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RESEARCH ARTICLE

ALTERNATE ZINC – NICKEL ALLOY COATING FOR HAZARDOUS CADMIUM

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Abstract

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Zn – Ni alloy deposition, cadmium, Surface characterisation, Corrosion resistance, Potentiodynamic polarisation, Corrosion impedance

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Shanmugasigamani Srinivasan Research on zinc – nickel alloy deposit from alkaline zincate cyanide free electrolyte was dealt to eliminate the use of potentially hazardous cadmium. To compare with cadmium separate deposition of cadmium from cadmium sulphate electrolyte was processed. Hull cell tests performed to determine the current density ranges with and without addition agents. SEM & EDAX, AFM, XRD observations indicated the deposit's surface morphology and percentage of zinc & nickel present in the alloy, surface topography and crystallographic orientation. Surface characterisation studies were evaluated for cadmium also. Weight loss methods, Potentiodynamic polarization, and electrochemical impedance spectroscopy correlations show zinc – nickel alloy coatings have a better corrosion resistance and are considered to be eco friendly replacement for cadmium coatings in corrosion resistant applications.

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1.Introduction

Corrosion resistance and excellent inherent lubricating properties with less corrosion products of cadmium put forth its utilization in fastener industries. Its toxicity lead to pursue an alternative zinc coating which protects steel substrates sacrificially, but zinc coating's performance in corrosion resistance is less than zinc – alloy coatings. Zinc alloy coatings such as Zn - Ni, Zn - Co, Zn - Fe have better corrosion performance than cadmium and zinc. Zinc alloy coatings from cyanide free alkaline zincates bath provides better corrosion protection than galvanised coatings as well as good throwing power than acid bath. The attack of pure zinc is preferred during corrosion and due to the dezincification rate the potential increased towards to steel than zinc- nickel alloy. Zinc – nickel alloy deposition has a potential of -680mv, closer to cadmium of -640mv, has higher corrosion resistance as well as better mechanical characteristics than other zinc alloy coating. Maximum protective ability was found to be 12 - 15% of nickel in zinc – nickel alloy. Zinc- Nickel alloy has micro hardness which is fit to be applicable for hard steel equipment manufacturing applications. [1-30]. Zinc- nickel alloy (12-15%) from non-cyanide alkaline zincate bath for corrosion resistance applications was deposited and compared with cadmium.

2. Experimental Techniques:

2.1. Methodology of zinc-nickel alloy and cadmium deposits

Treating zinc electrolyte with zinc dust after filtering, zinc stock solution was prepared. Dissolving nickel sulphate and then treated with suitable complexant to form complex for zinc – alloy deposition, nickel stock solution was prepared. Triethanolamine was used as complexants and it had been already reported in our previous studies on zinc – cobalt, zinc – nickel alloy deposition. Laboratory grade chemicals for zinc – nickel alloy deposition and operating conditions are shown in **table 1.** Cadmium electrolyte composition was tabulated in **table. 2**. In our previous study, we have optimized for the range 6 - 8% & in another study 10-12 % of nickel content in Zn – Ni alloy deposition. Present study envisaged 12 - 15% of nickel from zinc –nickel alloy electrolyte at lower pH than our previous studies. For alloy plating the above two electrolytes' stock solutions were mixed at required amount to get homogeneity of solution and pH was adjusted. Pure zinc anodes grade 99% purity (packed) used for deposition. Mild steel cathodes of 2cm^2 for cathode current efficiency measurements and for surface characterization measurements, were mechanically polished and degreased using solvents and electro cleaned using alkaline

treatment. Varying the nickel content, without and with addition agents, current density, temperature, etc., with stirring the electrolyte, the deposits obtained were analysed and results were evaluated. Cadmium was also deposited separately by using the composition of **table 2** and the deposits were analysed.

Correlating surface morphology, surface topography, crystallographic orientation and corrosion properties of zincnickel alloy coating with cadmium via XRD, SEM & EDAX, Potentio dynamic polarization, corrosion impedance meaurements, the results were investigated.

Zinc- Nickel alloy electrolyte composition
NICKEL STOCK
Nickel as sulphate - 2 15g/L
complexant - 40 200ml/L
- As required.
-10 - 12
- 30 - 60° C
$- 1 - 5 \text{ A/dm}^2$

TABLE :2 Cadmium electrolyte composition

Cadmium sulphate - 50-70g/l Sulphuric acid - 20 - 30 ml Gelatin - 10 - 20 g/l Sulphonated naphthalene - 5 -10g/l Temperature - Room temp Current densiy - 2 - 5 A/dm²

2.2. Current density identification

Hull cell tests were performed in the range of cathode currents 1A - 5A in a 267ml cm³ capacity cell to optimize the current density ranges according to the luster of the deposit and from Hull cell formula lowest and highest current density ranges were evaluated. Hull cell results with addition agents was diagrammatically represented as **Fig. 1.1** (a-e)

2.3. Cathode current efficiency

Mild steel cathodes of 2 cm² was exposed for deposition by applying different current densities as well as different temperatures from plain zincate bath, cadmium bath and zinc-nickel alkaline bath. Cathode current efficiencies at different current densities and different temperatures were calculated using current efficiency formula. Current efficiency with different current densities is represented in tabular format for the above corresponding deposits are given in the table.3,4,5 and diagrammatically represented in **Figs. 2,3** for plain zinc, cadmium and **Figs. 4,5** for zinc-nickel alloy.

2.4. Surface characterization of the deposits

Surface morphology, alloying elements and topography of zinc-nickel alloy & cadmium coatings were characterized from SEM, EDAX, AFM analysis. SEM is represented in **fig.6 (a-d)**. EDAX analysis of zinc and zinc – nickel alloy at different current densities were represented in **fig. 7 (.1-.3)** AFM analysis was shown at **fig.8 (.1-.12)** The crystallographic orientation and phase representation of the alloy system of cadmium and zinc- nickel coatings were observed by XRD instrument (XRD Pan analytical). Xrd pattern was shown in **fig. 9 (.1-.3)**

2.5. Corrosion resistance measurements

2.5.1. Weight loss method

This is simplest and most widely used method for evaluating corrosion rate of the electrodeposited component materials. (Zn - Ni alloy plated specimen & cadmium plated specimen). The specimens were cut into rectangular shape of an exposed area 5×3 cm² and subjected to pre-treatment process. The specimens were weighed electronic balance and suspended into 150 ml beaker containing 100 ml 3% NaCl solution. These beakers are kept in thermostat. After the specified time of immersion, The specimens were removed, washed in running water, dried, placed in desiccators to attain room temperature and weighed.

The corrosion rate was determined using the formula

Corrosion rate (mmpy) =8.76×w /D×A×T

Where

W is the weight loss in g D is the density in g/cc A is area of exposed in cm^2 T is the exposure time in hour mmpy is millimeter per year

Comparatively Zn-Ni alloy shows less corrosion rate than cadmium deposit.

2.5.2. Polarization measurements

Using the measurement of BAS IM Impedance analyzer, USA with Thales 4.18- USB softer the polarization were carried out in a conventional three-electrode cell with platinum counter electrode and a saturated calomel electrode coupled to a reference electrode. The working electrode was in the form of a square cut from zinc-nickel alloy deposited mild steel in which back side masked with tape. The working electrode area was 1×1 cm². For cadmium also separate polarization measurements from the deposited mild steel plates.

A glass cell was equipped with three electrodes connected to a potentiostat, after the potential becomes steady and it changes stepwise in the negative direction and then positive direction. Polarization measurements were graphically represented in **Fig.10**

2.5.3. Corrosion Impedance

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

EIS offers an advanced method of evaluation of the performance of metallic coating and organic barrier coatings. The apparatus required is three necked electrode cell, potentiostat and a frequency analyzer. Saturated calomel electrode serve as reference electrode, platinum as counter electrode and mild steel of area 1×1 cm² as working electrode using the instrument BAS IM6 Impedance Analyzer, USA with Thales 4.18- USB Software. A plot of Z vs Z["] for various frequencies gives a semicircle that cuts the real axis at higher and at a lower frequency Z corresponds to Rs + Rt calculated stern Geary equation. The double layer captaincies can determined from the frequency at which Z["] is maximum from the relation. Impedance data presented in the form Nyquist plot. It was diagrammatically represented in **fig.11**.

TABLE.3 EFFECT OF CURRENT DENSITY ON CATHODE CURRENT EFFICIENCY FOR PLAIN ZINC BATH

Current Density (A/dm ²⁾	Current Efficiency (%)	Thickness (Microns)
0.8	57	45
1.0	61	50
1.25	63	54
1.5	67	57

TABLE.4 EFFECT OF CURRENT DENSITY ON CATHODE CURRENT EFFICIENCY FOR CADMIUM BATH

		=
Current Density (A/dm ²)	Current Efficiency (%)	Thickness (Microns)
0.5	59	35
0.6	64	38
0.7	84	47
0.8	91	50

TABLE.5 EFFECT OF CURRENT DENSITY ON CATHODE CURRENT EFFICIENCY FOR ZINC-NICKEL BATH

Current Density (A/dm ²)	Current Efficiency (%)	Thickness(Microns)	NiSO ₄ .7H ₂ O
			Concentration(g/l)
0.6	51	22	5
0.75	66	28	5
0.8	44	26	7.5
1.0	58	31	7.5
1.0	43	31	10
1.25	49	35	10

Samples(Current Density A/dm ²)	Weight Loss (grams)	Corrosion Rate (mmpy)					
Cd (0.6)	0.0140	0.50					
Zn(0.6)	0.0780	0.38					
Zn-Ni(0.75)	0.0191	0.08					
Zn-Ni(0.8)	0.0149	0.06					

FABLE:6 Weight loss in grams of plated samples and corro	osion ra	ate
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Table 7: Potentio dynamic polarisation analysis data

(Current density A/dm ²)	E _{corr} Mv/SCE(volts)	$I_{corr} (A/cm^2) \times 10^{-4}$
Cd(0.6)	-868.6	19.8
Zn(0.6)	-1.07	68
Zn-Ni(0.75)	-844.9	14.7
Zn-Ni(0.8)	-865.6	15.2

Table :8 Electrochemical Impedance Spectra Analysis

Samples(Current density A/dm ²)	C _{dl} µF	R _{ct} ohms
Cd (0.6)	6.59	531.44
Zn(0.6)	3.96	239.17
Zn-Ni(0.75)	1.13	87.69
Zn-Ni(0.8)	2.30	93.39

3. RESULT AND DISCUSSION

3.1. Hull cell studies

Fig (1.1.a, 1.1.b, 1.1.c) shows dark grey colors were obtained at low current density areas only for zinc-nickel alloy coatings i.e. up to 2 A/dm^2 . At higher current densities white color was obtained.

Fig (1.1.d) shows grey colors were obtained for plain Zn bath. Fig (1.1.e) shows white color obtained for Cadmium bath at 2A current density.

This shows we can obtain good deposits of Zinc- Nickel alloy coatings even at higher current densities than zinc and cadmium.

3.2 EFFECT OF CURRENT DENSITY ON CATHODE CURRENT EFFICIENCY FOR PLAIN ZINC BATH

When current density increases current efficiency also increases in plain zinc electrolyte as shown in Fig.2 and the values were tabulated in table.3

3.3 EFFECT OF CURRENT DENSITY ON CATHODE CURRENT EFFICIENCY FOR PLAIN CADMIUM BATH

As current density increases current efficiency also increases in cadmium deposition also as shown in Fig.3 and Table 4

3.4 EFFECT OF CURRENT DENSITY ON CATHODE CURRENT EFFICIENCY OF ZINC-NICKEL BATH

Fig.4 and **Fig.5** shows when current density & concentration of nickel increases current efficiency decreases. It was because the presence of nickel ions in the bath. This may be due to rate of ionic diffusion of nickel and migration in to plating solution, unlike zinc and cadmium since both are single metal deposition. **TABLE.5** represents the diagrammatic features of **fig.4 & fig.5**

3. 5 Surface analysis:

3.5.1 SEM

Surface morphology of electrodeposited samples of zinc-Nickel at different concentrations are in **fig. 6 (a-d)** shown in SEM (Scanning Electron Microscope (SEM) & Energy Dispersive X-Ray Micro Analysis (EDAX) (Hitachi, Model: S3000H, Canada), (TESCON).

SEM shows ball like structures in zinc whereas in cadmium integrated rock like structures & Zinc – Nickel alloy at current density of 0.75 A/dm^2 , 0,8 A/dm^2 show semi fine grained uniform deposits.

3. 5. 2 EDAX

EDAX shows the elemental percentage of zinc from plain bath, zinc-nickel alloy from 7.5g/l nickel bath at 0.75 a/dm^2 , 0.8 a/dm^2 . The comparative table was prepared from EDAX was tabulated in **table 6.** and the diagrammatic representation was as shown in Figs 7.1, 7.2,7.3.

3.5.3. AFM

cadmium deposit shows columnar like structure at 3-dimensional view (Fig. 8.1) whereas at 2 -AFM of dimensional view (Fig. 8.2) it shows nodular as well as grain like structure. Deposit crystal peak and valley graph and average surface roughness profile was shown in Figs. 8.3 & 8.4

AFM of zinc-nickel alloy from 7.5 g/l at 0.75 a/dm² shows somewhat hccp platelet like structure due to the presence of zinc at 3-dimensional view (Fig. 8.5) whereas at 2- dimensional view (Fig. 8.6) it shows suppressed hccp integrated structure due to the presence of nickel in zinc nickel alloy deposit, peak and valley graph of deposit from AFM and average surface roughness profile was shown in Figs. 8.7 & 8.8

AFM of zinc-nickel alloy from 7.5 g/l at 0.8 a/dm² shows rod like structure arranged in a particular fashion due to the presence of nickel at higher concentration at 3-dimensional view (Fig. 8.9) whereas at 2-dimensional view (Fig. **8.10**) it shows step wise horizontal & vertical rod like structures due to the presence of nickel in zinc nickel allow deposit. Material peak and valley graph and average surface roughness profile was shown in Figs. 8.11 & 8.12

3.5.4. XRD

The phase structures of electrodeposits of zinc- nickel alloy were analysed by X-ray diffractometry (XRD, with X'PERT PRO PANalytical (Model: PW3040 160 X'Pert PRO, Netherlands). Electrodeposited Zn-Ni alloy has different phases; α - phase, a solid solution of Zn in Ni with an equilibrium solubility of about more than 79% Ni[31]; γ- phase, an intermediate phase with a composition Ni₅Zn₂₁; η- phase, a solid solution of Ni in Zn with less than 5 % Ni; δ -phase Zn₃Ni₅ appeared from η -phase to α - phase with increasing content of Ni. The fact from that the Zn from γ - phase is oxidized at two different potentials was related to the phase composition of alloys. When the deposit contains high amount of η -phase, this is dispersed among the intermediate of γ -phase, and after stripping of Zn from the solid solution, the remaining deposit was and easy to oxidize. However, in the absence of or with low amount of solid solution, the γ -phase forms a more compact structure with a lower value of exchange current density, and it is more difficult to oxidize. The composition of the alloy might suggest a pure γ -phase between 12% Ni and 15% Ni, with result that the Zn-Ni alloy coatings have very good corrosion resistance.

4. Corrosion resistance measurements

4.1. Chemical method (weight loss method)

The weight loss method shows that weight loss in various specimens which were subjected to experiment. The Cadmium plated sample at 0.6 current density show low corrosion performance than Zn and Zn-Ni plated samples as in TABLE 6. Zn-Ni plated sample 0.8 A/dm² stable in 3% NaCl electrolyte and weight loss is minimum due to Ni percentage significantly.

4.2. Electrochemical methods

4.2.1. Potentiodynamic polarisation analysis

TABLE 7 Shows the results obtained from polarization curves of (Fig.10) and Zn-Ni alloy coatings are improved in corrosion resistance when compared to bare zinc coating and Cadmium coating at same conditions. Improved corrosion resistance is noticed in the case of Zn-Ni deposits obtained at very low current densities levels. The results obtained are in concordance with impedance studies which is shown in Fig.11.

4.2.2. Electrochemical impedance spectra

The results of EIS were figured by Nquist plots as in Fig.11. Double layer Capacitance values(Cdl) and polarization resistance values (R_{ct}) were obtained from impedance. The values of R_{ct} and C_{dl} are listed in table 8. The R_{ct} values have remarkable for corrosion performance and C_{dl} values decreases with increase in corrosion performance.

HULL CELL PATTERN



Fig 1.1 Codes for Recording Hull Cell Pattern

(a) Hull Cell for $\rm NiSO_4$.7H_2O 5 g/l Concentration

(b) Hull Cell for $\rm NiSO_{4.}~7H_{2}O~7.5~g/l$ Concentration

(c)Hull Cell for NiSO4.7H2O 10 g/l Concentration

(d) Hull Cell for Plain Zn Bath

(e) Hull Cell for CdSO4 Bath

Fig.2 current efficiency versus current density of zinc







Fig.4 CURRENT DENSITY VERSUS CATHODE CURRENT EFFICIENCY OF 7.5 g/l NICKEL BATH



Fig.5 CURRENT DENSITY VERSUS different concentrations NICKEL BATH



Figs. 6 (a-d) zinc from plain zinc bath 9g/l, cadmium 5 g/l, 7.5g/l of Nickel at 0.75 A/dm², 0.8 a/dm²







Fig. 7.2 EDAX analysis of 7.5g/l of zinc-nickel alloy deposit at 0.75 a/dm²



Fig.7.3.EDAX SPECTRUM OF ZINC-NICKEL ALLOY DEPOSIT AT 0.8 A/dm²







Fig. 8.3

ISO 42	ISO 4287						
Amplitud	le parameter	s - Rougi	hness profile				
Rp	0.0847	um	Rp: Maximum Peak Height of the roughness profile.				
Rv	0.089	um	Rv: Maximum Valley Depth of the roughness profile.				
Rz	0.174	um	Rz: Maximum Height of roughness profile.				
Rc	0.0989	um	Rc: Mean height of the roughness profile elements.				
Rt	0.174	um	Rt: Total Height of roughness profile.				
Ra	0.0316	um	Ra: Arithmetic Mean Deviation of the roughness profile.				
Rq	0.0371	um	Rq: Root-Mean-Square (RMS) Deviation of the roughness profile.				
Rsk	-0.155		Rsk: Skewness of the roughness profile.				
Rku	2.32		Rku: Kurtosis of the roughness profile.				
Material Ratio parameters - Roughness profile							
Rmr	100	%	Rmr: Relative Material Ratio of the roughness profile.				
Rdc	0.068	um	Rdc: roughness profile Section Height difference				









ISO 42	87		
Amplitud	le parameter	s - Roug	hness profile
Rp	0.166	um	Rp: Maximum Peak Height of the roughness profile.
R∨	0.277	um	Rv: Maximum Valley Depth of the roughness profile.
Rz	0.443	um	Rz: Maximum Height of roughness profile.
Rc	0.194	um	Ro: Mean height of the roughness profile elements.
Rt	0.443	um	Rt: Total Height of roughness profile.
Ra	0.0735	um	Ra: Arithmetic Mean Deviation of the roughness profile.
Rq	0.0983	um	Rq: Root-Mean-Square (RMS) Deviation of the roughness profile.
Rsk	-0.998		Rsk: Skewness of the roughness profile.
Rku	3.80		Rku: Kurtosis of the roughness profile.
Material	Ratio param	eters - R	oughness profile
Rmr	100	%	Rmr: Relative Material Ratio of the roughness profile.
Rdc	0.133	um	Rda: roughness profile Section Height difference





Fig. 8.11

Rdc

0.163

Amplituc	le parameter	s - Roug	hness profile
Rp	0.198	um	Rp: Maximum Peak Height of the roughness profile.
Rv	0.185	um	Rv: Maximum Valley Depth of the roughness profile.
Rz	0.383	um	Rz: Maximum Height of roughness profile.
Rc	0.233	um	Rc: Mean height of the roughness profile elements.
Rt	0.383	um	Rt: Total Height of roughness profile.
Ra	0.0731	um	Ra: Arithmetic Mean Deviation of the roughness profile.
Rq	0.0876	um	Rq: Root-Mean-Square (RMS) Deviation of the roughness profile
Rsk	0.0784		Rsk: Skewness of the roughness profile.
Rku	2.28		Rku: Kurtosis of the roughness profile.
Material	Ratio param	eters - R	loughness profile
Rmr	100	%	Rmr: Relative Material Ratio of the roughness profile





Fig.9.1	XRD	PATTERN	OF	CADMIUM	DEPOSIT	(0.6	A/dm2)
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Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Crystal plane [h k l]
38.6010	82.09	0.3264	2.33055	2.51	[101] of Cd
62.5311	3276.40	0.1836	1.48418	100.00	[110] of Cd



Pos.	Height	FWHM	d-spacing	Rel. Int. [%]	Crystal plane
[°2Th.]	[cts]	[°2Th.]	[Å]		[h k l]
36.4253	128.20	0.3346	2.46665	17.76	[0 0 2]
38.8901	210.25	0.2007	2.31581	29.13	[100]
43.1681	721.75	0.2509	2.09570	100.00	[101]
54.5461	66.50	0.4015	1.68242	9.21	[102]
70.5438	164.00	0.3346	1.33505	22.72	[110]
82.0939	70.49	0.4015	1.17400	9.77	[112]
86.4466	46.90	0.4080	1.12478	6.50	[201]

FIG.9.2	XRD PA	ATTERN	OF	ZINC	DEPOSIT	(0.6	A/dm^{2}
110./.2			U			(0.0	(Mania)



Fig. 9.3 XRD PATTERN OF ZINC –NICKEL DEPOSIT (0.75 A/dm2)

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Crystal plane [h k l]
42.8047	887.78	0.2676	2.11265	100.00	[101] of Zn
62.1674	31.99	0.6691	1.49323	3.60	[110] of Ni

Conclusion: Research was aimed to identify the better environment-friendly replacements for hazardous cadmium to prevent corrosion. Corrosion resistance measurements such as weight loss method, polarisation analysis, electrochemical impedance spectra evaluate zinc- nickel alloy is superior in corrosion performance than cadmium and hence we can use this alloy for cadmium replacement applications.

References:

1.	L A S Silva, L. Sathler, Plating & Surface Finishing Dec 2003 :33-41
2.	M Schlesinger and M Paunovic, Electrodeposition of zinc and its alloy in "Modern Electroplating"
	, 4 th Edn., 555, 2000,, John Wiley & Sons New York
3.	Shanmugasigamani Srinivasan and Malathy Pushpavanam, J Appl Electrochem (2006) 36 : 315 -
	352
4.	Chandrasekar M S, Shanmugasigamani Srinivasan and Malathy Pushpavanam, J Solid State
	Electrochem (2009) 13 : 781 – 789
5.	E W Broomen, Plat Surf Finish, 80 (1993) 29 – 35
6.	A Krishniyer, M Ramasubramanian, B N popov, R. E. White, Plating & surface Finishing, Jan
	1999:99-103
7.	D E Hall, Plating Surf Finish, 70 (1983) 59
8.	B N popv, M Ramasubramanian, S N Popova, R E White, K M yin, J chemical Society Faraday
	Ttransactions, 92(1996), 4021
9.	J Divisek, P Malinowski, J Merge, H Schmitz, Int J Hydrogen Energy, 13 (1988) 141 – 145
10.	H Ashassi - Sorkhabi, A Hargrah, N Paruini - Ahmadi, J Manzoori, Surface & Coatings

	Technology, 140 (2001) 278
11.	C E Lehmberg, Ph.D. Thesis, Sheffield Hallam University, 1998
12.	T Akiyama, H Fukushima, ISIJ Int. 32 (1992) 787 – 9
13.	F.Elkhatabi, M sarret, C muller, Journal of Electroanalytical chemistry., 404, (1996),45
14.	C Muller, M Sarret, M Benballa, Electrochimica Acta, 46 (2001) 2811
15.	S. Rajendran, S. bharathi, T vasudevan, Transactions of the Institute of Metal Finishing ,78 (2000)129-134
16.	R Ramanauskas, L Nuleshkova, L Maldonado, P. Dobrvolskis, Corros Science, 40 (1998) 401
17.	F.I. Danilov, I A shevlyakov, T E Sknar, Russian Journal of Electrochemistry 35 (1999) 1322
18.	G Roventi, R Fratesi, Surface & Coatings Technology, 82 (1996) 158
19.	D D Penin, Stability constants of metal – Ion complexes, Part B: Organic Ligands, 1979, Pergamon, Oxford
20.	J B Bajat, Z Kacacarevic – Popovic, V B Miskovic – Stankovic, M D Maksimovic, Progress in Organic Coatings, 39 (2000) 127
21.	Z Zhou, T J O'Keefe, Surface & Coatings Technology, 96 (1997) 191
22.	M Ishihara, H Yumoto, K Akashi, K Kameri, Materials Science & Engineering, B38 (1996) 150
23.	K Yamakawa, H Fujikawa, Curr Jpn Mater Res, 16 (1996) 1 – 9
24.	D.G.Block, Eur. Patent 0649918A1,1995
25.	R G Baker, A C Holden, Plat Surf Finish, 72 (1985) 54 – 57
26.	Shanmugasigamani Srinivasan and Malathy Pushpavanam, TIMF, 84 (2006) 326 - 331
27.	Shanmugasigamani Srinivasan and Malathy Pushpavanam, TIMF, 86 (2008) 122
28.	M Gavrila, J P Millet, H Mazile, D Marchandise and J M Cuntz, Surf Coat Technol, 2000, 123, 164
29.	C C Hu, B Tsay and C H Allen, Electrochim Acta, 2003, 48, 907
30.	Duprat, J J; Kelly, Mike; "Dedicated processes for electroplating on fasteners", Fasteners
31.	Technology International, Aug (2010) 56-60
	C Muller, M Sarret, M Benballa, J electroanal chem. (2002),519,85