

"Some Studies on the Parameters for the New Bath for Protection of Steel from Corrosion"¹

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Summary

In this study, dealt with the electrodeposition of zinc from slightly acidic citrate baths in an attempt to find the optimum bath composition and electrodeposition conditions for this process. The experiments revealed that the optimum bath composition contains: $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 100, tri-sod.citrate 50 and citric acid 20 g l^{-1} and this was denoted as Zn-10 bath. The optimum operating conditions for zinc deposition from Zn-10 bath were: $i_{d.c.} = 2 \text{ Adm}^{-2}$, $t = 20 \text{ min.}$, $\text{temp.} \cong 25^\circ\text{C}$ and $\text{pH } 5.0$ under such conditions, the bath was characterized by a cathodic current efficiency of 96.94%, throwing power 13.43 %. As in most Zn plating baths, the throwing power of citrate bath is poor. In order to improve the throwing power of the Zn-10 bath, some organic compounds were added and tested. It was found that addition of 0.05 g l^{-1} SGN1 gave the best result. Specially, improves on the smoothness and brightness of zinc deposits.

The zinc plate from the optimum Zn-10 bath form hexagonal crystals and this was confirmed from the X-ray diffraction data. The microhardness of zinc plated from Zn-10 bath is generally high and affected strongly by the operating conditions.

Key Words:

Electrodeposition, Electroplating, Optimum Bath, Throwing Power, Anodic Stripping Voltammetric(ASV), Potentiodynamic Cathodic Polarization, Microhardness, Cathodic Current Efficiency(CCE or f).

¹ For the paper in Arabic see pages (167-168).

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1. Introduction:

The corrosion resistance of pure zinc deposits is not satisfactory under more corrosive environments, particularly in a very humid atmosphere. It was found that addition of cobalt to zinc was so effective in the improvement of the corrosion resistance of galvanized steel production^(1, 2, 3, 4).

Too, the zinc and his alloys^(4, 5) are characterized by their high degree of corrosion protection of steel in automobile^(6, 7, 8), aerospace⁽⁹⁾, and electronic industries⁽¹⁰⁾. In addition, its possible use as a less polluting alternative to cadmium coatings⁽¹¹⁾.

In the present study, zinc was electrodeposited onto steel substrates from citrate baths. Attempts had been done in order to obtain a sound and satisfactory deposits from an optimum bath. The effect of operating variables such as: bath constituent, concentrations of zinc ions, current density, pH, and temperature on the electrodeposition of zinc was studied. In addition, the effect of some addition agents on the process of zinc electrodeposition from these baths was studied. Baths used for the electrodeposition of zinc are presented in **Table 1**.

2. Experimental work

All the plating baths and reagents used were made from annular chemicals and doubly distilled water. The compositions of the examined baths for zinc electrodeposition are given in **Table 1**. For electrodeposition, a steel cathode and platinum sheet anode each of dimensions **(2.5 cm x 3.0 cm)** was used. The plating cell used was a rectangular Perspex trough **(10 cm x 3.0 cm)** provided with vertical grooves, on each of the side walls, to fix the electrodes. Before each run, steel cathode was mechanically polished with different grade emery papers, 600, 800, 1000 and 1500 and then washed with distilled water, rinsed with ethanol and weighed. Direct current (d.c) was supplied by d.c. power supply model **(GPS-3030D)**. The Cathodic current efficiencies f were determined with the help of Cu-coulometer, ($f = \mathbf{Wt}_{\text{exp}} / \mathbf{Wt}_{\text{theo}}$) where \mathbf{Wt}_{exp} is the weight of the deposit obtained experimentally and $\mathbf{Wt}_{\text{theo}}$ is the weight of the deposit calculated theoretically according to Faraday's law. Most of the experiments were carried out at 25 ± 2 °C. The plating duration was 20 minutes.

The throwing power (T.P.) of the solution was measured using Haring-Blum rectangular Perspex cell fitted with one anode between two parallel cathodes where the ratio of the far to the near distance was (5:1). The percentage throwing power was calculated from Field's formula⁽¹²⁾

$$T.P\% = \frac{L - M}{L + M - 2} \times 100$$

where L is the current distribution ratio or linear ratio (5:1) and M is the metal distribution ratio of the near to the far cathodes.

In some cases, the values of M were measured as a function of L over a wide range of linear ratios varies between (1:1) and (5:1). The throwing index (T.I.) of each bath was considered as the reciprocal of the slope of the M versus L plot⁽¹³⁾.

A potentiostat / Galvanostat (**EG&G model 273**) controlled by PC was used for the stripping voltammetric measurements. All potentials were measured relative to a saturated calomel electrode (SCE).

Potentiodynamic anodic stripping voltammetric curves were carried out in conventional electrolytic cell, containing a platinum sheet cathode (**2.5 cm x 3 cm**) as a working electrode, a saturated calomel reference electrode and a platinum wire as a counter electrode. Deposition of Zn from the plating bath was carried out on the platinum sheet cathode at a constant deposition potential = - **1100 mV (SCE)** for constant different plating times (**50-400 Sec.**). At the end of each deposition time, stripping analysis was performed immediately in the same plating bath (in situ) by sweeping the potential to more anodic potentials at a potential sweep rate of 5mVs^{-1} .

The surface morphology of the zinc electrodeposits was examined using a **scanning electron microscopy (SEM) (JOEL- JEM 1200 EX II Electron microscope)**. The structure of zinc deposit from the selected bath on steel cathodes was examined by **X-ray** diffraction analysis using **Philips** diffractometer (**40 kV, 25 mA**) with **Ni** filter and **Cu K α** radiation.

The microhardness of the zinc deposit was measured by means of a **Shimadzu** microhardness tester. In all tests a 25 g f load was employed and the hardness was expressed as the Vickers hardness (H_v) in kilograms-force per square millimeters.

In some experiments, the thickness (d) of the deposited metal, in microns was calculated from the relation:

$$d = \frac{Q \times i \times t \times f}{60 \times \delta}$$

where, Q (g A⁻¹ h⁻¹) is the electrochemical equivalent of the metal; i (A dm⁻²) is the plating current density, t (min.) is the plating time, f % is the cathodic current efficiency percent and δ (g cm⁻³) is the density of metal. This density δ for Zn is 7.13 (g cm⁻³).

Results and discussion

1- Cathodic Current Efficiency:

The cathodic current efficiency f % of Zn from citrate baths is generally high but less than 100% as a result of simultaneous discharge of hydrogen. The effect of some operating variables on the cathodic current efficiency f % was studied. For example, **fig. 1** shows the effect of increasing Zn²⁺ ion content in the bath. The efficiency increases gradually with Zn²⁺ ion concentration up to =100 g l⁻¹, then tends to level off. The improvement of Zn deposition efficiency could be due to the decrease in its deposition potential with increasing its ion concentration **fig. 1**.

However, **Table 2** shows the effect of pH on f %. Within the pH range studied (3.7 - 6.0), the highest f % is obtained at pH = 5.0.

According to the above data, the optimum bath is Zn-10 bath which produced satisfactory and sound deposits, it contains: ZnSO₄ 100, tri-sod. citrate 50 and citric acid 20 g l⁻¹ at pH = 5.0 (adjusted by adding drops from NaOH solution). Using this optimum bath composition, the effect of some operating variables such as the applied current density and temperature on the f % was studied.

Table 3 illustrates that with increase of current density an increase in f % is observed.

The effect of temperature of the optimum bath on f % can be seen in **Table 4** Increasing temperature has higher depolarizing effect on hydrogen discharge than on Zn discharge and therefore one might expect a decrease in f % for Zn deposition with raising temperature. It is worth while to mention here that at temperature higher than 50°C, the citrate

bath becomes unstable and turbid. Therefore, no experiments were performed at temperature higher than 50°C.

Addition of SLS or SGN1 improves greatly the brightness of the zinc deposited from citrate bath. The effect of these addition agents individually or in a mixture on $f\%$ was studied. The data in **Table 5** reveal that the $f\%$ is slightly decrease in presence of either SLS, SGN1 or a mixture of them.

2- Surface Morphology and Structure of The Deposits:

The Zn deposit produced from the optimum bath Zn-10 is very adhere to the steel substrate and has a metallic luster.

X-ray diffraction measurements were conducted on the as-deposited zinc from bath Zn-10 at pH 5.0, $i_{d.c.} = 2 \text{ A dm}^{-2}$, and $t = 20 \text{ min}$. The data show that Zn is deposited under these conditions in a polycrystalline form with hexagonal structure with different orientations (**Table 7**). The anodic stripping voltammetric analysis show that the as-deposited Zn is crystallized in one phase since the anodic scan exhibits only one peak as shown in **fig. 6**.

The surface morphology of the as-deposited zinc from the optimum bath Zn-10 was examined by using scanning electron microscope **SEM** as a function of the most effective operating variables such as current density and pH. The samples were prepared at 25°C by electrodeposition for 20 minutes and the corresponding electron micrographs are shown in **fig. 7**. As shown by SEM, the surface of the zinc deposited from the optimum Zn-10 bath is fully occupied by irregular grains **fig. 7a**. These grains contained packets of hexagonal lamina each with a pronounced layered texture.

A comparison between (**fig. 7 a and b**) depicts that the decrease of current density from 2 to 1 A.dm^{-2} is accompanied by the formation of flat leaf-like grains dispersed between fine grained-deposits on the surface.

On the other hand, on decreasing pH value form 5.0 to 3.7, a relatively coarser-grained electroplate was obtained, **fig. 7 c**. This could be attributed to the fact that the electrodeposition of zinc at low pH values is associated with cathodic depolarization **fig. 7 b**. The decrease in cathodic polarization reduces the nucleation rate and favors the growth rate.

3- Microhardness of the Deposits:

The microhardness of the zinc deposits from the citrate bath under different operating variables was measured and the results are listed in **Table 6**. The data display that the microhardness of zinc is generally affected by the prevailing conditions. The highest value of the microhardness is given for Zn-5 bath which contain zinc sulphat and tri-sod. citrate.

However, addition of citric acid to the bath decreases the hardness of the deposits. This decrease of hardness could be attributed to the fact that addition of citric acid decrease cathodic polarization, and consequently decreases the number of active sites of nucleation. Therefore, produces coarse-grain which is characterized by low hardness.

An increasing in hardness was observed when the current density was decreased from 2 to 1 Adm^{-2} . However, a moderate value of hardness is obtained for the zinc deposited from the optimum bath Zn-10.

4-Throwing Power and Throwing Index of the Bath:

It is known that acidic zinc baths are characterized by poor values of throwing power^(14, 15). In some cases, negative values of T.P. were obtained. This means that the weight of the deposit at the far cathode is even less than predicted for primary current distribution.

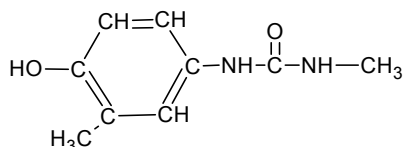
Tables 2-5 includes the results of T.P.% calculated by means of Field's formula at different operating conditions while **figs. 2-5** illustrate the linear plot between metal distribution ratios M and linear ratio L, the reciprocal of their slopes (throwing index T.I.) were used as indicator of T.P. of the bath and include in the same Table. Increasing current density, improves T.P. of the bath this increase of T.P. could be assigned to the increase of polarization as a result of increasing current density. On reverse, elevation of temperature has the effect of decreasing T.P. and T.I as a result of decreasing polarization even though elevation of temperature increases the conductivity of the solution. This result indicates the greater effectiveness of polarization on throwing power of the bath.

Increasing pH leads to a remarkable increase of T.P. and T.I. This improvement in T.P. could be attributed to the increase of cathodic polarization with increasing pH. Increasing the cathodic polarization

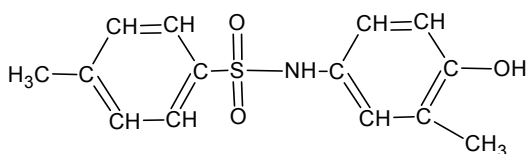
results in a better distribution of the current density between far and near cathode.

However, in order to improve the T.P. of the optimum bath, (T.P=13.43%) some organic compounds were added to the bath separately. The data on **Table 5** and **fig. 2** depict that these organic additives improve greatly the T.P.% reaching in some cases to a value of 41.9 % by using very small concentration 0.05 g l⁻¹ of SGN1.

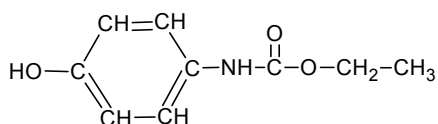
The structures of some organic compounds are used in the search:



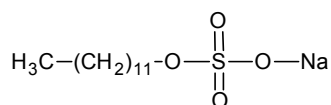
SGN 1



SGN 2



SGN 3



SLS

Table 1: Composition of the zinc electroplating solutions.

Bath No.	Concentrations (g ^l ⁻¹)							C (conductivity) (Ω ⁻¹ .cm ⁻¹)	pH
	ZnSO ₄ 7H ₂ O	citric acid	tri-sod. citrate	SLS	SGN.1	SGN.2	SGN.3		
Zn- 1	60	-	-	-	-	-	-	14.73	5.35
Zn- 2	80	-	-	-	-	-	-	17.44	5.25
Zn- 3	100	-	-	-	-	-	-	19.99	5.20
Zn- 4	100	-	20	-	-	-	-	22.44	5.15
Zn- 5	100	-	50	-	-	-	-	29.17	5.15
Zn- 6	100	10	-	-	-	-	-	21.42	2.40
Zn- 7	100	20	-	-	-	-	-	23.05	2.25
Zn- 8	100	20	50	-	-	-	-	28.25	3.70
Zn- 9	100	20	50	-	-	-	-	30.90	4.50
Zn-10	100	20	50	-	-	-	-	33.04	5.00
Zn-11	100	20	50	-	-	-	-	36.11	6.00
Zn-12	100	20	50	0.5	-	-	-	"	5.00
Zn-13	100	20	50	-	0.05	-	-	"	5.00
Zn-14	100	20	50	-	-	0.05	-	"	5.00
Zn-15	100	20	50	-	-	-	0.05	"	5.00
Zn-16	100	20	50	0.5	0.05	-	-	"	5.00
Zn-17	100	20	50	0.5	-	0.05	-	"	5.00
Zn-18	100	20	50	0.5	-	-	0.05	"	5.00

Table 2 : Effect of pH on the cathodic current efficiency, throwing power and throwing index of bath Zn-8.

(Time= 20 min., $i_{d,c} = 2 \text{ Adm}^{-2}$)

pH	f %	T.P.%	T.I.
3.7	88.24	- 1.72	0.943
4.5	93.65	---	---
5.0	96.94	13.43	1.344
5.5	94.31	---	---
6.0	90.04	---	---

Table 3 :Effect of current density on the cathodic current efficiency, throwing power and throwing index of bath Zn-10.

(Time= 20 min., pH = 5.0)

$i_{d,c}$ (Adm ⁻²)	f %	T.P.%	T.I.
0.33	85.63	---	---
0.66	92.52	- 0.37	0.99
1.00	92.50	---	---
1.33	93.75	---	---
1.66	93.89	---	---
2.00	96.94	13.43	1.34

Table 4 : Effect of temperature on the cathodic current efficiency, throwing power and throwing index of bath Zn-10. (Time= 20 min., $i_{d.c} = 2 \text{ Adm}^{-2}$, pH = 5.0)

Temperature°C	f %	T.P.%	T.I.
25	96.94	13.43	1.34
35	95.27	---	---
50	94.80	09.87	1.26

Table 5 : Effect of addition agents on the cathodic current efficiency, throwing power and throwing index of baths. (Time= 20 min., $i_{d.c} = 2 \text{ Adm}^{-2}$, pH = 5.0)

Bath No.	f %	T.P.%	T.I.
Zn-10	96.94	13.43	1.34
Zn-12	93.0	29.91	1.98
Zn-13	---	37.68	---
Zn-14	---	37.80	---
Zn-15	---	41.92	1.98
Zn-16	90.04	---	---
Zn-17	89.39	---	---
Zn-18	89.22	38.69	2.26

Table 6 : Microhardness and thickness for zinc deposit, under different conditions of baths constituent, pH and current density. (Time= 60 min., $i_{d.c} = 2 \text{ Adm}^{-2}$, pH = 5.0).

Bath No.	V. H(Kg f mm ⁻²)	d(μ m)
Zn-5	578	31.59
Zn-8	395	36.77
Zn-10	426	33.24
Zn-10*	521	9.50

Zn-10* : The same as Zn- 10, only the current Density was decreased to 1 A.dm^{-2} .

Table 7 : X- ray diffraction data of the electrodeposited zinc from citrate bath Zn-10. (Time= 20 min., $i_{d.c} = 2 \text{ Adm}^{-2}$, pH = 5.0).

2 θ	d (A°) observed	I / I _o	h k l	Structure
38.76	2.3213	17.9	100	hexagonal
43.02	2.0908	29.3	101	
70.43	1.3357	100	004	
81.93	1.1749	25	112	
86.26	1.1267	10.1	201	
123.93	0.8727	8.1	210	
127.37	0.8593	51.2	211	

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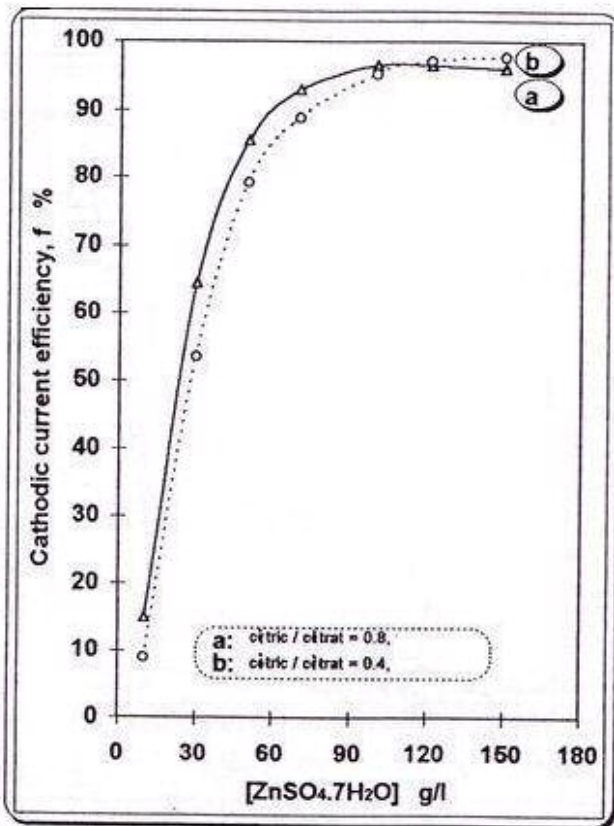


Fig. 1 : The effect of [ZnSO₄.7H₂O] on the cathodic current efficiency and the changed ratio of [citric \ citrate] at constant pH = 5.

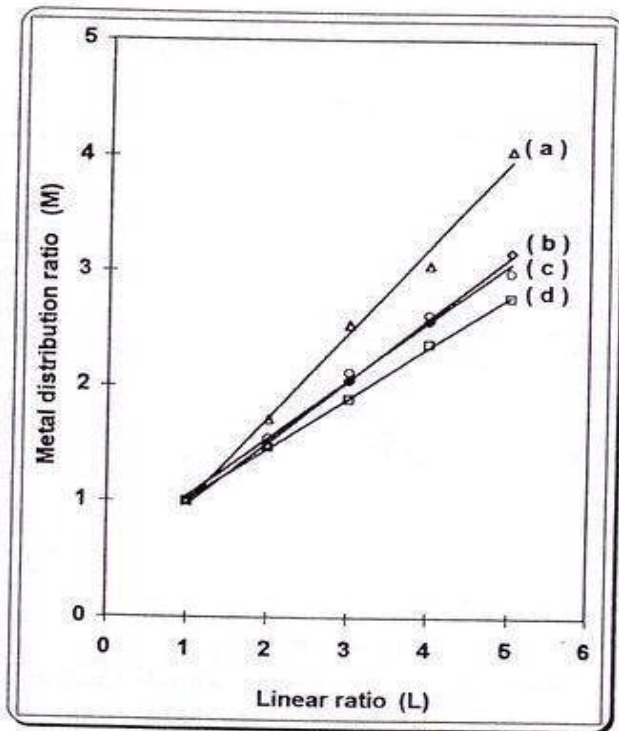


Fig. 2 : Effect of addition agents on the throwing index for Zn-deposition from Zn-10 baths (Zn-10 curve a, SLS curve b, SGN1 curve c, and SLS + SGN1 curve d).

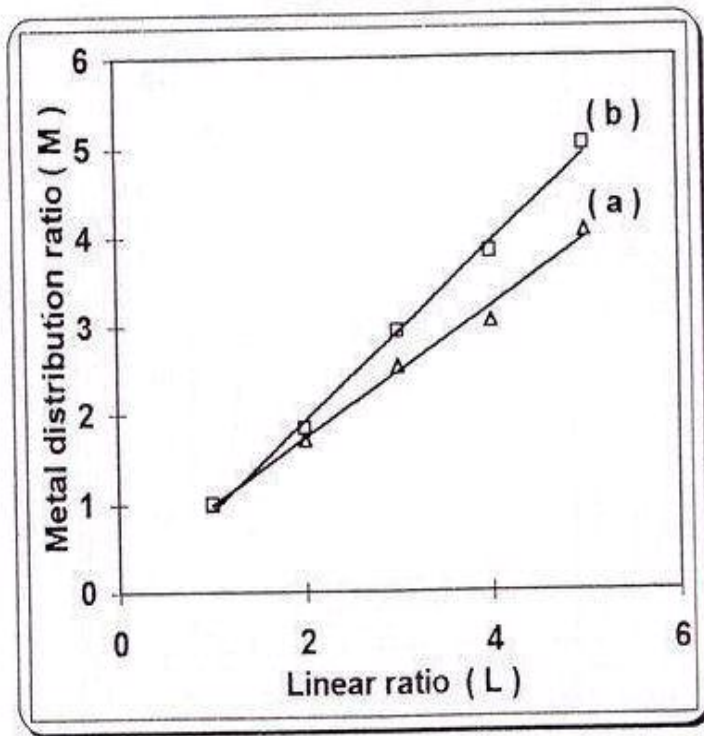


Fig. 3 : Effect of current density on the throwing index for Zn-deposition from Zn-10 bath at ($i_{d,c}=2 \text{ Adm}^{-2}$ curve a and $i_{d,c}=0.66 \text{ Adm}^{-2}$ curve b)

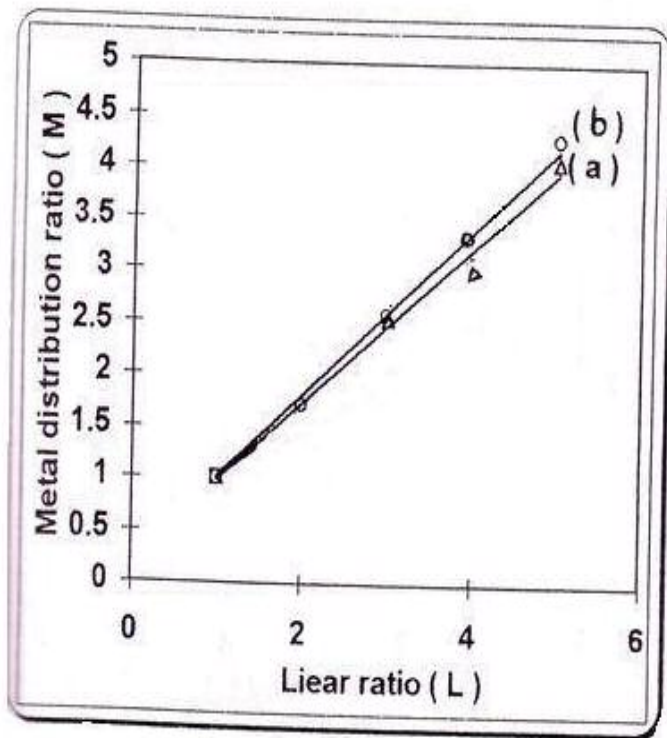


Fig. 4 : Effect of temperatur on the throwing index for Zn-deposition from Zn-10 bath at (T =25 °C curve a, and T= 50°C curve b).

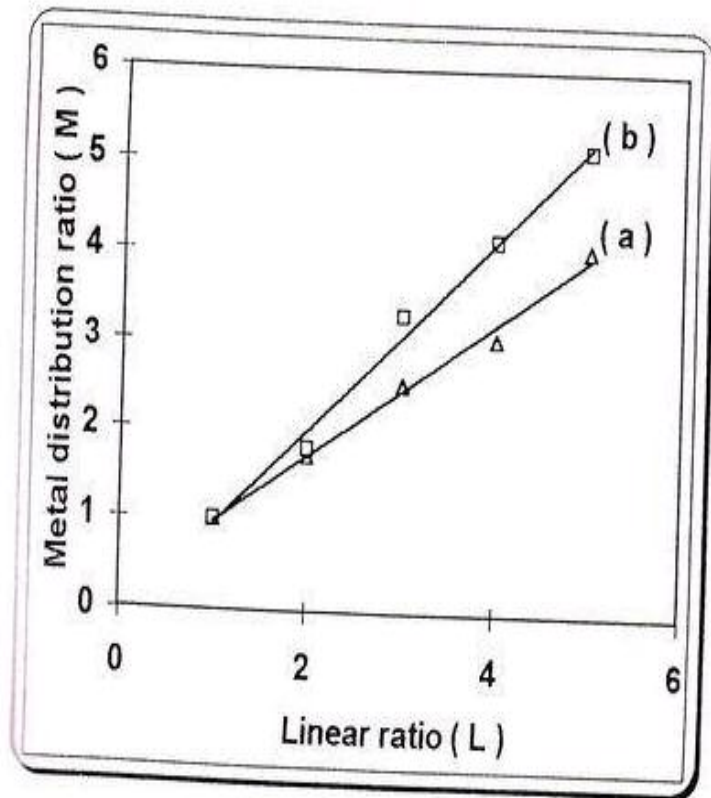


Fig. 5 : Effect of pH on the throwing index for Zn-deposition from Zn-10 bath at (pH = 5 curve a and pH = 3.7 curve b).

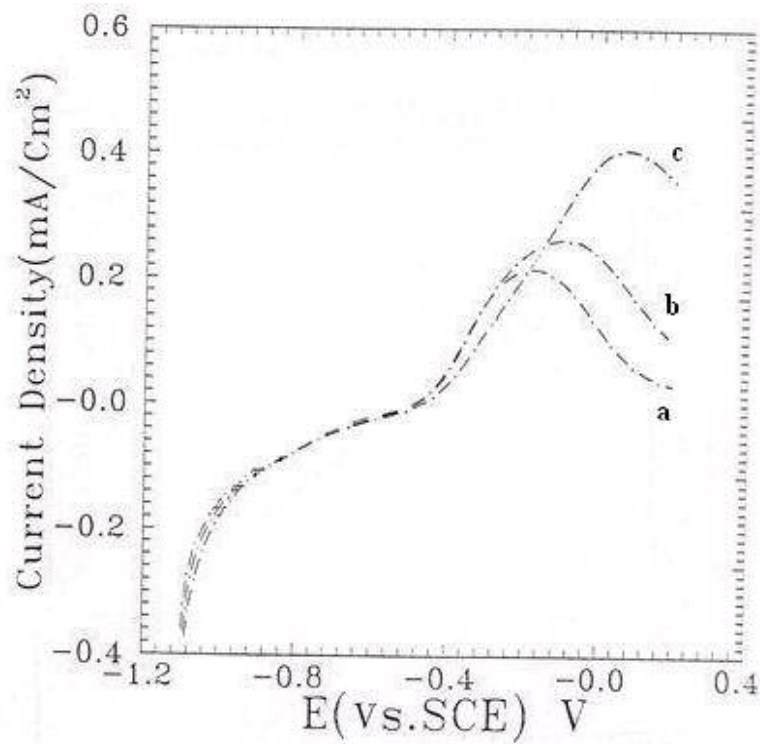


Fig. 6 : Anodic stripping voltammograms of a Zn deposit obtained from solution bath Zn-10 at deposition potential -1100 mV and different deposition time : (50 sec. curve a, 100 curve b and 400 sec. curve c, at scan rate = 5 mVs^{-1}).



Fig.(7):Photomicrographs of Zinc deposited from (Zn- 10) bath

Fig.(7)-a: Zinc deposited from (Zn- 10) bath, X = 1500 (Time = 20 min, $i_{d.c} = 2 \text{ Adm}^{-2}$, pH = 5.0).



Fig.(7)- b: Zinc deposited from (Zn- 10) bath, X = 1500 (Time = 20 min, $i_{d.c} = 1 \text{ Adm}^{-2}$, pH= 5.0).



Fig.(7)- c: Zinc deposited from (Zn- 8) bath, X = 1500
(Time = 20 min, $i_{d.c} = 2 \text{ Adm}^{-2}$).

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