermis Linn leaf extract- 10ml/l. Matte white deposits are obtained at the current density of 0.8-4A/dm^2. The Current efficiency and the throwing Power of Zinc Electrodeposited carbon steel from optimized bath is found to increase than in the case of zinc deposits on carbon steel from basic bath.

Key words: Additive, Current density, Current Efficiency, Hull Cell, Lawsonia inermis linn, Throwing power, Zinc elctrodeposition

1 Introduction

The use of zinc-plated articles is increasing due to its sacrificial protection of steel from corrosion. This sacrificial protection is due to the fact that the zinc is a less noble metal and cathodically protects the steel even in places where the deposit is damaged. Zinc coatings are obtained either from cyanide, non-cyanide alkaline or acid solutions [1], [2], [3], [4], [5], [6]. It is very economical to deposit and worldwide supplies are high [7]. Zinc is non-toxic and it is safe in contact with food. Other employed depositing solutions, apart from acid solutions, are those based on cyanide baths and to a lesser extent fluoborate, alkaline zincate and pyrophosphate [8].

Cyanide zinc baths are the most widely used, have high throwing power, which is one of the important factors in zinc plating. However, due to their toxicity and the stringent regulations against water pollution and costly effluent disposal, non-cyanide and low-cyanide baths have been investigated and used for commercial plating[9],[10].

Good deposition depends mainly on the nature of bath constituents. The Presence of additive is an important factor that promotes adequate industrial **deposits.** Some of these smoothen the deposit over a wide current density range and the other addition agents influence the production of bright deposits. Therefore, it is essential to develop the bath with a single additive that could produce a quality deposit. A number of organic additives are reported in the literature, which fall into two categories – the carrier additive and the brightener. Generally, the carrier additive would enable grain refinement and the brightener additive would have a complementary effect in producing bright deposits. Since most of the formulations are proprietary in nature, a detailed study to explore a viable combination of the additives becomes essential [11],[12],[13],[14]. Our earlier communication [15] dealt with the development of a ecofriendly bath with ethanolic extract of Lawsonia inermis Linn. Leaf . 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[16]. The principal colouring substance of henna is a red orange coloured molecule (lawsone, 2-hydroxy1,4-napthoquinoine) having molecular formula, C10H6O3 and M.P. 190°, present in dried leaves in a concentration of 1–1.4%w/w [17], [18], [19]. 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) [20]. 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. 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. The use of aqueous Lawsonia inermis leaf extract under different experimental working parameters/conditions in this study is an attempt to further extend these previous Investigations.

2. EXPERIMENTAL METHODS

2.1. Preparation of zinc coatings

All the solutions are prepared from AR grade chemicals and double-distilled water. The standard Hull cell of 267-ml capacity is used to optimize the bath constituents and bath variables [21]. The Hull cell experiments with the bath solution given in Table 1 are carried out without agitation. The pH of bath solution is measured using a digital pH meter (Equipetronix, model: 7020) and adjusted with 10% sulphuric acid or sodium bicarbonate solution. Zinc plate of 99.99% purity is used as anode and activated each time by immersing in 10% HCl followed by water wash. Mild steel (AISI-1079, composition C 0.5%, Mn 0.5%, P and S 0.05% and rest Fe) plates of standard Hull cell size are mechanically polished using emery paper (320-800 grit size) to obtain a smooth surface and degreased by

dipping in boiling trichloroethylene. The scales and dust on the steel plates are removed by dipping in 10% HCl solution and then subjected to electrocleaning process. These steel plates are washed with distilled water and used for the experiments as such. After electrodeposition the plates are subjected to bright dip in 1% nitric acid for 2-3 s followed by water wash and drying. The nature and appearance of zinc deposit is carefully observed and recorded through
Hull cell codes (Figure 1).

2.2. Preparation of Extract;

The Lawsonia inermis Linn leaves are dried at room temperature; ground to powder and 2Kg of the obtained powder is macerated in water (1:2) as solvent for 48 hrs. After maceration, the suspension is centrifuged and the extract is collected and filtered using Whatmann No. 1 filter paper. The liquid extract is concentrated by distilling off the solvent and then evaporating the solvent to dryness on a water bath to remove nearly 90 % of water from the extract and amount of the extract is calculated and kept at 4^{o}C for further use. This aqueous extract is used for doing the Hull Cell experiments.

2.3. **Current efficiency and throwing power Measurements**

The cathodic current efficiencies (CCE) as the percentage of the total current usually employed for the cathode deposition of the metal. This is calculated from the relationship

$$\% \text{ CCE} = \frac{\text{Wt. of the metal actually deposited}}{\text{Wt of the metal calculated from the quantity of electricity is passed}} \times 100$$

Electrodeposition is carried out for 10 min in each case.

Throwing power (TP) is measured using Haring-Blum cell. A porous zinc anode is placed between two plane parallel steel cathodes filling the rectangular cell cross section. The cathodes distance ratio is 5:1 from the central anode. . The percentage throwing power is calculated from Field's formula [22].

3. RESULTS AND DISCUSSION

Zinc electrodeposits offered very good corrosion resistance to carbon steel metal parts because of its sacrificial protection. Though Zinc electrodeposits could be obtained from different types of electrolytes, acid sulphate electrolyte is preferred by their fast deposition rates compared to cyanide electrolyte. Good deposition obtained on the cathode surface mainly depends on the nature of the bath constituents. Generally plating bath contains conducting salts, buffering agents, complexing agents and metal ions. Among these the complexing agents effectively influenced the deposition process, solution properties and structure of the deposit. These actions are specific and varied with respect to the pH, nature of anion, temperature and other ingredients of the medium. Thus, Hull Cell is used to study the effect of aqueous L. inermis L. leaf extract during electrodeposition of Zinc on Carbon steel.

3.1 Hull Cell Studies;

Effect of aqueous Lawsonia inermis Linn leaf Extract:

Table 1 shows the Basic bath composition. Basic bath solution give coarse dull deposit between the current density range of 1 and 3.5 Adm^{-2} at 1A cell current (Figure 1). To improve the nature of deposit, L.inermis Extract is added to the bath solution. With increase in the concentration, the nature of deposition improved and became semi bright.

At a concentration of 10mlL^{-1} of L.inermis Extract, the Hull cell panels are bright between the current density range of 1 and 4 Adm^{-2}.With further addition of L. inermis Extract, the nature of the deposit became burnt at higher current density region. Therefore, on the basis of the above observations, the amount of L.inermis Extract is kept at 10mlL^{-1} as optimum. The Hull cell patterns are shown in Figure 1A. Further experiments are carried out by keeping the amount of L.inermis extract at 10 ml L^{-1}.

Bath composition	Concentration g/l	Operating conditions
Zinc Sulphate	240 gL^{-1}	Temperature:30^{o}±2 ^{o}C
Sodium Acetate	30 gL^{-1}	Anode: Zinc metal (99.99% pure)
Aluminium Sulphate	30 gL^{-1}	Cathode:Carbon steel
pH	3.5-4.5	

TABLE-1

Basic Bath Composition And Operating Conditions For Zinc Electrodeposition

Key for Hull Cell Diagram:

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

Bu	St &D	un

4 3.5 1 0 Adm^{-2}

Fig 1A

Hull Cell Diagram – Effect of L.Inermis Extract

10ml

Br	un

4 1 0A/dm^{-2}

Effect of Zinc sulphate

To find out the effect of Zinc ion, the Zinc sulphate concentration is varied from 15-250 gL^{-1} keeping Henna Extract at 10mlL^{-1}. At low current density region of 1-2 Adm^{-2}, streaky deposits and at high current density range of 3-4 Adm^{-2}, burnt deposits are obtained (Fig 1B).With increase in the concentration of Zinc sulphate the brightness range is extended to higher and lower current density regions. At a concentration of 70gL^{-1}, a satisfactory bright deposit is obtained. Above this concentration of Zinc sulphate, no improvement in the nature of deposit is observed. The concentration of Zinc sulphate is fixed at 70gL^{-1} as optimum.

Fig 1B
Hull Cell Diagram: Effect of Zinc Sulphate

70g/L

Br	un

4 1 0 A/dm^{-2}

Effect of Sodium acetate

Sodium acetate is added to increase the conductance of the bath solution. The concentration of sodium acetate is varied from 2-50gL^{-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 are found to be reduced with increase in the concentration of sodium acetate and at 14gL^{-1}; the deposit is bright over a current density range of 1.5-3.5Adm^{-2}. Further increase in the concentration (>14gL^{-1}) do not introduce any effect on the nature of deposit and on the conductance also. So, the concentration of sodium acetate is fixed at 14 gL^{-1} in the bath solution. (Fig 1C)

Fig 1C
Hull Cell Diagram: Effect of Sodium Acetate

14g/L

Bu	Br	Gr	Un

4 0 A/dm^{-2}

Effect of Aluminium Sulphate:

Aluminium Sulphate is varied from 2-50gL^{-1}. At lower concentrations, the Hull cell panels has shown semi bright deposit at low current density region and burnt at high current density region. The semi bright and burnt regions are found to be reduced with increase in the concentration of Aluminium sulphate and at 18 gL^{-1}, the deposit is bright over a current density range of 1-3.5 Adm^{-2}.Further increase in the concentration(>18 gL^{-1}) do not introduce any effect on the nature of deposit and on the conductance also. So, the concentration of Aluminium sulphate is fixed at 18 gL^{-1} in the bath solution. (Figure.1D)

Fig 1D
Hull Cell Diagram- Effect of Aluminium Sulphate

18 g/L

Bu	Br	Un

4 1 0 A/dm^{-2}

Effect of pH

To know the effect of pH, the pH of the bath solution is varied from 2-5. At higher pH, the Hull cell panels has-shown burnt deposit at high current density region. At pH 4, satisfactory deposit is obtained. At lower pH (<4), the specimens has dull deposit at low current density region. From the above observations, the pH of the bath solution is kept at 4 as optimum. (Figure. 1E).

Fig 1E
Hull Cell Diagram- Effect of pH

pH- 4

Bu	Br	St	P

4 2 0Adm^{-2}

Effect of Temperature:

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

Fig 1F
Hull Cell Diagram- Effect of Temperature.

303K

Br	P

4 1 0A/dm^2

Effect of current:

The Hull cell experiments are carried out at different cell currents (1-3A) for 10 min using optimum bath solution. It is found that at a cell current of 1A the deposit is bright in the current density range 0.8-3 Adm^{-2}.At a cell current of 2A, the deposit is bright in the current density range of 2-4 Adm^{-2}. At a cell current of 3A the deposit is bright over the current density range between 3 and 4 Adm^{-2}. (Figure. 1G)

Fig 1G
Hull Cell Diagram- Effect of Cell Current

Bu	Br	

4 1A 1 0A/dm^2

Optimized Bath:

By varying the components in the Basic Bath in the above manner, an optimized bath is formed. This optimized bath contained 10 ml of Henna Extract. The bath composition and operating conditions are given in Table 2

TABLE -2
Optimised Bath Composition and Operating Conditions for Zinc Electrodeposition

Bath composition	Conc. (gL^{-1})	Operating conditions
$ZnSO_4$ $Al_2(SO_4)_3$ CH_3COONa Lawsonia inermis Linn. Leaf extract	70 gL^{-1} 18 gL^{-1} 14 gL^{-1} 10mlL^{-1}	Anode:Zinc Metal (99.99%pure) Cathode: Carbon steel Temperature: 303K pH : 4 Plating time :30min Bright current density range : 0.8-4Adm^{-2} Cell Current in Ampere :1A

3.2. Effect of Current Density on Current Efficiency During Zinc Electrodeposition on Carbon Steel

Current efficiency or cathode efficiency in electrodeposition is expressed as the percentage of the total current usefully employed for cathode deposition of the metal. Current efficiency of Zinc electrodeposited carbon steel obtained from Basic Bath, and Optimized bath are measured at various current densities. At lower current density (1Adm^{-2}), the current efficiency of Zinc electrodeposited carbon steel obtained from Basic Bath and Optimized bath are found to be 50 % and 75% respectively. At a current density range of 1-4Adm^{-2}, the efficiency is found to be increased and reached high at $2Adm^{-2}$. The Efficiency obtained are 70% and 99% respectively. Further increase in the current density is found to decrease the efficiency (Table 3). This shows the absence of hydrogen evolution at a current density range of $1\text{-}4Adm^{-2}$, after this hydrogen evolution has started.

H. Geduld, in his Metals Hand Book, (9th edn.) explained that the high cathode current efficiency of 96-98% is produced only by Acid- Chloride baths and this is most important property of this bath and he expressed that there is no other zinc plating system that approaches this extremely high efficiency at higher current densities. This present study on Zinc Electrodeposition in the presence of L.inermis L. leaf extract proved that even acid sulphate Zinc electrolyte brought out this efficiency in the presence of Additive, leaf extract. The high cathode efficiency combined with the quick brightening action provides faster plating tendency and increases productivity. The high efficiency can lead to productivity increase of 15-60% over cyanide baths.

TABLE -3
Effect of Current Density on Current Efficiency During Zinc Electrodeposition on Carbon Steel

Current Density (Adm^{-2})	Current Efficiency (%)	
	BASIC BATH	OPTMIZED BATH
1	50	75
2	56	99
3	70	80
4	65	76
5	62	47

3. Determination of Throwing Power

Throwing Power refers to the degree of uniformity of metal distribution on a cathode. Throwing power for basic bath and optimized bath is measured by using Haring Blum Cell at different current densities. It is found that the optimized bath has shown greater throwing power than Basic bath. At lower current density, throwing power for basic bath and optimized bath are found to be 18.4 % and 27.5 % respectively.

Further increase in current density, increases the Throwing Power and attains the maximum of 21.1% and 40.2% respectively at $2Adm^{-2}$. (Table V.3.). Thorough literature survey reveas the presence of additive increases the throwing power on zinc electrodeposition. The values obtained for optimized bath have proven the effect of additive on throwing power during Zinc electrodeposition.

TABLE 4
Effect of Current Density on the Throwing Power

Current Density (A/Dm^{-2})	Throwing Power (%)	
	Basic Bath	Optimized Bath
1	18.4	27.5
2	21.1	40.1
3	23.2	36.6
4	25.5	35.2
5	26.8	27.8

4. CONCLUSION

Optimised bath composition for zinc electrodeposition is given in the Table 5

TABLE 5
Optimised Bath Composition and Operating Conditions for Zinc Electrodeposition

Bath composition	Conc.(g/L)	Operating conditions
$ZnSO_4$ $Al_2(SO_4)_3$ CH_3COONa Lawsonia inermis Linn. Leaf extract	$70\ gL^{-1}$ $18\ gL^{-1}$ $14\ gL^{-1}$ $10mlL^{-1}$	Anode: Zinc metal(99.99%pure) Cathode: Carbon steel Temperature:303K PH: 4 Plating time:30min Bright current density range : $0.8\text{-}4Adm^{-2}$ Cell Current in Ampere:1A

The Zinc deposits on carbon steel obtained from this optimized bath has shown better characteristic properties than the zinc deposits obtained from Basic Bath. Matte white deposits are obtained at the current density of $0.8\text{-}4A/dm^2$. This confirms the influence of Lawsonia inermis Linn. Leaf extract on electrodeposition of Zinc. The Current efficiency and the throwing Power of Zinc Electrodeposited carbon steel from optimized bath is found to be increased than in the case of zinc deposits on carbon steel from basic bath.

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