CHAPTER-4

ELECTRODEPOSITION OF ALLOYS (NICKEL-ZINC)

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ELECTRODEPOSITION OF ALLOYS

4.1 Introduction :

Although metals are highly valued in the pure state, they are usually not strong enough to satisfy the demands of structural and mechanical engineering. However, if the metals are judiciously alloyed, we get materials with requisite properties to overcome the above difficulties of the present day. Also, codeposition of metals results in an appreciable reduction in metal cost. Now-a-days, alloys can be used for decorative purposes, in view of their special and variable colour effects.

Alloy is a metallic solid containing two or more different elements, at least one of which is a metal.

Characteristics of alloys :

1) Hardness and strength : Alloys are generally stronger than pure metals. For example, the addition of 1% carbon increases the tensile strength of pure iron by ten times. Addition of a little arsenic makes lead so hard that it is used for bullets.

2) Electrical conductivity : Alloys are generally poor conductor of heat and electricity as compared to pure metals. For example, presence of even traces of impurities in copper reduces its conductivity to a large extent. That is why copper is purified to 99.99% for use as electrical conductors.

3) Resistance to Corrosion : Alloys are generally more resistant to corrosion. For example, pure iron is rusted even in moist air; whereas stainless steel, an alloy of Fe with Cr is even acid proof.

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4) Melting and boiling points : Melting and boiling points of an alloy are generally lower than those of its constituent elements. For example, the melting point of 'solder', an alloy of Ph and Sn is much lower than those of Pb and Sn.

There are number of methods for the manufacture of alloys; as follows :

1. Fusion

2. Electro - deposition

3. Reduction method

4. Powder metallurgy

Electrodeposition of metals and alloys is the purpose of the study. Here electrodeposition consists in simultaneous deposition of the component metals from the electrolyte containing their solution mixture by passing electricity. For example, brass is obtained by the electrolysis of a mixed solution of copper and zinc cyanides dissolved in potassium cyanide.

Theproblems arising in the deposition of alloys are the composition of the solution, the choice of electrodes (anodes in particular) and the conditions of operations in order to secure the required composition in the deposited alloy. The chemical equivalent of the two constituents influences their proportion in the deposit, so the solution will not necessary contain the alloy constituents in the same proportion as that of the required alloy deposit. Further

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anode and cathode efficiencies are not likely to balance and this leads to variation in the composition of the solution. To avoid this insoluble anodes are used.

4.2 : <u>Simultaneous deposition of Metals : Simultaneous</u> <u>discharge of cations</u> :

In order to deposit two metals simultaneously at a cathode it is necessary that the two metals have same deposition potentials. This means that the concentrations of the two ions in solution must be so adjusted that the potentials of the two metals, which are different, are brought together. Such adjustment is usually not possible with solutions of simple salts of the metals, it is possible by converting the metal ions to complexes. (M & P)

If a solution contains two cations, there is a possibility that simultaneous discharge may occur; this problem is very interesting in the electrodeposition of alloy. But this problem is also very important in the deposition of single metals, since aqueous solutions always contain hydrogen ions. Were if not for a variety of complicating factors, such as the influence of one metal on the deposition potential of the other, the situation would in principle be relatively simple, provided the discharge potentials of the two ions were the same, simultaneous deposition would occur.

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For example, the reversible potential of a metal 'A' in a solution of its ions of activity a_A^+ , i.e. of the electrode A, A⁺, would be given by

$$\mathbf{E} = \mathbf{E}_{\mathbf{A}}^{\mathbf{O}} - \frac{\mathbf{R} \mathbf{T}}{\mathbf{Z}_{\mathbf{A}} \mathbf{F}} \quad \ln \mathbf{a}_{\mathbf{A}} + , \dots \qquad (1)$$

and the theoretical discharge potential E dis is equal to -E i.e.

E dis. =
$$-E_A^O + \frac{RT}{Z_A F} \ln a_A + ----$$
 (2)

In order to obtain the actual discharge potential, it is necessary to include the over voltage $"W_A"$, and so it follows that

$$E_{dis} = -E_A^O - W_A + \frac{RT}{Z_A F} \qquad \ln a_A + \dots \qquad (3)$$

If the solution contains two cations, one of which may be the hydrogen ion, then provided there is no interaction in solution or in the deposit, simultaneous deposition will occur when the two discharge potentials, e.g. of A and B, become equal, that is, when

$$-E_{A}^{O} - W_{A} + \frac{RT}{Z_{A}F} \ln a_{A}^{+} = E_{B}^{O} + \frac{RT}{Z_{B}F} \ln a_{B}^{+} --- (4)$$

The subject of simulatenous discharge may be divided into two aspects, e.g. first when it is desired to deposit two metals simultaneously, e.g. in alloy deposition, and second, when simultaneous deposition is to be avoided, e.g. in electroanalytical work. An examination of equation (4) shows that there are in general, three ways in which the discharge potentials ? of two cations may be brought together : (a) if the standard potentials are approximately equal and overvoltages are small (b) if the standard potentials are different, but the overvoltages vary sufficiently to compensate for this difference, and (c) if the differences in reversible potential and overvoltage are compensated for by differences in activities (concentrations) of the ions.

4.3 : Influence of plating parameters in Alloy Deposition :

Independent parameters in alloy deposition, as in all deposition, processes are current density, temperature, pH agitation, and concentrations of bath constituents. Normally, these must be more properly controlled in alloy plating than in single metal plating, because it is likely that a change in any one will affect one metal more than the other and thus changes the composition of the alloy. Exact effects can be determined only by experiment. Current efficiency, addition agents, base metal, throwing power and anodes have a prominent role in alloy deposition

Many alloy deposition baths (i.e. simple and complex, organic solvent baths) are possible,

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4.4 Electrodeposition of Nickel - Zinc Alloys :

Zinc was used as a constituent of brass for 2,000 years before being recognized as a separate element. Zince is divalent and amphoteric. The metal is slowly oxidized in air moisture. It reacts with mineral acids and at elevated temperatures with the halogens. It also reacts with potassium hydroxide or sodium droxide forming zincates together with evolution of hydrogen. Zinc forms a complex ion with excess ammonia.

Zinc (as metal) is used for numerous purposes. The major use is in galvanizing i.e. coating (Hot dipping) of various iron and steel surfaces with a thin layer of zinc to retard corrosion of the coated metal.

About 35% of the world production is used to protect iron and steel. Various processes are important commercially : hot dip galvanizing in which objects are immersed for a short time in baths of moletn zinc. In all cases, the protective zinc layer is partly alloy with the ferrous substrate, and adheres very strongly.

The aim of the present work is to make an attemp for systematic, exhaustive and quantitative study on electrodeposition of binary alloy of Nickel and Zince and to establish optimum conditions to obtain the best quality deposit.

Howver good quality deposits were reported from ammonical bath containing Nickel sulphate, Zinc sulphate boric acid, Glucose. The current efficiency of the process is not high. The influence of the following parameters are studied in details to establish the optimum conditions under each system.

1) Composition of the bath (Electrolyte Concentrations).

2) Temperature.

3) Current density

4) Duration of electrolysis

5) Electrode distance

6) Addition agents.

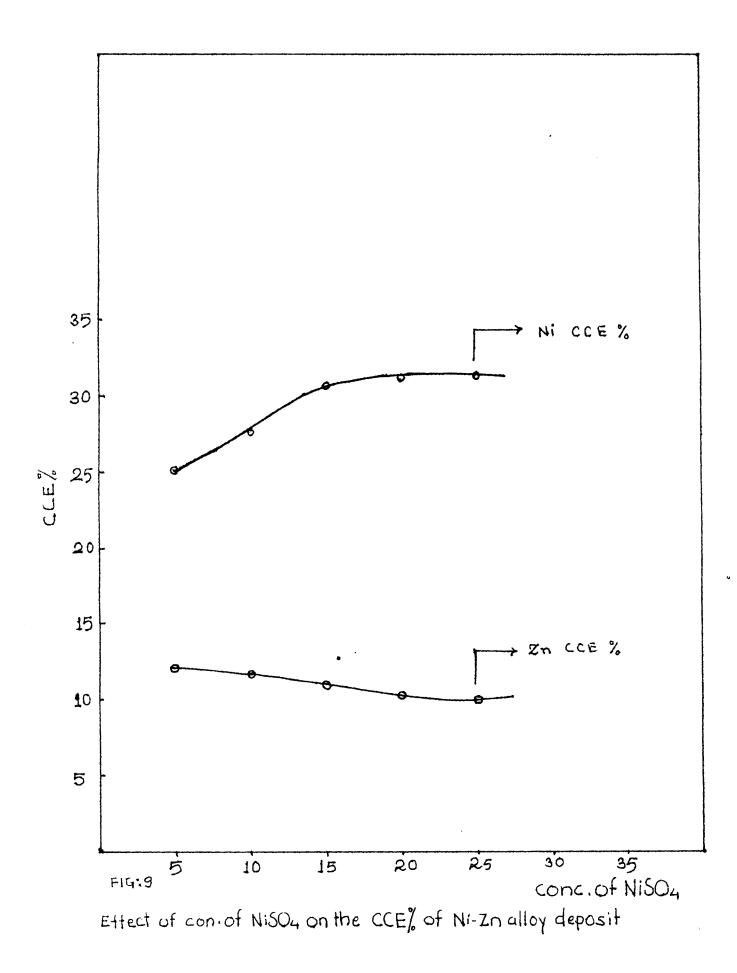
With the help of certain addition agents, we have succeded in obtaining alloy deposit of high quality and properties which may bring about a radical change in plating industry. Considering increasing cost of noble metals, inclusion of silver or gold in traces in the solution has evolved a new method of obtaining an alloy deposit.

percentage				20 minutes		Nature of deposit	Dirty black	nonaanerent Dull white adherent	Uniform, adherent, silver white deposit	Dull white	-do-			
ent and	ب	100 m l	1m 0(••			37.15 D	40.10 D	42.47 U s	44.70 D	43.08			
etal content	alloy deposit.	1 gm per 100 ml	25 ml per 100 ml	Electrolysis		Zn CCE %	12.11 37	11.78 40	11.27 42	10.28 44	10.38 43			
n the n		Boric acid :	••	of		CCE %	25.04	28.32	31.20	32.39	32.70			
sulphate on the metal	the Nickel-Zinc	2) Boric	4) Ammonia	6) Duration		itent deposit Zn	28.57	25.92	23.53	19.15	20.45			
of nickel	(CCE%) of	00 mJr J.	.ps/sq		cms.	Metal cou <u>in alloy</u> Ni	66. 67	70.37	73.53	72.34	72.72			
ncentration	current efficiency	: 10 gms/100 mFrJ.	ty : 2.4 amps/sq.	25 ⁰ c	distance : 4 c	Wt. of deposit gms.	0.021	0.027	U. 034	0.047	00.044		۲۰ ویورد ۱۹۵۸ ۱	
The effect of concentration of	cathode current	Zinc Sulphate	Current density	Temperature :	Electrode dis	Wt. of copper deposited in coulo- meter oms.		0.072	0.096	0.106	0.105	ion.		
TABLE NO.9 : The	catl	1)	3) (5) 1	7) I	Concm. of Nickel sulphate per 100 ml	10	15	20 *	25	35	Optimum condition.		
TABL						Sr. no.		5	'n	4	ŝ	dC *		

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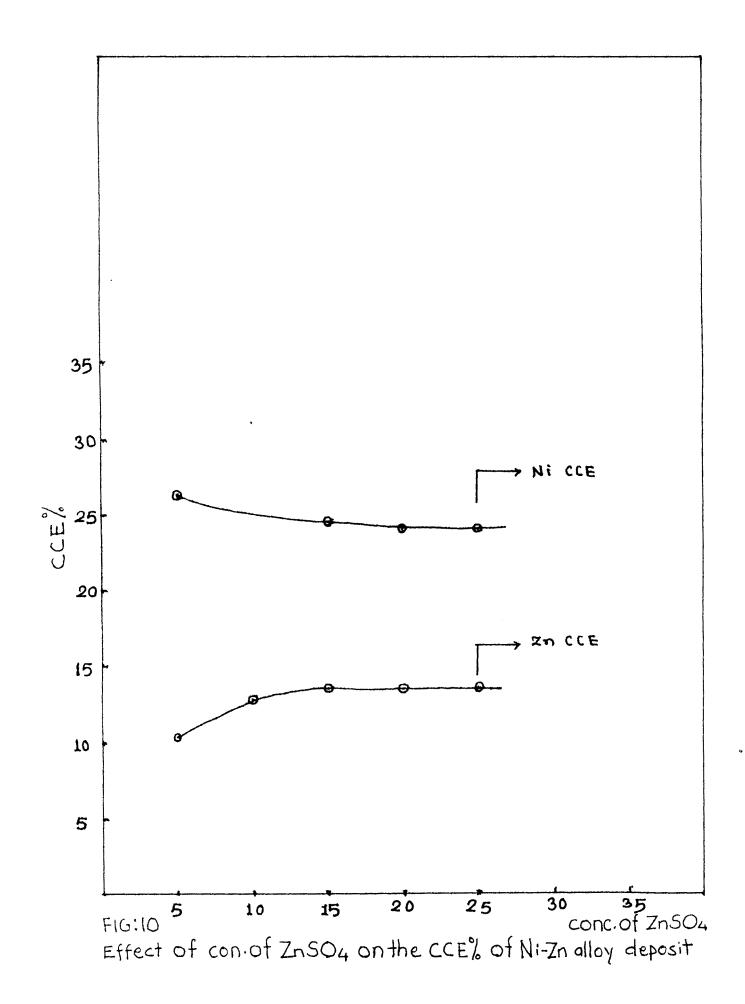
: The effect of concentration of Zinc sulphate on the me	cathode current efficiency (CCE %) of the Nickel-Zinc alloy deposit.	1) Mickel Sulphate : 20 gms per 100 ml 2) Boric acid : 1 gm per 100 ml	3)Current density : 2.4 amps/sq.dm. 2) Ammonia : 25 ml per 100 ml	5)Temperature : 25 ⁰ c 6) Duration of Electrolysis : 20 minutes	7)Electrode distance : 4 cms.	nc. of Wt.of Wt. of Metal content CCE % Total Nature of .nc sulphate copper deposit in alloy CCE % deposit .r 100 ml depositedr- gms. deposit	in coulometer gms.	5 0.144 0.050 70.00 24.00 26.08 10.11 36.19 Slightly non adherent, dark black at edges	10 0.086 0.034 73.53 26.47 31.20 12.70 43.96 Slight improvement.	15 * 0.125 0.044 65.91 21.81 24.90 13.57 38.47 Uniform, bright, adherent	20 0.125 0.046 63.04 31.11 24.86 13.57 38.43 Dull white, adherent.	25 0.126 0.047 63.83 31.112 24.86 13.57 36.49 Black,slightly non-adherent.	Optimum condition.
TABLE No.10 : TI	0	1)	3)C	5)1	()	Conc. of Zinc sulph per 100 ml		Ŋ	10		50 4	25	timum condi
TABLJ						Sr. no.		7	2	ო	4	ហ	do • *

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nt and percentage	loy deposit.	2)Zinc sulphate : 15 gms/100 ml	4)Current density : 2.4 amps/sq.d.	6)Duration of Electrolysis : 20 minutes.		Nature of deposit		Slight non adherent dull white.	Slight improvement	Uniform, adherent	Dull white, adherent	I do I	
al conte	Zinc al	c sulpha	ren t den	ation of		Total JJE %		29.84	31.54	31.91	32.53	31.64	
the met	lickel -	2)Zine	4) Cur	6)Dura		CCE%	zn	10.90	13.35	13.13	13.25	12.56	
: The effect of concentration of Ammonia on the metal content and percentage	cathode current effeciency (CJE%) of the Nickel - Zinc alloy deposit.	20 gms per 100 ml	00 m l		cms.	Metal content CC in alloy deposit	Ni Zn Ni	65.63 34.3 8 18.94	58.82 38.23 18.19	56.75 35.14 18.78	57.50 35.0 19.28	58.54 34.15 19.08	
concentra	c effecie	••	gm per 1	25 ⁰ c	••	Wt. of deposit		0.032	0.034	0.037	0.040	0.041	
he effect of c	athode current	1)Nickel Sulphate	3)Boric aciã : 1	5)Temperature : 2	7)Electrode distance	Wt. of copper deposited-	rin coulom eter gas.	0.110	0.118	0.120	0.128	0.135	
TABLE NU.1G : 1	0	1) N	3) B	5) I	7)E	Conc. of Ammonia per 100	Ţu.	10	15	20 *	25	30	
TABL						sr. no.		r\$ ~1	7	ю	4	ហ	

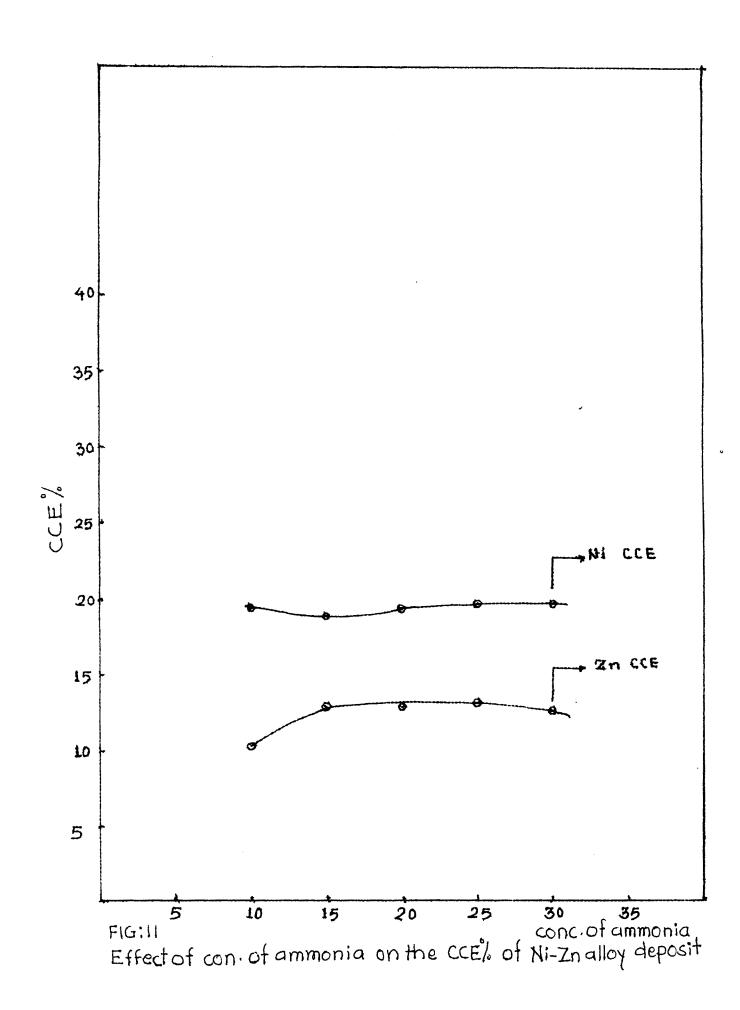
* Optimum condition.

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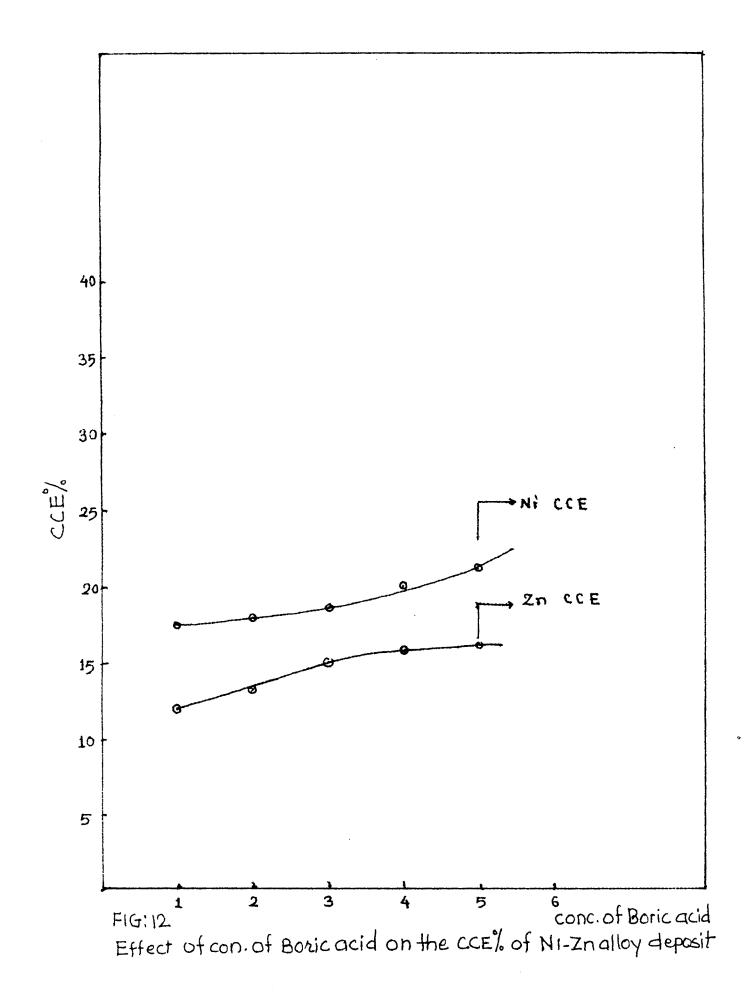
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			<pre>v ()C. 0+equ[5</pre>	ame ner 100 ml	2) Zinc	nhate : 15 משג/100 ml
		TUTTER	> 	amos/	Amon	: 20 ml
	5)		0 20			n of Elec
	()		distance :	4 Cills.		
Sr. No.	Amount of Boric acid in gms	Wt. of copper posite	Wt. of Metal de-deposit in a depo	letal content CCE% in alloy deposit	% Total CCE %	Nature of deposit
		in coulo- meter gms	<u>i</u> N	Zn Ni	Zn	
1)	1	0.110 0.030	.030 60.00	33.33 17.56 12.12	12 29•68	Non adherent, black
2)	7	0.115 0.	0.033 57.58	39.40 17.73 13.70	70 31.43	Adherent but blackish at the edges.
3)	3 * \$.	0.120 0.038	.038 57.89	39.47 18.92 15.14	14 34.06	Adherent, bright
4)	4	0.122 0.	0.040 57.50	37.50 20.23 15,54	54 35.77	Dull white
5)	ß	0.123 0.	0.042 59.52	40.48 21.81 16.74	74 33.55	Blacks adherent

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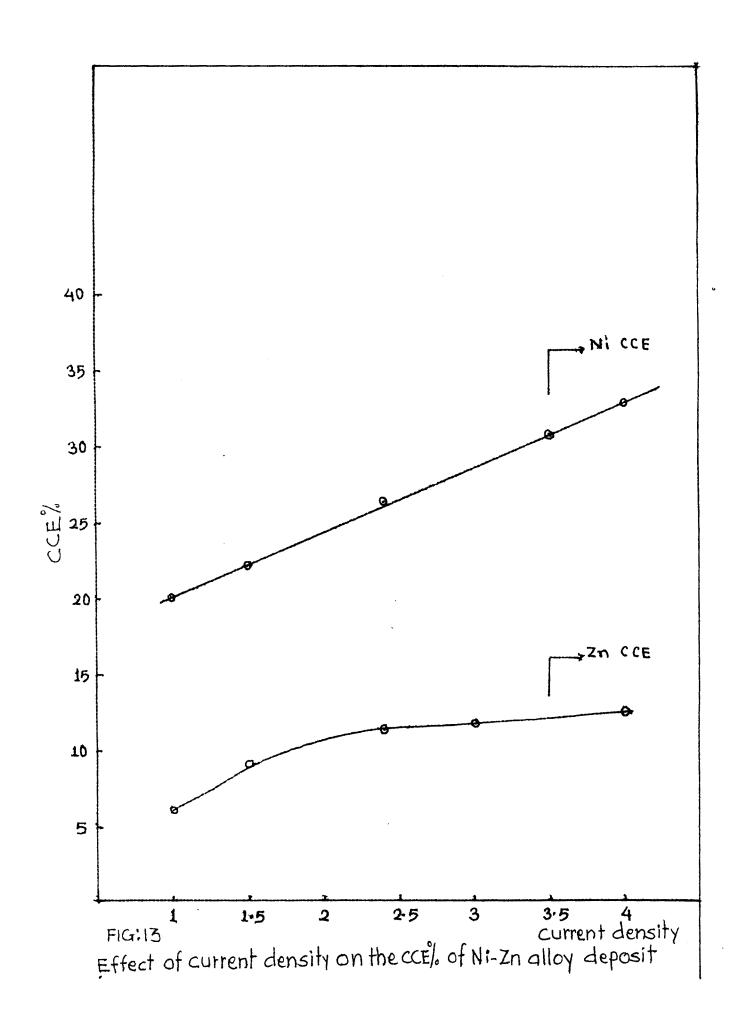
 al content and percentage cathode el - Zinc alloy deposit. 2) Zinc sulphate : 15 gms/100ml 4) Amnonia : 20 ml per 100 ml 6) Duration of Electrolysis : 20 minutes 	Nature of deposit	Non adherent black Adherent slight black with bluish ting at edges Adherent white, uniform Adherent white, black patches Blackish at the edges.
it and alloy ulphat a : 2(on of	Total CCE %	26.18 31.44 38.29 43.56 45.97
1	CCE % Zn	6.06 9.09 11.46 12.26 12.75
the metal the Nickel 100 ml 2) 4) 6)	in	20.12 22.35 26.83 31.30 33.22
	tal content alloy posit Zn 1	20.00 25.71 26.92 24.63 25.29
	in del del	75.00 71.42 71.15 71.01 74.71
<pre>clurrent iency (0 phate : 2 pms c : 250c distance</pre>	t wt. of deposit	0.020 0.035 0.052 0.069
<pre>: The effect of Jurrent current efficiency (1) Nickel Sulphate : 3) Boric acid : 3 gms 5) Temperature : 25⁰c 7) Electrode distance</pre>	wt. of copped depositedrin coulometer gms	0.080 0.120 0.148 0.168 0.210
13	Current density amps. per sq. dm.	1 1•5 2•4 * 4•2 4•2
TABLE NO.	Sr. No.	1) 2) 4) 5)

* Optimum condition. × Micropholograph - 7

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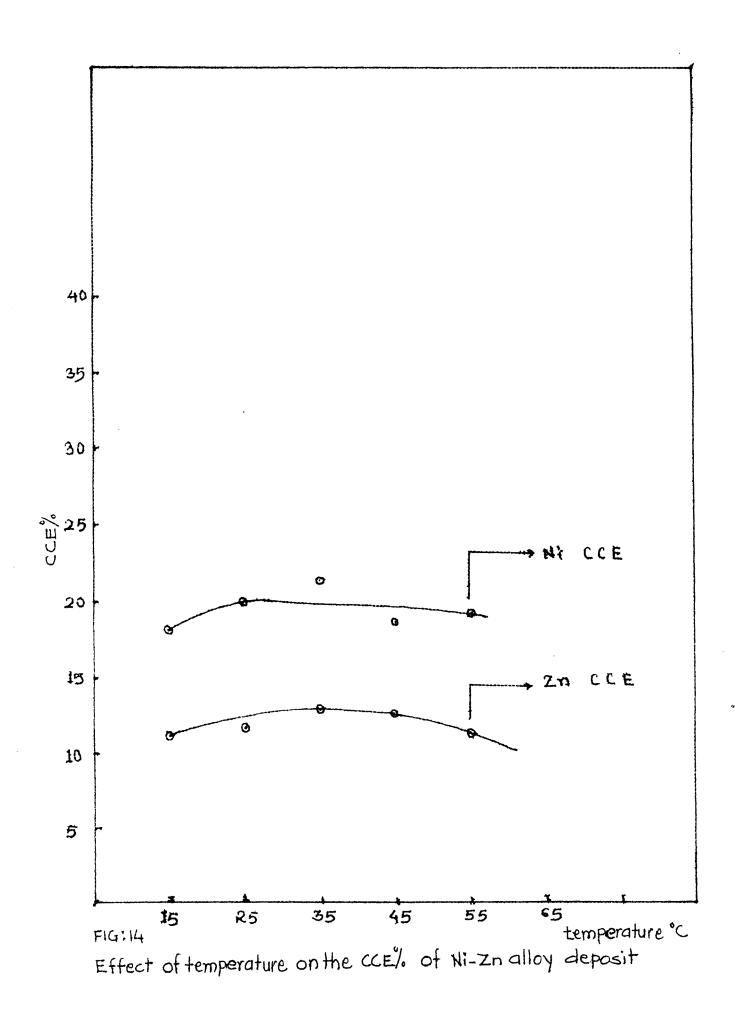


<pre>1) Nickel Sulphate : 20 3) Boric acid : 3 gms pe 5) Anmonia : 20 ml per 1 7) Electrode distance : 7) Solution : 20 ml per 1 7) Electrode distance : 7) Electrode distance</pre>	er 100 ml 2) Zinc sulphate ml 4) Current densi 6) Duration of E 6) Duration of E 6) Zuration of E content CCE% Total oy t Zn N1 Zn 34.29 18.16 11.13 29.34	ce : 15 gms / 100 ml sity : 2.4 amps / sq.d.m Electrolysis : 20 minutes Nature of Deposit
 3) Boric acid : 3 gms per 5) Ammonia : 20 ml per 100 7) Electrode distance : 4 8 9 9<td>ml4) Current densi6) Duration of E6) Duration of E6) Duration of Econtent<</td><td>: 2.4 amps ctrolysis : ture of Depo</td>	ml4) Current densi6) Duration of E6) Duration of E6) Duration of Econtent<	: 2.4 amps ctrolysis : ture of Depo
<pre>5) Ammonia : 20 ml per 10 7) Electrode distance : 4 7) Electrode distance : 4 Temperature Wt. of Wt. of Me deposit- gms dep edrin coulome- ter gms 15 0.130 0.035 62.86 15 0.145 0.042 64.29 35 * * 0.160 0.050 66.00</pre>	6) Duration of E content CCE% Total oy t Zn Ni Zn 34.29 18.16 11.13 29.34	•• Q
7) Electrode distance : 4 Temperature Wt. of Wt. of Mt. of Mt. of deposit Temperature Wt. of Mt. of Mt. of Mt. of deposit 0c deposit-gms deposit 15 0.130 0.035 62.86 15 0.130 0.035 64.29 35 * x 0.160 0.050 66.00	ontent CCE% Total Y Zn Ni Zn 4.29 18.16 11.13 29.34	
TemperatureWt. ofWt. ofMe0ccopperdepositin0cdepositgmsdepdepositgmsdepedrincoulome-Niter gmster gmsdep250.1300.03562.8635 * ×0.1600.05066.00	ontent CCE% Total Y Zn Ni Zn 4.29 18.16 11.13 29.34	
edrin coulome- ter gms 15 0.130 0.035 62. 25 0.145 0.042 64. 35 * % 0.160 0.050 66.	Zn Ni Zn 4.29 18.16 11.13 29.34	
15 0.130 0.035 25 0.145 0.042 35 * × 0.160 0.050	18.16 11.13 29.34 19.08 11.10 21.08	
25 0.145 0.042 35 * × 0.160 0.050	10 00 11 10 31 08	Non adherent, dull White
35 * ½ 0.160 0.050	00.10 01.11	Dull white, adherent
	34.00 22.13 12.67 37.01	Uniform, adherent. bright.
	37.50 18.38 12.45 30.93	Slight blackish at edges
5 55 0.145 0.041 63.41	34.15 19.24 11.70 30.94	Black, spatchy, unsatis- factory

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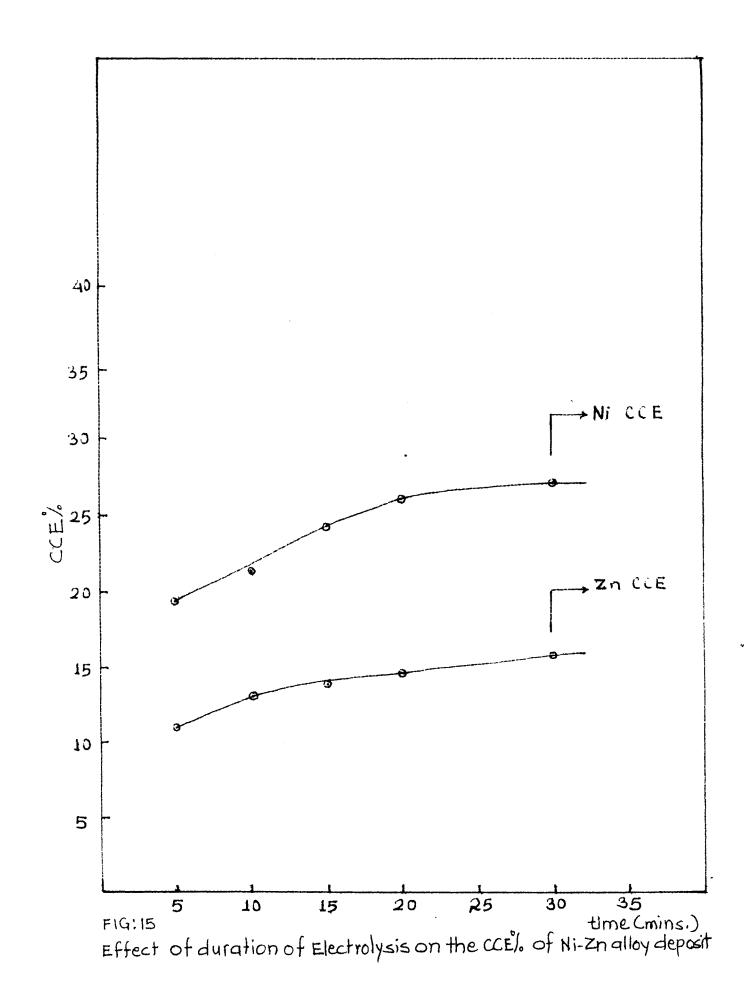
raded no. 1. The effect of Duration of electrolysis on the metal content and percentage	(CCE %) of the Nickel - Zinc alloy deposit.	ml 2) Zinc sulphate : 15 gms \cancel{z} 100 ml	4) Current density : 2.4 amps/sq.d.	6) Temperature : 35 ⁰ c		CCE % Total sit CCE % Nature of deposit Ni Zn		25 19.51 11.01 30.52 Non adherent,black	33 21.45 12.75 34.21 Adherent,slight improvement	00 24.30 13.71 38.02 Adherent,w hit e, with blue at edges	00 25.76 14.53 40.05 Uniform,bright good	B0 26.30 15.72 42.02 Dull white, adherent.
of electrolysi	itency (CCE %)	20 gms per 100 ml	per 100 m l.	· 100 ml	: 4 cms.	Metal content in alloy deposit Ni Zn		62.50 31.25	63.33 33.33	72.00 36.00	64. 00 32.00	66.71 34.80
: Uuràtion	ent eff é ci	**	: 3 gms	20 ml per 100 ml	distance	Wt.of deposit gms.		0.016	0• 030	0• 050	0.075	0.082
. Me erredt or	cathode current eff é c	1) Nickel Sulphate	3) Boric acid	5) Armonia :	7) Electrode distance	Wt.of copper depositedrin	conlometer gms.	0.055	0.095	0.159	0.200	0.216
TABLE NU. LO						Duration of Electrolysis minutes		ß	10	15	20 * %	30
						Sr. no.		-1	2	ო	4	IJ

* Optimum condition.

*. Microphotograph - 9

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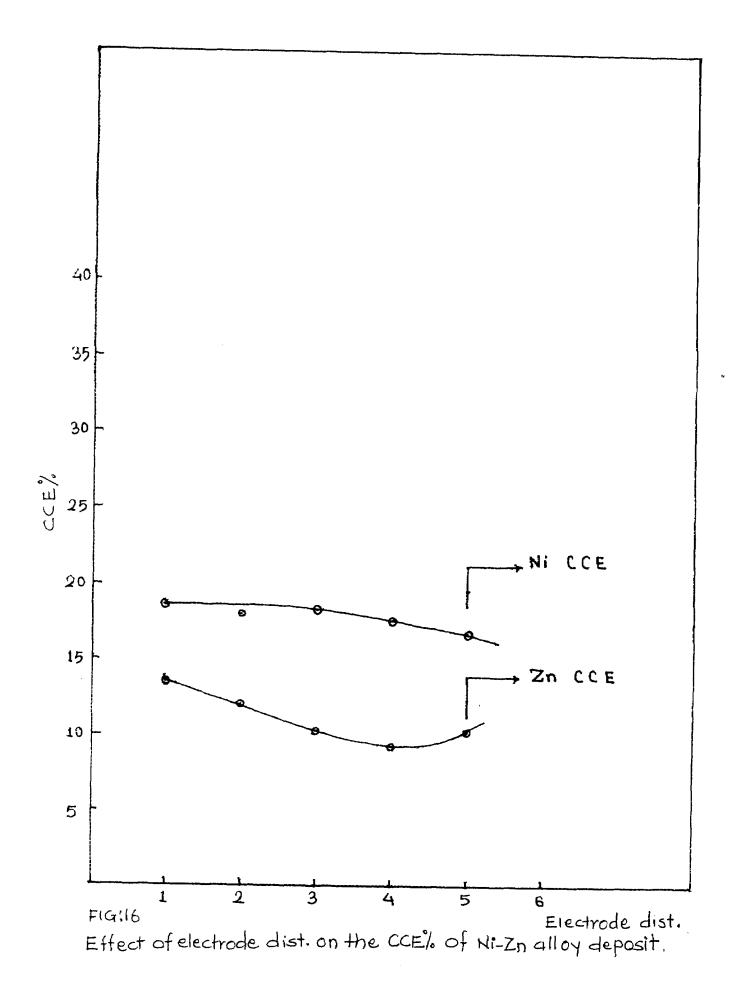
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: The effect of Electrode distance on the metal content and percentage cathode current efficiency (CCE%) of the Nickel-Zinc alloy deposit.	1)Nickel Sulphate : 20 gms per 100ml. 2) Zinc sulphate : 15 gms/100 ml	3)Boric acid : 3 gms per 100 ml 4) Current density : 2.4 amps/ sq.dm	5)Ammonia : 20 ml per 10 0 ml 6) Temperature : 35 ⁰ c	7)Duration of Electrolysis : 20 minutes.	Wt.of Wt. of Metal content CCE % Total Nature of conner deposit in alloy deposit CCE % deposit	tedrin gms. Ni Zn Ni Zn eter	0.130 0.037 59.46 37.6 6 18.62 13.04 31.66 White.adherent	0.132 0.039 58.97 33.33 18.17 11.93 30.63 -do-	0.129 0.036 61.11 30.56 18.30 10.33 28.63 improvement in quality of deposit, good	0.130 0.036 58.34 27.78 17.31 9.32 26.63 Dull white.	0.128 0.037 62.12 30.62 17.20 10.12 27.32 -do-	t i ⊂n
TABLE No.16 : The cur	1)1	3)E	5)4	7)1	Electrode W distance o		1	3	* m	4	ŝ	Obtimum condition.
TABLE					Sr.		ħ	0	m	4	S	+40



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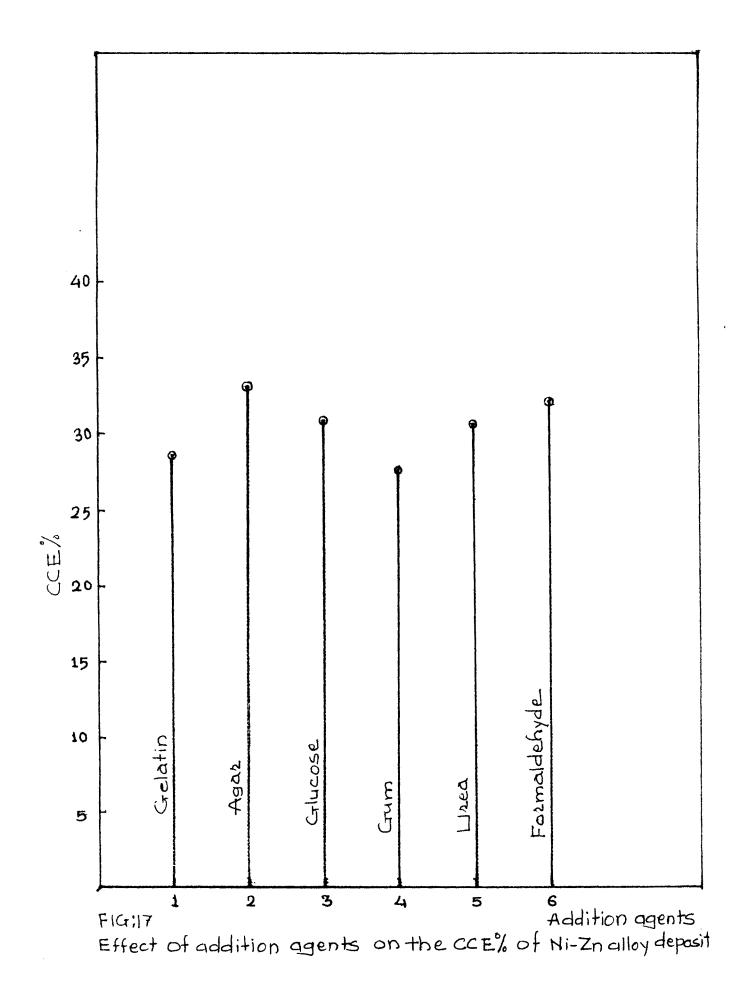


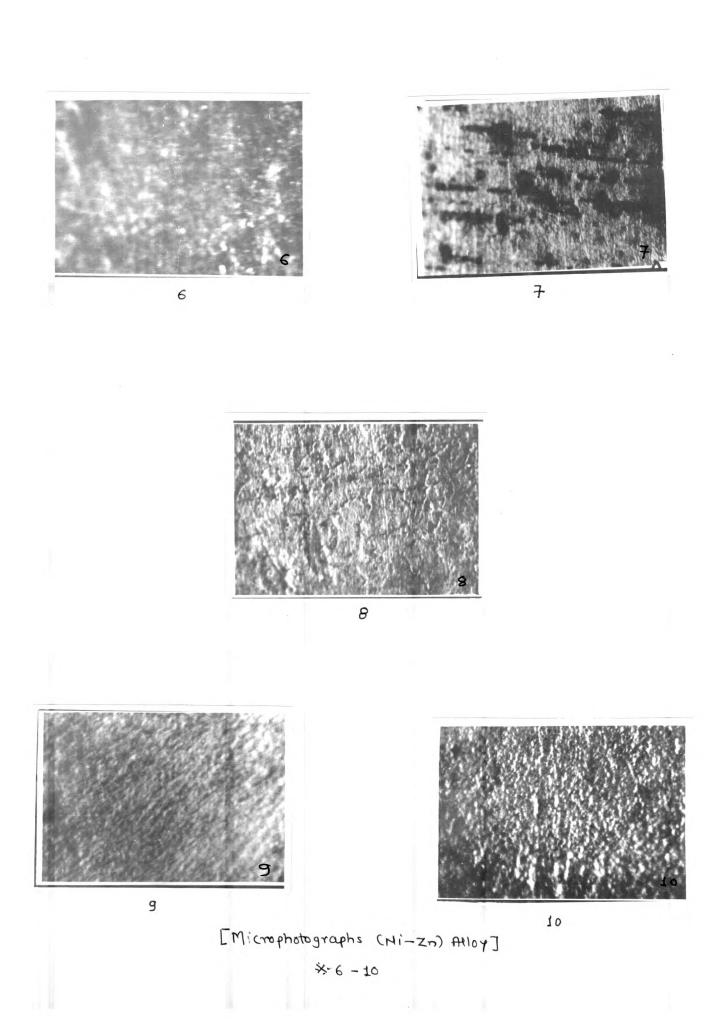
	0.17 : The effect of Addition agents, on the metal content and percentage cathode current efficiency (CCE%) of the Nickel-Zinc alloy deposit.	1)Nickel Sulphate : 20 gms per 100 ml 2) Zinc sulphate : 15 gms / 100 ml	3)Boric acid : 3 gms per 100 ml 4) Current density : 2.4 amps/sq.d	5)Ammonia : 20 ml per 100 ml b à Temperature : 35 ⁰ c	7)Duration of Electrolysis : 20 minutes 8) Electrode distance : 3 cms.		depositedrin gms. comlometer gms.	latin 0.125 0.034 61.76 32.35 18.03 10.66 28.69 No improvement in quality	ar 0.125 0.038 6053. 36.84 19.75 13.57 33.32 -do-	ucose * 🔆 0.140 0.040 72.50 25.00 22.23 8.65 30.88 Bright, white adherent uniform	m 0.180 0.034 67.64 26.47 18.99 8.39 27.38 Smooth,slight bright	ea 0.128 0.036 63.89 33.33 19.28 11.36 30.64 - do -	rmalde- 0.129 0.037 67.57 33.33 20.80 11.27 32.07 - do -	
Add Add Guun For For For		1) N	3)B	5)A	D(1	Addition agents	•	Gelatin	Agar	Glucose * 🖓	Gum	Urea	Formalde- hyde	

* Optimum condition. * Micropholograph - 10

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SUMMARY

: NICKEL - ZINC SYSTEM (OPTIMUM CONDITIONS) :

The influence of the Physico-chemical factors upon the nature and magnitude of the Ni-Zn alloy deposit has been shown in the previous Table Nos. 9 to 17 and graphically in Figs. 9-17. The ranges over which parameters were studied and optimum conditions arrived at any experiments are summerised below :

F	arameters studied and Range	Optimum condition
1.	Composition of the bath	
	a) Concn. of Nickel Sulphate	20 gms per 100 ml of
	5-35 gms per 100 ml of the	the solution.
	solution.	
	b) Concn. of Zinc sulphate 5-35	15 gms per 100 ml of
	gms per 100 ml of the solution.	the solution.
	c) Concn. of Ammonia 10-35 ml	20 ml per 100 ml of the
	per 100 ml of the solution.	solution.
	d) Boric acid, 1-5 gms per	3 gms per 100 ml of the
	100 ml of the solution.	solution.
2.	Current density, 1 to 4.2 gmps.	2.4 amps per sq.dm.
	per sq.dm.	0
3.	Temperature $15^{\circ} - 55^{\circ}c$.	35°C ·
4.	Duration of Electrolysis 5-30 minutes.	20 minutes.
5.	Electrode distance 1-5 cms.	3 cms.

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Table 4.5 Results & and Discussion (/4.9 - 4.17 : Fig. 4.9 - 4.17)Nickel - Zinc Alloys.

The effect of different variables on the composition of the deposit, cathode current efficiency (CCE) and the nature of the deposits is described below :

1) Effect of Nickel Sulphate concentration

(CF Table 4.9, Fig. 4.9)

Nickel sulphate concentration was varied from 5 gms to 35 gms. per 100 ml. of the solution. When the concentration of Nickel in the bath was increased, its content in the deposits also increased to some content. Increase of electrolytic concentration furnishes more metallic ions and consequently increases the rate of nuclei formation and reduces the evolution of hydrogen at the cathode. This results in a uniform, fine grained and smooth deposit with greater efficiency. Higher nickel content in the bath produced dull white, unsatisfactory deposit. Similarly at low concentration of the nickel, the deposits obtained were nonadherent. Zinc content in the deposit decreased with increase in the concentration nickel sulphate. CCE of nickel increased from 25% to 38% while that for zinc decreased proportionately. The optimum condition for nickel sulphate concentration was 20 gms per 100 ml when the deposits obtained were adherent and uniform.

2) Effect of Zinc Sulphate concentration (CF Table 4.10, Fig. 4.10)

The concentration of zinc sulphate was changed from 5 gms. to 35 gms. per 100 ml of the solution. The zinc content in the alloy deposit was increased from 24% to 31%. This increases in the zinc content was followed by a consequent increase in the efficiency upto 15 gms. of zinc sulphate, after which the efficiency practically remained constant. The nickel content in the alloy deposit as well as its CCE, in general, decreased with increases in the concentration of zinc sulphate. The as deposits obtained at lower as well/higher concentration of zinc sulphate, were nonadherent and black. The optimum condition selected was 15 gms per 100 ml of zinc sulphate.

3) Effect of concentration of Ammonia :

(CR Table 4.11, Fig. 4.11)

Ammonia mainly acts as the solvent. The amount of Ammonia has been varied from 10 ml to 35 ml per 100 ml. for low concentration range the deposits obtained were nonadherent. The quality of deposit improves at 20 ml of Ammonia per 100 ml. However, above this concentration of Ammonia dull deposits were obtained. The optimum condition was obtained at 20 ml of Ammonia per 100 ml.

4) Effect of concentration of Boric acid :

(CF Table 4.12, Fig. 4.12)

Boric acid has marked effect on the nature of the deposit and especially on CCE. As concentration of Boric acid was increased the total CCE was also increased. Hence the effect of boric acid was studied, using concentration between 1 gm to 5 gms per 100 ml of the solution. Bright, uniform and satisfactory deposits were obtained at 3 gms per 100 ml. The deposits became dull when the concentration was further increased. The metal content as well as CCE increased with increase in the concentration of boric acid. The optimum condition for boric acid concentration was 3 gms per 100 ml.

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- 5) Effect of current density :

(<u>CF Table 4.13, Fig.4.13</u>)

Increase in current density normally tends to increase the proportion of the less noble metal in the alloy deposit. Some addition agents may reverse this generalization, by having more effect on the polarisation behaviour of one metal than on the other. The extent of the change is normally greater in simple salt solutions than in complex solutions.

Using a bath of optimum composition, current densities varing from 1 to 4.2 amps, per sq.dm. were studied. In the lower region of current density (1 amps per sq.dm.). The deposits were nonadherent and black, but with an increase in current density upto 2.4 amps. per sq.dm. more shining, uniform and adherent deposits were obtained. Above this current density, the deposits turned black and showed burning effect. At higher current density the deposit becomes loose, especially at the edge due to the metal ion concentration near the cathode and evolution of hydrogen. In general the weight of deposit and total CCE increased with increase in current density. The optimum condition for current density was 2.4 amps per sq.dm.

6) Effect of Temperature :

(CF Table 4.14 and Fig.4.14)

The temperature range studied was $15^{\circ} - 55^{\circ}c$ under optimum conditions of the composition and C.D. It was seen that, the quality of deposit improved on raising the temperature to $35^{\circ}c$ and then decreased with further rise of temperature. Increase of temperature on one hand favours diffusion and tends to produce a fine grained uniform deposit, but on the other it increases the rate of crystal growth, decreases the hydrogen over voltage, favouring evolution of the gas and causes the precipitation of basic salts, resulting in a coarse, poorly adherent and dark deposit. At mode rate temperatures the influence of the former factor is predominating while at higher temperatures letter ones are increasingly operative. Zinc content in the alloy deposit and CCE increased slightly, while the Nickel content in the alloy deposit and its CCE decreased proportionally with an increase in the temperature, usually tends to decrease the proportion of more noble metal in the alloy plate. However, the variation being very small the point need not be stressed further.

7) Effect of duration of Electrolysis :

(CF Table-4.15 and of Fig. 4.15)

At the optimum composition, current density and temperature, the duration of electrolysis was varied from 5 minutes to 30 minutes. The cathode current efficiency of the deposit was found to increase from 31% to 41% over the whole range of duration studied. The metal contents both Nickel and Zinc increased in general with increase in the duration of electrolysis. The nature of the deposits, were found unaffected for different periods, except at 5 minutes nonadherent deposits were obtained. At 20 minutes the deposit was bright, uniform and adherent, hence optimum condition for duration of electrolysis was obtained at 20 minutes.

8) Effect of distance between electrodes :

(<u>CF.Table 4.16 and Fig.4.16</u>)

The distance between cathode and anode was changed between 1-5 ams. It was noticed that the character of the deposit was not affected to any appreciable extent, either qualitatively or quantitatively, excepting that the cathode current efficiency tends to decrease with increase in the distance between cathode and anode. At 3 cm distance between electrodes gives fine deposit.

9) Effect of addition agents :

(CF. Table 4.17 and Fig. 4.17)

The addition agents listed in Table 4.17 were introduced singly to the bath under the optimum conditions and the effect was studied. In presence glucose, gum and urea the quality of deposit was considerably improved and bright white, smooth adherent deposits were obtained. The deposits obtained in presence of glucose was bright, adherent and uniform.

It is well-known that even small quantities of certain substances added to a depositing solution markedly influence, the structure of the resulting deposit. These are called as addition agents. Most of them are colloidal in nature and they form disperse system with the electrolyles. They produce beneficial change in the character and structure of the deposit. Small quantities of colloidal addition agents may cause the metal to collect as very small crystals and produce smooth uniform and adherent adherent deposit. Also, current density on the cathode surface is never perfectly uniform.