Electroless Nickel Plating Formulation For Automotive And Mechanical Parts

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Electro less plating processes are considered to be much convenient, cheaper and best for deposition on parts with lot of holes, cleavages, bents, curves, abnormal shapes, threading etc., effectively and economically.

Electro less plating uses a redox reaction to deposit metal on an object without the passage of an electric current. Redox reactions involve Reduction and Oxidation reactions. One metal is reduced from its salt and other one gets oxidized to its metallic salt.

Electro less plating technique is being used for many decades. They involve reduction of a complexed metal using a mild reducing agent, typically formaldehyde.

For example, mirrors can be manufactured using this reaction:

$R\text{-}CHO + 2\ [Ag(NH_3)_2]OH \rightarrow 2\ Ag(s) + RCOONH_4 + H_2O + 3\ NH_3$ where R is an organic group or hydrogen. The reaction deposits a shiny coat of elemental silver on the walls of the container.

Electro less plating is an autocatalytic reaction. Autocatalytic reactions are chemical reactions, in which at least one of the reactant is also a product. And a chemical reaction in which a product (or a reaction intermediate) also functions as a catalyst. In such a reaction the observed rate of reaction is often found to increase with time from its initial value.

Being autocatalytic and electrochemical redox process, the formulation and control on the stability of bath, consistency of deposition and maintenance of bath become critical and sometimes difficult too. As probability of settling down of the bath leading to the deposition of metals-"Seeding"- on the walls, pipes and other parts of the plating vessel / tank is very high, resulting loss of metal, constituents of plating solution, forcing to clean the tank and pipes making loss in chemical cost and time.

Of course, one need not require to use electrical energy and metallic anodes for electro-less plating of metal, as it is autocatalytic process with reduction of metal in presence of a catalyst of noble metal. But the formulation, maintenance of solution, plating tank design and arrangement of heaters, cooling coils, agitation system etc., become very critical, to obtain consistent plating quality, uniform rate of deposition of metal with constant productivity, as metal ion to be released and plated on the required part uniformly and the depleted metal to be added as per the depletion rate from the plating solution. Apart from these the surface preparation, catalytic preparation of surface receptive to get adherent electro less plating of metal etc., needs special attention.

Advantages with electro less plating include:

1. No investment and maintenance cost on D.C. Power sources viz., rectifiers, dynamo etc., as this process does not use electric current.
2. Even coating on parts surface may be achieved with uniform in thickness on uneven surfaces.
3. No sophisticated jigs or racks are required.
4. There is flexibility in plating volume and thickness.
5. The process will plate recesses, bents, sharp edges, cleavages and blind holes with stable thickness.
6. Chemical replenishment can be monitored automatically.

7. Complex filtration method is not required
8. Matte, Semi Bright or Bright finishes can be obtained.
9. Rack and barrel plating is possible.
10. No investment on metallic anodes as electrodes.

The following list of metals may be deposited by electro less plating technique on various substrates is as given below:

Metals deposited by electro less plating technique are: 1. Copper, 2. Nickel, viz., a. Nickel-Boron alloy b. Nickel-phosphorus alloy, c. Nickel-Teflon composite, Nickel-Sic,Nickel-Al_2O_3 etc., 3 Arsenic, 4.Cobalt, 5.Chromium, 6.Iron etc., on various substrates and are as depicted below:

1.Electro less copper is deposited on ferrous metals and non-ferrous metals,viz.,brass, bronze, apart from non-conductive substrates- ABS plastics and other plating grade plastics, Glass epoxy material of Printed Circuit Boards, Ceramics, SiO_2 etc., and catalyst used is a solution containing $Pdcl_2$ and $Sncl_2$ with Hcl and reducing agent is formaldehyde-HCHO.

$$CuSO_4 + 2HCHO + 4NaOH \rightarrow Cu + Na_2SO_4 + H_2 + 2H_2O + 2HCOONa$$

2a. Electro less Nickel is deposited on ferrous metals viz., iron, tool steel or mild steel with or without an undercoat of electro-less Copper. The catalyst used is a solution containing $Pdcl_2$ and $Sncl_2$ with Hcl. Reducing agents used are Sodium hypophosphite or Boron hydride.

2b. Electro less Nickel on tool steel with or without an undercoat of copper, is to improve abrasion resistance and on brass, bronze or copper electrical parts and switches of auto parts, mobile phone components and other electrical and electronics devices, components etc., to improve conductivity with reduced contact resistance. Hence, the applications of electro less copper and electro less nickel are very wide.

2c. Apart from these other specialty electro less plating is reported in the literature viz., Nickel with Teflon of 5, 7, 9 % , Nickel with SiC, Nickel with diamond etc. for special applications of auto parts and other parts to improve their properties and applications-hardness, abrasion resistance, wear resistance etc.

2d. For aerospace applications, new developments are taking place on electro less plated composites.

History of Electro less Nickel plating:

The EN plating of metallic nickel from aqueous solution in the presence of hypophosphite was first noted as a chemical accident by Wurtz in 1844.

In 1911, Roux reported that metal was inevitably precipitated in the powder form; however these works were not in practical applications. In its early stage, progress in the field remained slow until World War II. In 1946, Brenner and Riddell developed a process for plating the inner walls of tubes with nickel-tungsten alloy, derived from the citrate based bath using an insoluble anode, which brought out the unusual reducing properties of hypophosphite.

The U.S. Patent Office says that the patent it issued in 1950 differed from the earlier patent in that Roux reaction was spontaneous and complete, while the Brenner and Riddell process was a controlled catalytic process so that deposition occurred only on catalytic surfaces immersed in the bath.

Brenner later wrote that his patent was an accidental discovery similar to the work of Wurtz and Roux, but said that he took out a patent to protect U.S. government rights. In fact, a declassified U.S. Army technical report written in 1963 goes on extensively about Wurtz and Roux work, and gives more of the discovery credit to them than to Brenner. This plating process was attributed to the action of chemical reduction of Ni ions.

During the 1954-59 period, Gutzeit at GATC (General American Transportation Corporation) worked on full scale development of electro less plating by chemical reduction alone, as an alternate process to conventional electroplating.

Initially, the co-deposition of particles was carried out for electrodepositing Ni-Cr by Odekerken, during the year of 1966.

In that study, in an intermediate layer, finely powdered particles like aluminum oxide, polyvinyl chloride (PVC) resin were distributed within a metallic matrix. A layer in the coating is composite but other parts of the coating are not.

The first commercial application of their work used the electro less Ni-SiC coatings on the Wankel internal combustion engine and another commercial composite incorporating poly tetra fluoro ethylene (Ni-P-PTFE) was co-deposited, during the year of 1981. However, the co-deposition of diamond and PTFE particles was more difficult, than the composites incorporating Al_2O_3 or SiC. The feasibility to incorporate the fine second phase particles, in submicron to nano size, within a metal/alloy matrix has initiated a new generation of composite coatings.

Probable Mechanism of eNi deposition:

As per Scholder and Heckel, the deposit consist of a mixture of pure metal and metallic phosphides. They suggest the following reaction:

$NiO + H_3PO_2 \rightarrow Ni + H_3PO_3$

$3H_3 PO_2 \rightarrow H_3PO_3 + 2P + 3H_2O$

$2Ni + P \rightarrow Ni_2P_6$

The author did not connect the reduction of Ni with the evolution of H_2.

Luke's theory, gives a satisfactorily explanation of the simultaneous reduction of Nickel and hydrogen, as follows:

$H_2PO_2^{--} + H_2O \rightarrow HPO_3^{2--} + 2H^+ + H^{--}$ (in acid solutions)

$H_2PO_2^{--} + 2\ OH^{--} \rightarrow HPO_3^{2--} + H_2O + H^{--}$ (in alkaline solutions)

$Ni^{2+} + 2\ H^{--} \rightarrow Ni^0 + 2H$

$H^+ + M^{--} \rightarrow H_2$

Many theories are proposed for the mechanism of electroless deposition of Ni, as the deposition is complicated process.

Table.1: Types of Electro less Nickel Deposits with different Phosphorus Content

No	Type of Deposit	Phosphorus content in deposit %	Heat treatment temperature in °C	Hardness in Rockwell C	Remarks
1	LPEN- Low Phosphorus e Ni	2 to 5	As plated 400 to 425°C for 1 hour	Up to 60 Maximum Hardness	Uniform coating, most resistant to alkaline environments,best solder-ability
2	MPEN- Medium Phosphorus e Ni	6 to 9	--- 375 to 400°C for 1 hour	--- Maximum Hardness	Best appearance
3	HPEN- High Phosphorus e Ni	10 to 13	375 to 400°C for 1 hour	> 65	Super corrosion protection, most resistant to acidic environments
4	e Ni with PTFE	-----	As plated	----	Increased lubricity and low reflectivity

Electroless nickel can also be rendered non-magnetic, making it the optimal choice for electromagnetic shielding.

A great importance of electroless Nickel plating is its ability to produce deposits with a very high degree of thickness uniformity. It is much beneficial when coating on complex parts with critical dimensions, such as ball valves or threaded components. This is because of the fact that no current is involved and the associated problems of current distribution do not arise.

Formulations on Electro less Nickel on copper:

Several formulations on EN plating are tried and in this technical paper, the most successful formulation on electro less Nickel is discussed in details after continuously using in large scale production of mechanical and automobile parts for more than one year period.

The following Bath-I was selected from literature, as it was giving good results for electro less Nickel plating on Copper and electro less copper coated steel parts and it is as given below: .

Bath-I :

1) Nickel Chloride **$NiCl_2 .6H_2O$** – 20 grams per liter

2) Sodium Hypophosphite, **$NaH_2PO_2.H_2O$**– 15 grams per liter

3) Acetic Acid, **CH_3COOH** – 20 ml per liter

4) DL- Malic Acid, **CH_2 (COOH).CH (OH).COOH** -20 grams per liter

5) Glycine **NH_2CH_2COOH** – 5 grams per liter

6) Boric Acid H_3BO_3 -- 2 grams per liter

pH – 6.5 to 6.7 (Adjusted with NaOH & Hcl)

Temperature – 70 to 72 ^{o}C

Time to get 5 to 6 microns of eNickel on Copper – 25 to 30 minutes

Process Sequence:

The Process sequence followed for non-ferrous metal parts made of copper, brass and bronze, is as given:1) Degrease 2) Alkaline Cleaner 3) Swill 4) Acid dip 5) Swill thoroughly 6) Pre-Activator 7) Activator 8) Swill 9) Post-Activator 10) Swill thoroughly 10) Electro-less Nickel Plating 11) Swill 12) Hot water dip 13) Dry.

The Process sequence followed for ferrous metal parts made of steel, tool steel etc., with electro less copper coating is as given: 1) Degrease 2) Alkaline clean 3) Swill 4) Acid dip 5) Swill thoroughly 6) Pre-activator 7) Activator 8) Swill thoroughly 9) Post activator 10) Swill 11) Electro-less copper plating 12) swill 13) Electro-less Nickel Plating 14) Swill 15) Hot water dip 16) Dry

The Process sequence followed for ABS plastics with electro less copper coating is as given: 1) Chromic acid etching 2) Swill 3) Swill thoroughly 4) Pre-activator 5) Activator 6) Swill thoroughly 7) Post activator 8) Swill 9) Electro-less copper plating 10) swill 11) Electro-less Nickel Plating 12) Swill 13) Hot water dip 14) Dry.

After electroless Nickel Plating further thicker deposit of bright nickel is deposited as follows:

1. Jig and load 2. Watts nickel Plating (5 to 10 minutes to get 4 to 5 microns) 3.Swill 4. Bright nickel plating for 25-30 mts to get 20 microns of Nickel 5.Swill 6.Bright chromium plating for 10 mts. 7. Swill 8. Dry 9. Unload.

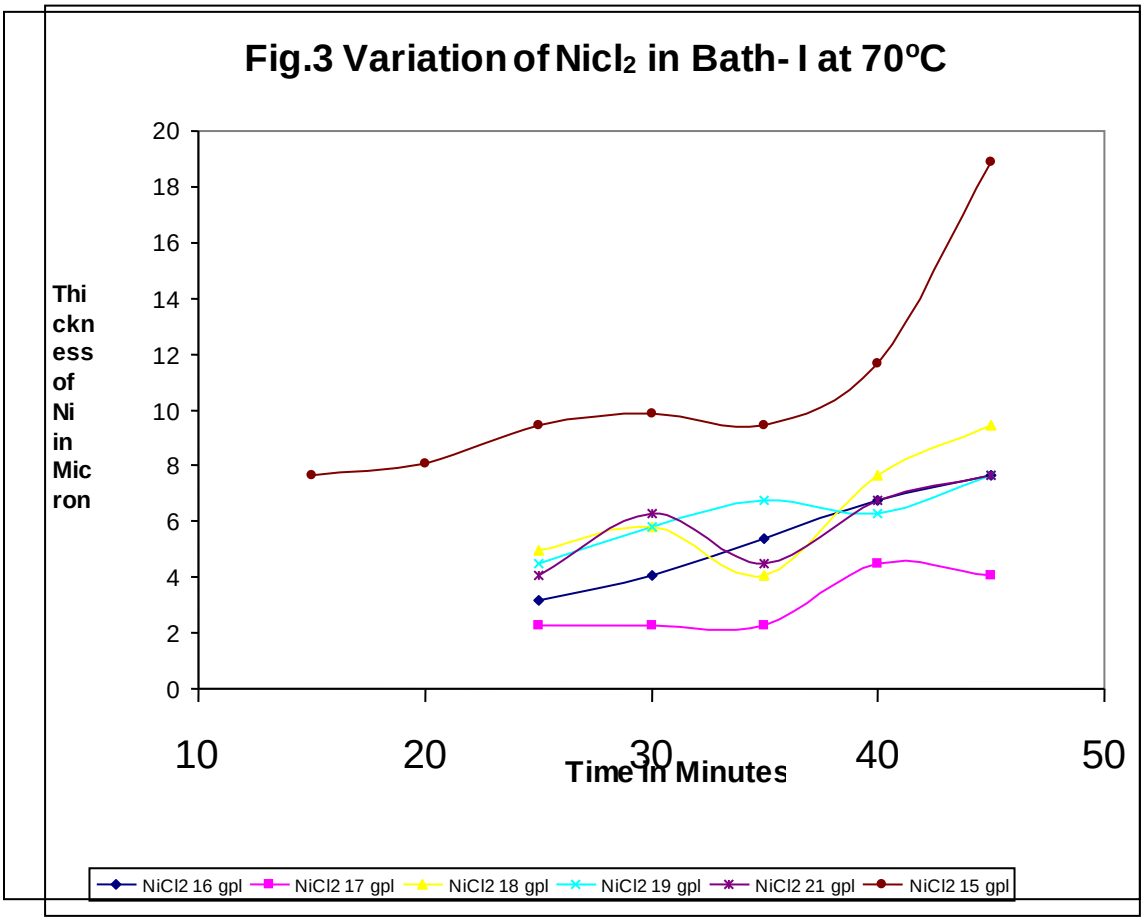
This Bath.1- is further studied thoroughly by varying the various ingredient chemical compositions. Graphs are plotted to find out the optimum condition to get the best & fast results of deposition of electro less Ni deposit on copper.

Every time one chemical ingredient out of 6 chemicals are varied of concentration & studied at temperature of 70 ^{o}C, 75 ^{o}C and 80 ^{o}C .

Cleaned, pre-weighed 1”x1” sized copper specimens are used throughout the experiment & the deposit thickness of Nickel is obtained & calculated by weight gain method. This is cross-checked with X-ray fluorescence thickness tester & the results are within ± 5 %.

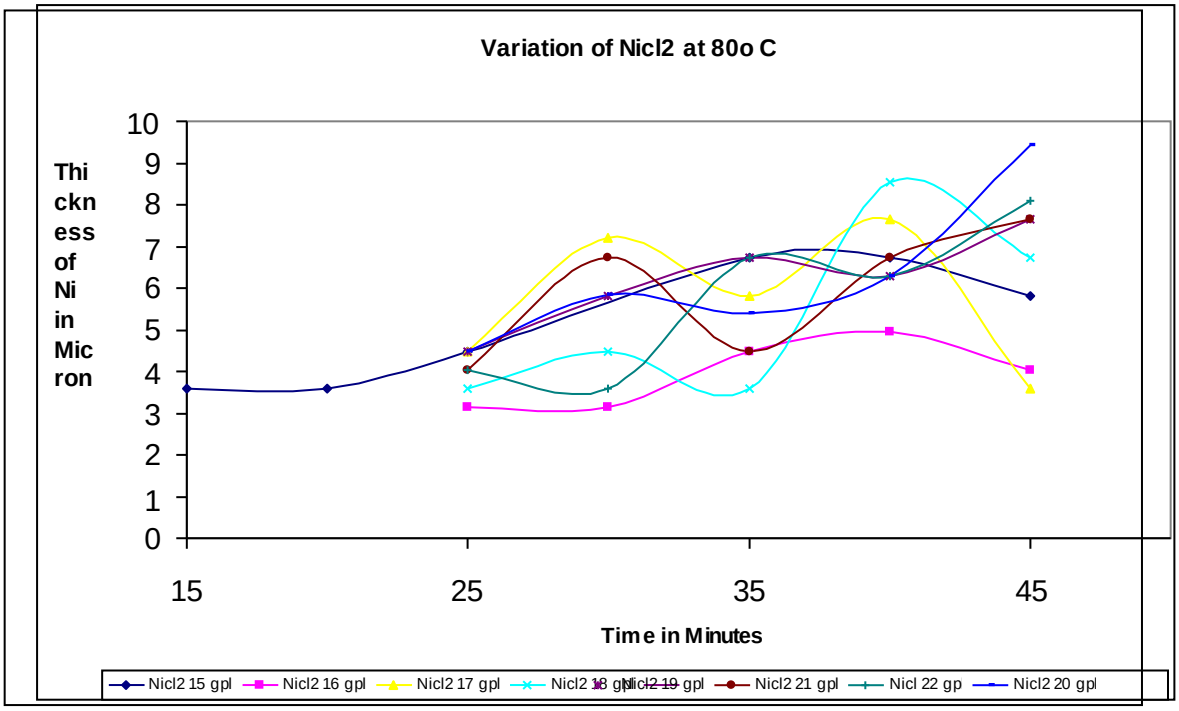
difference. The graphs are plotted with the results of thickness obtained by weight-gain method, to find out the optimum condition of the chemical composition of the bath.

Fig.3: Variation of Nickel Chloride in Bath-I at 70 ^{o} C



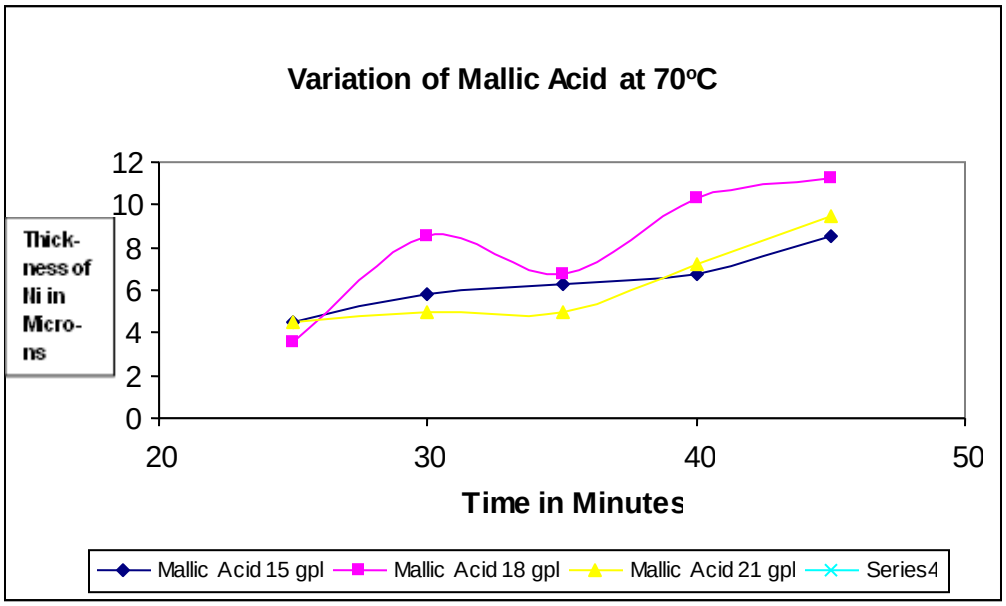
Note: In Fig.3, Optimum is 15 grams per liter of Nickel Chloride in Bath-I at 70ºC deposits 9 microns of Nickel in 30 minutes.

Fig. 4: Variation of Nickel Chloride in Bath-I at 80 ° C



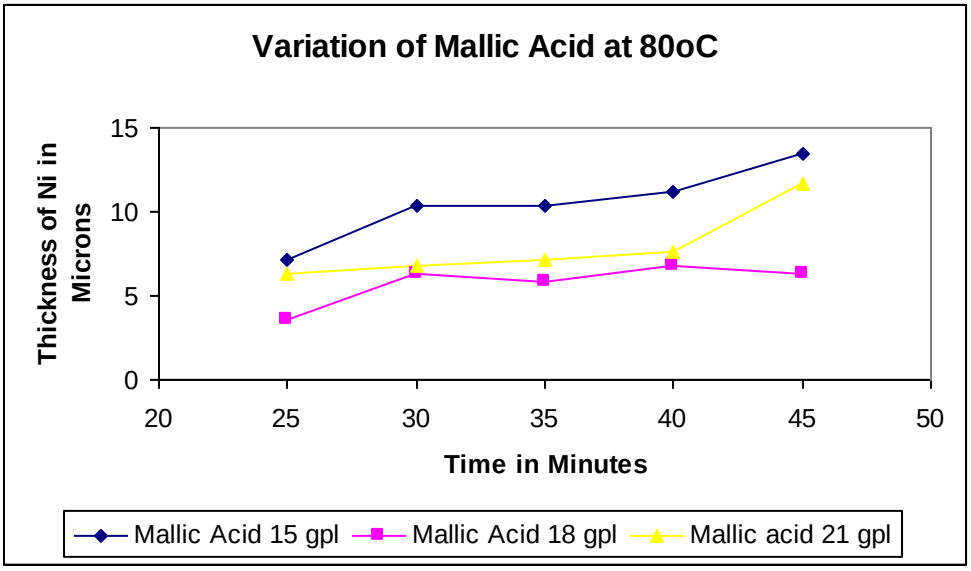
Note: In Fig.4: Optimum is 17 grams per liter of Nickel Chloride in Bath-I at 80 ° C deposits 7 microns of Nickel in 30 minutes

Fig. 5: Variation of Mallic Acid in Bath-I at 70 °C



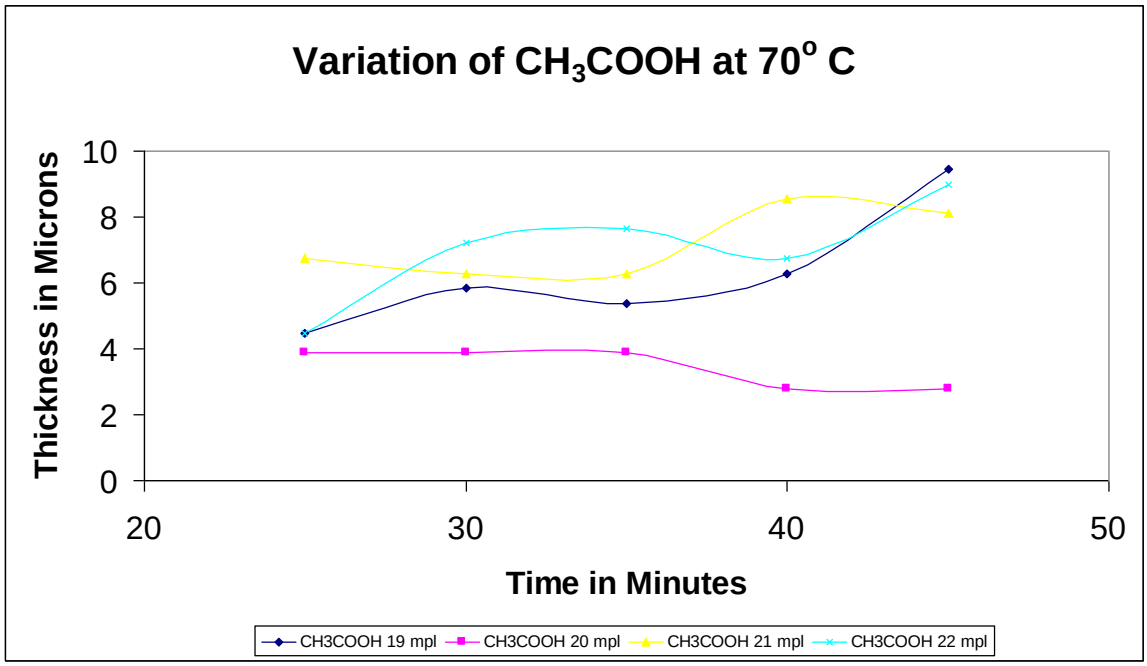
Note: In Fig.5: Optimum is 18 grams per liter of Mallic Acid at 70 ° C, deposits 9 microns of Nickel at 70°C, in 30 minutes.

Fig. 6 : Variation of Mallic Acid in Bath-I at 80 ºC



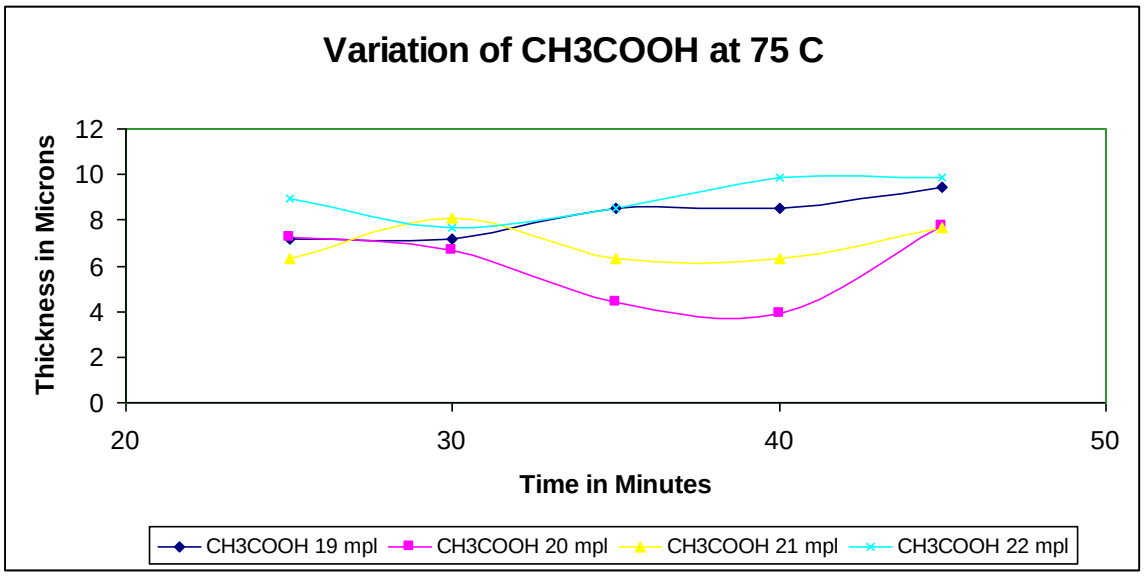
Note: Optimum is 15 grams per liter of Malic Acid gives 11 microns of Nickel in 30 minutes

Fig. 7. Variation of Acetic Acid in Bath-I at 70ºC



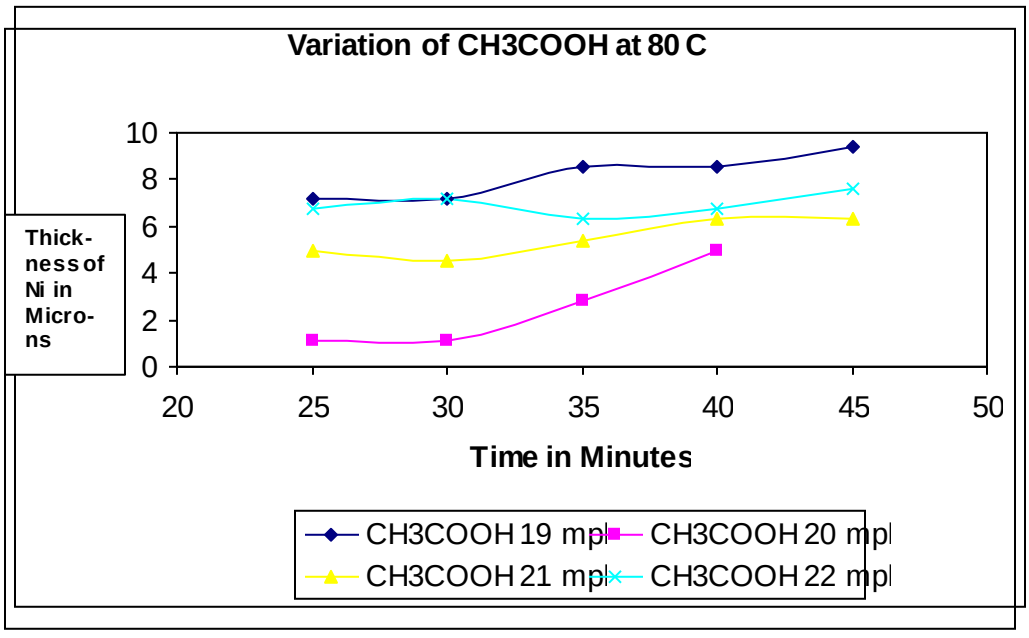
Note: Optimum is 22 ml per liter of Acetic Acid gives 7 microns of Nickel at 70ºC in 30 minutes.

Fig. 8: Variation of Acetic Acid in Bath-I at 75 ºC



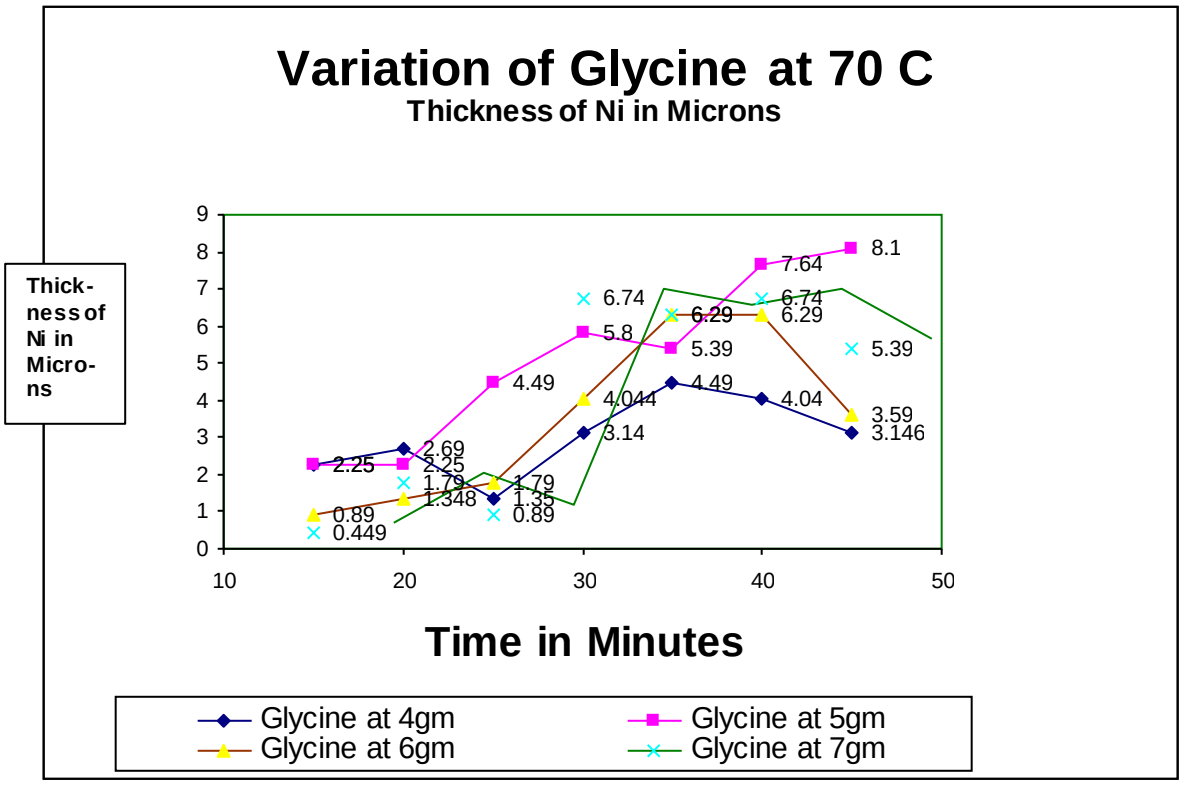
Note: Optimum is 21ml per liter of Acetic Acid gives 8 microns of Nickel at 75°C, in 30 minutes

Fig. 9: Variation of Acetic Acid in Bath-I at 80 ° C



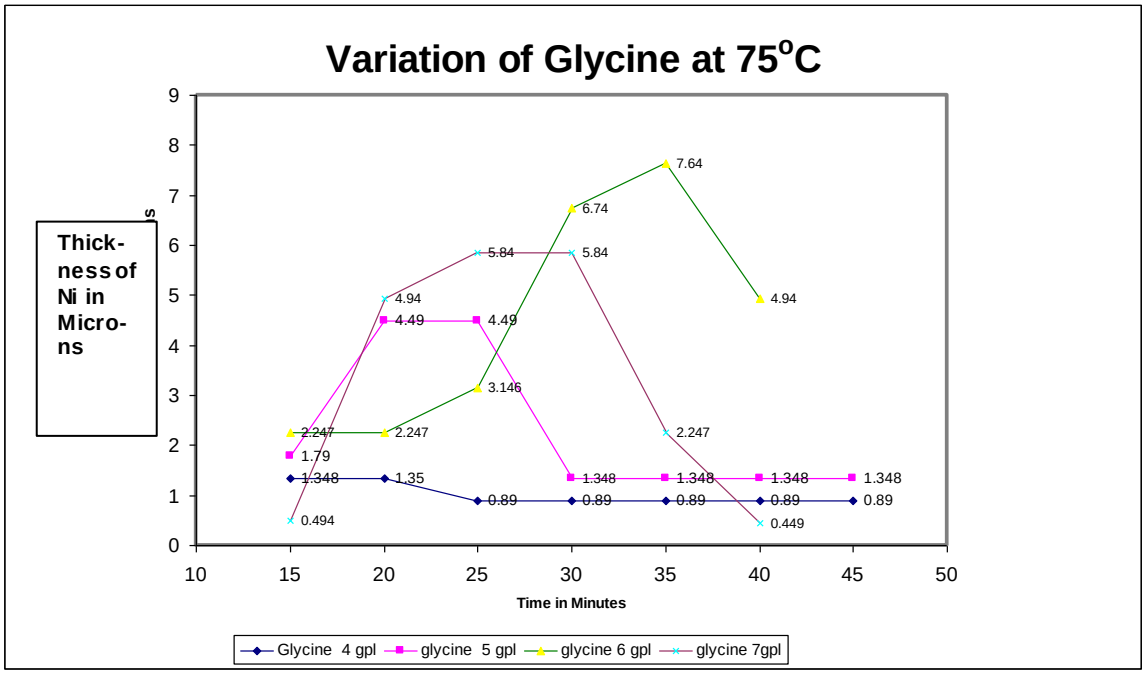
Note: Optimum is 19 ml per liter of Acetic Acid gives 8 microns of Nickel at 80°C, in 30 minutes

Fig. 10: Variation of Glycine in Bath-I at 70 ºC



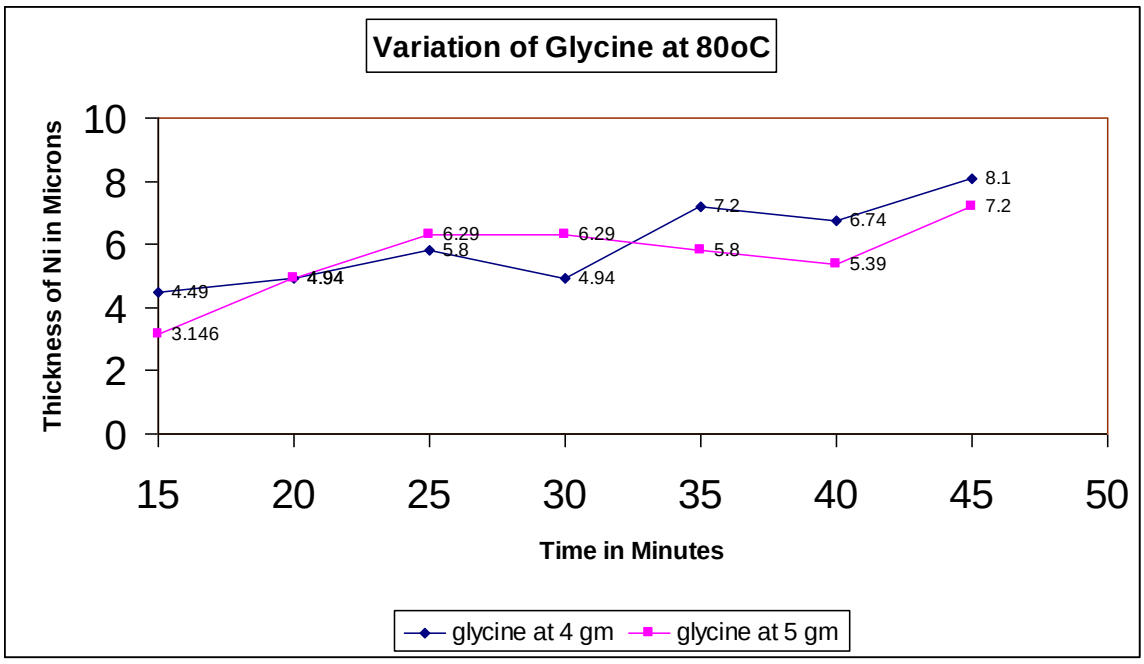
Note: Optimum is 7 grams per liter of Glycine gives 6.74 microns of Nickel at 70ºC, in 30 minutes

Fig.11: Variation of Glycine in Bath-I at 75 ºC



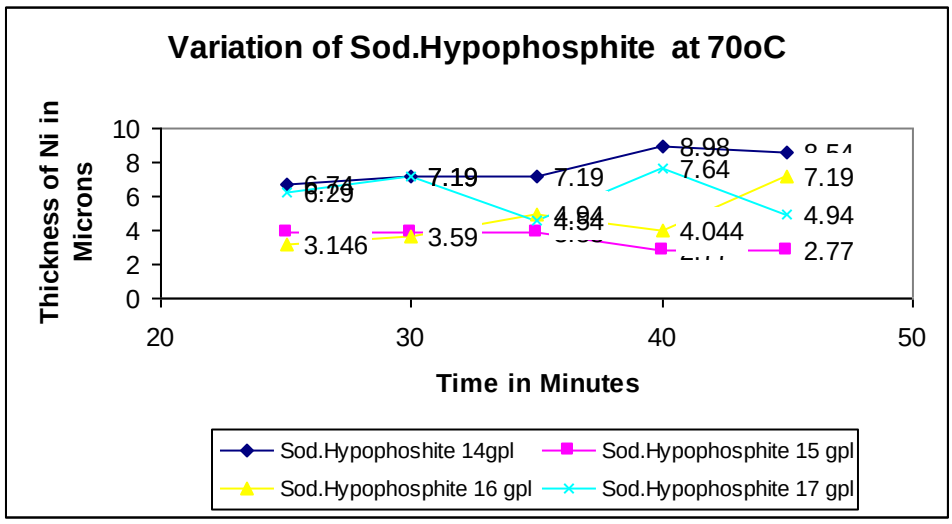
Note: Optimum is 6 gram per liter of Glycine gives 6.74 microns of Nickel at 75ºC, in 30 minutes

Fig.12: Variation of Glycine in Bath-I at 80 º C



Note: Optimum is 5 grams per liter of Glycine gives 6.29 microns of Nickel at 80ºC, in 30 minutes.

Fig.13: Variation of Sodium Hypophosphite in Bath-I at 70 º C



Note: Optimum is 14 grams per liter of Sodium Hypophosphite gives 7.19 microns of Nickel at 70ºC, in 30 minutes.

These optimum results are as depicted in Table.2

Table.2: Depiction of optimum composition of eNi Bath-II

No	Chemical constituents of Electro less Nickel Bath	Grams/liter or ml/liter	Optimum Condition	Thickness in microns	Remarks
1	NICKEL CHLORIDE **$Nicl_2.6H_2O$** (in gram/liter)	15	70°C; 30 min	9.0	
2	SODIUM HYPOPHOSPHITE **$NaH_2PO_2H_2O$** (in gram/liter)	14	70°C; 30 min	7.19	
3	ACETIC ACID **CH_3COOH** (in ml/liter)	22	70°C; 30 min	7.0	80°C;30 min: 8 microns of Ni at 19 ml/l
4	DL-MALLIC ACID **$CH_2(COOH).CH(OH)-COOH$** (in gram/liter)	18	70°C; 30 min	9.0	80°C;30 min: 11 microns of Ni at 15 gm/l
5	GLYCINE **NH_2CH_2COOH** (in gram/liter)	7	70°C; 30 min	6.74	
6	BORIC ACID **H_3BO_3** (in gram/liter)	2	------	-----	
7	Temperature	70° C-72° C	30 minutes		
8	pH	6.8 to 6.9	--------		
9	Time	30-40 minutes			

Optimum Composition of eNi bath (Bath II):

Nickel Chloride, $Nicl_2.6H_2O$ – 15 gram per liter

Sodium Hypophosphite, $NaH_2PO_2H_20$– 14 grams per liter

Acetic Acid, CH_3COOH – 22 ml per liter

DL-Malic Acid, CH_2 (COOH). CH (OH). COOH-18 grams per liter

Glycine, NH_2CH_2COOH – 7 grams per liter

Boric Acid, H_3BO_3 -2 grams per liter

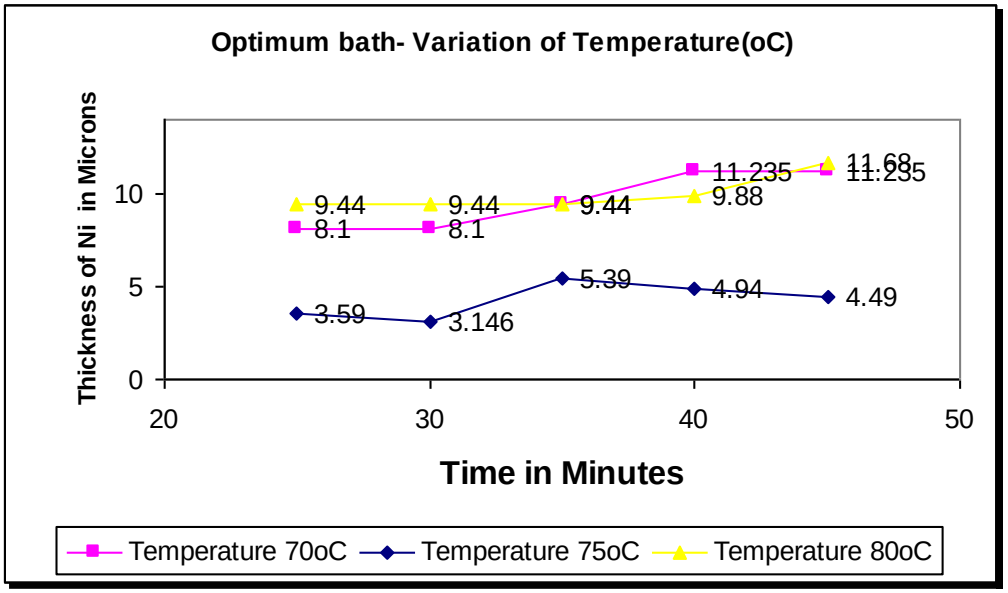
pH – 6.8 to 6.9 (Adjusted with NaOH & Hcl)

Temperature – 70 to 72 ° C

Thickness: 6.74 to 9.0 microns of Ni in 30 minutes

Time- 30 to 35 minutes

Fig.14: Variation of Temperature in Optimum Bath-II



Note: Optimum temperature of 80°C gives 9.44 microns of Nickel in 25 minutes, in the Optimum composition of bath, given below:

Final (optimum) Composition of eNi bath at 80 ° C (after study on temparature:

Nickel Chloride, $Nicl_2 .6H_2O$ – 15 gram per liter

Sodium Hypophosphite, $NaH_2PO_2H_20$– 14 grams per liter

Acetic Acid, CH_3COOH – 22 ml per liter

DL-Malic Acid, CH_2 (COOH). CH (OH). COOH-18 grams per liter

Glycine, NH_2CH_2COOH – 7 grams per liter

Boric Acid, H_3BO_3 -2 grams per liter

pH – 6.8 to 6.9 (Adjusted with NaOH & Hcl)

Temperature – 80 to 82 ° C to get 9.44 microns of Nickel

Time- 25 to 30 minutes

This bath was prepared & used for 12 months to verify & establish the results and it was consistent in giving the thickness of 8-9 microns of Nickel at 80 ° C in 25-30 minutes.

Composition of Nickel Deposit:

The deposited Nickel was subjected to EDAX analysis to know the composition. The results are as shown in Fig15 & 16. Inclusion of Phosphorus is clearly seen in EDAX plots. The deposit contains 12.23 to 13.74% of Phosphorus.

Fig.15. EDAX Analysis of Composition of eNickel deposit

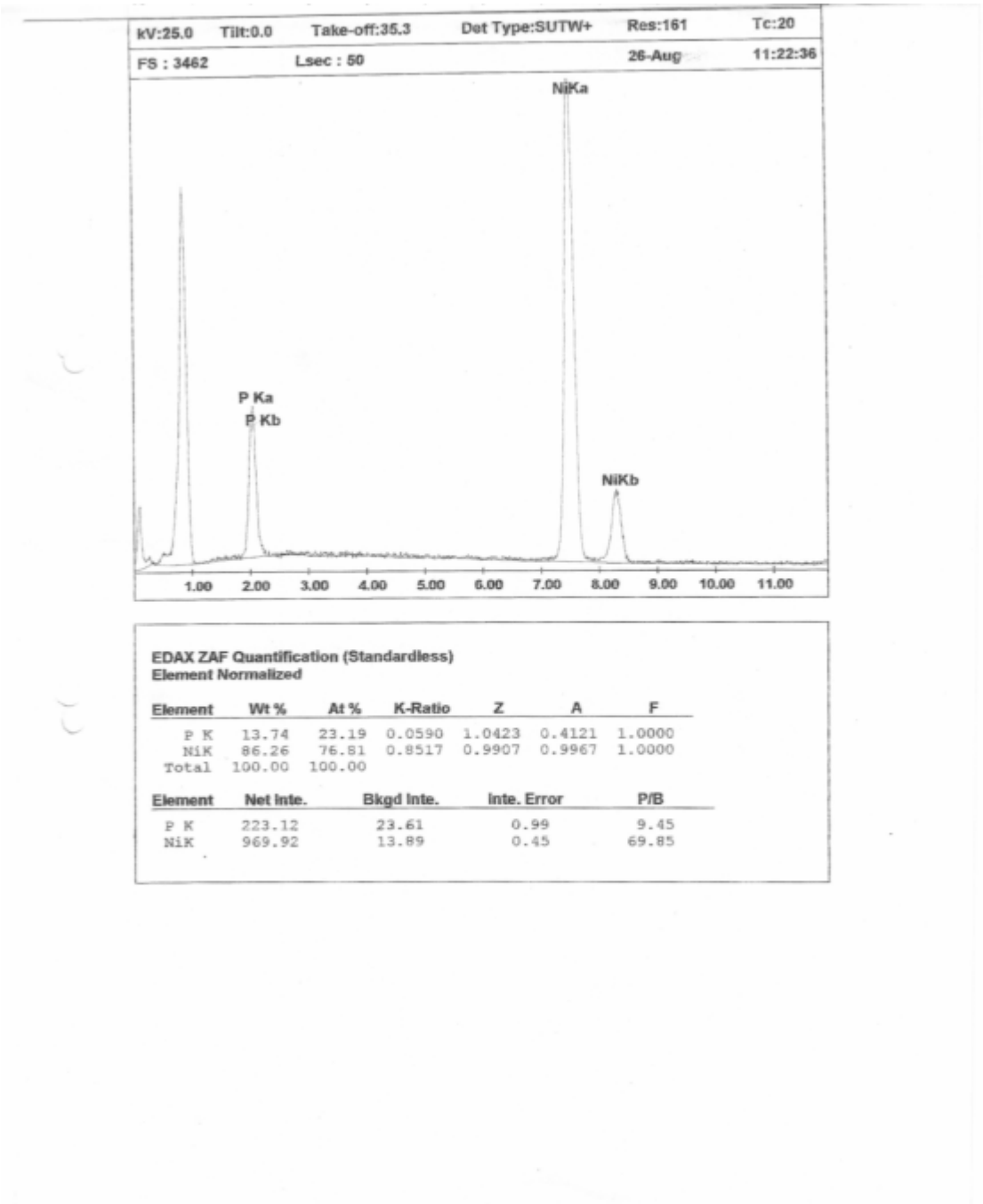
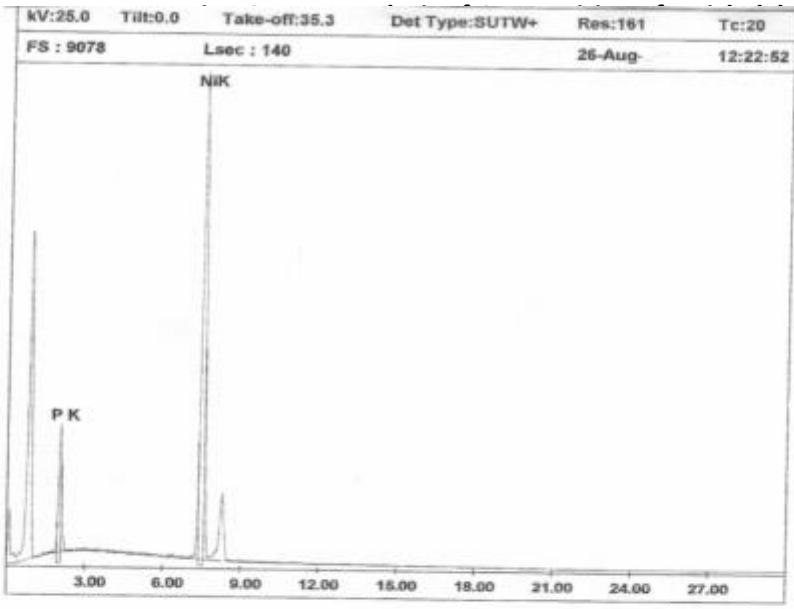


Fig.16:EDAX analysis of composition of eNickel Deposit



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
P K	12.23	20.89	0.0520	1.0431	0.4076	1.0000
NiK	87.77	79.11	0.8678	0.9917	0.9970	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
P K	179.82	20.80	0.66	8.65
NiK	904.10	13.18	0.28	68.60

These optimum results are as depicted in Table.3

Table.3: Depiction of optimum composition of eNi Bath-III

at optimum temperature of 80°C to 82°C

No	Chemical constituents of Electro less Nickel Bath	Grams/liter or ml/liter	Optimum Condition	Thickness in microns	Remarks
1	NICKEL CHLORIDE **$NiCl_2 .6H_2O$** (in gram/liter)	15	70°C; 30 min	9.0	Very Good
2	SODIUM HYPOPHOSPHITE **$NaH_2PO_2.H_2O$**(in gram/liter)	14	70°C; 30 min	7.19	Good
3	ACETIC ACID **CH_3COOH** (in ml/liter)	22	70°C; 30 min	7.0	80°C;30 min: 8 microns of Ni at 19 ml/l
4	DL-MALLIC ACID **$CH_2(COOH).CH(OH)-COOH$** (in gram/liter)	18	70°C; 30 min	9.0	80°C;30 min: 11microns of Ni at 15 gm/l Very Good
5	GLYCINE **NH_2CH_2COOH** (in gram/liter)	7	70°C; 30 min	6.74	Retards the speed
6	BORIC ACID H3BO3 (in gram/liter)	2	------	-----	
7	Temperature	80°C - 82°C	30 minutes		
8	pH	6.8 to 6.9	--------		
9	Time	30-40 minutes			

This formulation is much useful for large scale production of Electro less Nickel plating in rack and barrel plating of auto and industrial components.

Properties of eNi deposits obtained:

1. Plating thickness ranges from of 8.5 to 9 microns, obtained in 25 to 30 minutes. Thickness was checked by weight gain method and verified by x-ray fluorescence thickness test equipment.

2. The phosphorus co-deposited is 12.23 to13.74 %.
Further the P content in the deposit may be reduced by way of change in sodium hypophosphite content in the solution.

3. Baking or heat treatment after plating has resulted in hardness as high as 70 Rc.

4. Salt Spray Corrosion Test (1000 hours for high phosphorous containing eNi deposits; 250 hours for mid-phosphorous containing eNi deposits)

5. Mechanical Wear:

The abrasion resistance of electro less nickel is very good in lubricated wear situations and the wear index numbers of different deposits are as in Table.4 obtained from the Taber Abrader/ Abraser.

Table.4: Comparison of wear index numbers from Taber Abrader:

No	Type of Deposit	Heat treatment Temperature C	Wear Index Number	Remarks
1	Electro less Nickel (as deposited)	-----	9.6	Good
2	Electro less Nickel	300	4.4	
3	Electro less Nickel	500	2.7	
4	Electro less Nickel	650	1.3	
5	Electrolytic Nickel from Watts Bath (as deposited)	-----	14.7	
6	Electrodeposited Hard Chromium (as deposited)	------	2.0	

Advantages with this bath are:

1. Rack and Barrel plating are possible
2. Masking is possible for selective surface plating. Masking was performed by either screen printing with ink, peelable solder mask film or by photo-printing.
3. The deposited eNi contains 12.23-13.74 % P which is highly recommended for hardness requirement of the deposit after heat treatment.
This is achieved by heat treatment of the deposited eNi at C for 1.5 to 2 hrs.
4. Bath may easily be maintained and restarted after dummy plating at any time, after adding the chemicals after analysis and adjusting pH to working pH.

Maintenance of eNi Bath:
Analysis Methods

The bath contents may easily be maintained by periodic analyses and addition of chemical ingredients of the bath. The critical constituents to be analysed are 1) Nickel or Nickel chloride and 2) Sodium hypophosphite, in this case.

1.Nickel Concentration:

Reagents Required:

a. Conc. Ammonia A.R.

b. Murexide indicator: Grind 0.2 gm of murexide A.R with 100 gms of Sodium chloride A.R in a mortar to a fine powder and store in a clean glass or polyethylene bottle; label properly with contents and date.

c.0.05 M EDTA $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$

Disodium salt of Ethylene Diamine Tetra Acetic acid standard solution:

Dissolve 10 gms of Sodium Hydroxide-NaOH A.R. in 200 ml of DI water placed in 1 litre volumetric flask. Weigh 18.6 gms of disodium ethylene diamine tetra acetic acid EDTA A.R. and record the exact weight. Transfer this to the flask and stir to dissolve fully. Dilute to the mark with DI water, mix well and transfer this to a clean polyethylene container, label it with molarity of EDTA with date.

M of EDTA = weight of EDTA / 372

Procedure:

1. Pipette 2 ml of plating solution in a 250 ml capacity Erlenmeyer flask.

2. Add 100 ml of DI or distilled water.

3. Add 10 ml of conc. Ammonia.

4. Add 0.2 gram of Murexide indicator.

5. Titrate with 0.05 M EDTA standard solution with swirling the flask while adding the EDTA solution. Color change is from yellow to purple end point.

6. Note down the volume of EDTA consumed.

Calculation:

Amount of Nickel present = ml of EDTA solution X Molarity of EDTA X 29.35 = grams /liter --"A"

(Note: Atomic weight of Ni = 58.69 and Molecular weight of $Nicl_2.6H_2O$ = 237.70)

Amount of $Nicl_2.6H_2O$ present: = "A" (237.70 / 58.69) = "A' x 4.05 = grams / liter

2. Nickel Chloride $Nicl_2.6H_2O$

Reagents required:

a.20% Ammonium acetate-CH_3COONH_4: Dissolve 200 gms of ammonium acetate CH_3COONH_4, in 1000 ml of DI water in a clean glass beaker, by stirring. Store it in a glass or polyethylene bottle; label it with contents and date.

b. Sodium chromate-Na_2CrO_4 indicator: Add 2.0 gms of Sodium chromate in 100 ml of DI water and dissolve it fully by stirring. Transfer it and store in a clean polyethylene bottle, label with contents and date.

c. 0.1 N Ag NO_3 (silver nitrate) standard solutions: T ake 700 ml of distilled water in a 1 liter volumetric flask and add 5 ml of Conc. HNO_3. A.R. Add 17 gms of silver nitrate Ag NO_3, stir well to dissolve completely. Dilute to the mark with distilled water, after mixing well. Store in an amber colored glass bottle, label with concentration and date. This has to be standardized with 0.1 N KCl (Potassium chloride), as below:

1. Pipette out 25 ml of 0.1N KCl into an Erlenmeyer flask

2. Add 25 ml of DI water and 5 ml of 20% ammonium acetate

3. Add 1 ml of sodium chromate indicator.

4. Titrate with silver nitrate with swirling till the precipitated silver chromate turns pink.

Normality of Ag NO_3 = ml of KCl X Normality of KCl / ml of Ag NO_3

Procedure for $Nicl_2.6H_2O$:

1. Pipette 5 ml of plating solution in a 250 ml capacity Erlenmeyer flask.

2. Add 100 ml of De ionized or distilled water.

3. Add 10 ml of 20% ammonium acetate.

3. Add 2 ml of sodium chromate indicator solution.

4. Titrate with 0.1 N Ag NO_3 standard solution to a permanent faint pink end point, due to the formation of Silver chromate. Ag_2CrO_4.

5. Note down the volume of 0.1 N Ag NO_3 consumed.

Calculation:

ml Ag NO_3 X Normality of Ag NO_3 X 23.75 = grams / litre of $Nicl_2.6H_2O$ --"B"

Note: Molecular weight of $Nicl_2.6H_2O$ = 237.70; Atomic weight of Ni = 58.69

2.Sodium Hypophosphite Concentration:

Reagents Required:

a) Concentrated hydrochloric acid, L.R. or A.R. Grade

b) 1% Starch indicator solution:
Make slurry of 3 gm of soluble starch in a small volume of cold water and add this to about 300 ml of boiling water and stir well to mix thoroughly. Boil for 3 to 5 minutes. Cool to room temperature and store it in a clean glass or polyethylene bottle with proper label with date. A pinch of mercuric oxide may be added to prevent mold growth.
c) 0.1 N Iodine (standard volumetric solution):
Dissolve 40 grams of KI (Potassium Iodide) in 30 ml of Distilled water in a 250 ml beaker. Weigh accurately 12.69 grams of Iodine crystals and dissolve in the above KI solution by stirring till it completely dissolves. Transfer this solution into a 1000ml capacity volumetric flask and make it up to the mark with distilled or DI water. Transfer this solution in a brown coloured bottle and keep in darkness inside the desk after labelling with the concentration of iodine solution with grams per litre and date.

Standardize this solution with 0.1 N As_2O_3 solution as follows:

Standardization of I_2 solution:
0.1N.As_2O_3 solution:
Take 30 grams of Arsenic oxide in a weighing bottle. Heat this at 110^oC for 2 hours. Cool this in a desiccator. Add 4 grams of KOH in 50 ml of DI water placed in a 250 ml beaker. Dissolve this by stirring. Weigh out 4.9 to 5.0 grams of As_2O_3 and record the exact weight. Add and dissolve this in the above KOH solution, which is heated to luke warm temperature. When completely dissolved carefully add 50% H_2SO_4 solution drop-wise, until the solution is neutral to phenolphthalein (dissolve 1 gram of phenolphthalein in 100 ml of isopropyl alcohol and store it in a dropper bottle) indicator and become colourless. Cool and transfer it to a 1000 ml capacity volumetric flask and make it up to the mark with distilled or DI water. Transfer and store this in a glass or polyethylene bottle with labelling indicating concentration, grams per litre and date.
Procedure:
Pipet 25.0 ml of As_2O_3 solution to 250 ml capacity Erlenmayer flask and add about 2 gms of sodium bicarbonate,50 ml of distilled or D.I water and 2 to 3 drops of 1% starch indicator. While swirling, titrate with iodine to first blue end point that remains at least for 30 to 60 seconds.
N = ml of As_2O_3 X N of As_2O_3 / ml of I_2.

d) 0.1 N $Na_2S_2O_3.5\ H_2O$- Sodium thiosulphate solution:

Dissolve 24.8 grams of $Na_2S_2O_3.5\ H_2O$ in 700 ml of previously boiled and cooled distilled or DI water in 1000 ml volumetric flask. Stir, dissolve and dilute it to make up to the mark. Mix well and transfer it to a glass or polyethylene bottle. Label it with normality and gm/L of $Na_2S_2O_3.5\ H_2O$ with date and keep.

Standardize 0.1 N $Na_2S_2O_3$ with 0.1N KIO_3 solution as follows:

Preparation of 0.1 N KIO_3 solution:

Pipet 25.0 ml of KIO_3 Potassium Iodate standard solution in a 250 ml Erlenmeyer flask. Add 30 ml of distilled or DI water and 1 gm of KI-Potassium iodide and 10 ml of 25% H_2SO_4 solution. Titrate with swirling with the above O.1 N Sodium thiosulphate solution to a pale yellow colour. Add 2 ml of starch reagent and continue titration until blue colour disappears.
Calculation: N of $Na_2S_2O_3$= ml of KIO_3 x N of KIO_3 / ml of $Na_2S_2O_3$
Preparation of Standard KIO_3 solution:
Dry about 30 gms of KIO_3 AR in a weighing bottle at 180^oC for 2 hours and cool it in a desiccator. Dissolve 1 gm of NaOH and 10 gm of KI in 200ml of distilled water in a 500 ml beaker. Weigh out 3.5 gms of KIO_3 and add it to the beaker and stir to dissolve. Transfer this solution to a 1000ml volumetric flask and make it up to the mark. Store this in a glass bottle and label it with N. of KIO_3 and gms / L of KIO_3.
N of KIO_3 = weight of KIO_3 / 35.67

Procedure for analysis of Sodium Hypophosphite :

1. Pipette 5.0 mls of bath (previously cooled) into an iodine flask.
2. Add 50mls concentrated hydrochloric acid.
3. Pipette 50.0mls 0.1 N iodine into flask. Stopper flask and shake.
4. Leave in a dark cupboard for 30 minutes.
5. Titrate with 0.1 N sodium thiosulphate to a pale straw colour.
6. Add a few drops of freshly prepared 1% starch indicator solution and continue titration to a clear end point.
7. Record ml of thiosulphate.

Calculation:
g/L sodium hypophosphite = {(ml of I_2 X N of I_2) - (ml of thio x N of thio)} x 10.6

Abbreviations used:

DI = De-ionized water; A.R. = Analytical Reagent; wt = weight; gm(s) = gram (s); ml = milliliter; N = Normality; M = Molarity; gpl or gms/L = grams per liter; mpl or ml/L = milliliter/Liter.

Maintenance of working solution:

Once analysed the lesser amount may be compensated by adding the solution of Nickel chloride and Sodium hypophosphite.

Stock solution A:
Dissolve the following chemicals in 10 litres of DI water and store in 2 X 5 litres capacity PVC carboys with lid in a cool place with label as Solution “A” with date:
1. Nickel chloride- 150 gms.
2. DL- Malic Acid- 180 gms

3. Boric Acid - 20 gms

Stock solution B: Dissolve the following chemicals in 10 litres of DI water and store in 2 X 5 litres capacity PVC carboys with lid in a cool place with label as Solution "B" with date:

1. Sodium hypophosphite – 140 gms
2. Acetic Acid – 220 ml
3. Glycine -- 70 gms

The stock solutions "A" and "B" can be kept separately for 3 to 6 months if properly stored with lid.

Solution "A" and "B" to be added as per analysis report, after removing the load. Adjust the solution to the required pH.

Not advisable to add chemicals when the load or job is in the tank, which may lead to rough deposits of eNi and or spontaneous precipitation of Nickel as sponge, at high temperature of working bath.

Precautions to be taken before shutting down and start up of the working bath:

1. Before shutting down, cool the solution below the working temperature, say 50^{o} to 55^{o}C and add 100 ml of Glycine solution (1gm per liter of Glycine stock solution) to the working electro less Ni bath to avoid the possible auto-deposition of Ni on the walls of the process vessel, pipes, cooling coils etc. With this precaution, the bath can easily be maintained for more than 100 days.

2. Reduce the pH below the working pH before shutting down the bath.

3. Always check the pH by electrometric method by using a suitable pH meter.

4. When the solution is not in use, it has to be covered with a suitable lid and do not allow dust particles falling in the bath.

5. No job or dummy should be left unattended in the bath, while shutting down.

6. For better results and stable life of bath, the solution may be cooled and transferred to a clean storage tank with mild air agitation, to store when the bath is idle.

7. No traces of activator should enter the bath.

8. Before start of the bath, analyze the Ni content & sodium hypophosphite content and pH. As per analytical report, add required Nickel chloride solution, Sodium hypophosphite solution, adjust pH with 10% NaOH or 20% Hcl solution and heat the solution to working temperature.

9. Do not add maintenance chemical solution when the job is inside the solution. Remove the job and add necessary chemical solutions with stirring to maintain the bath.

10. Keep the hanging hooks and jigs clean; strip them and clean before loading the job.

11. Do not carry drag out solution along with the job to the working solution. This is to maintain pH of the working solution.

12. Check the pH of solution for every batch of plating and if required adjust it with NaOH or hydrochloric acid solution. While adding 10% NaOH solution, stir well and do not

allow the formation of nickel precipitate of $Ni(OH)_2$;this may dissolve by continuous stirring with agitation.

13. Start plating on the dummy for 20-25 minutes and then the regular job may be loaded for eNi. plating.

14. Mild air-agitation with rod movement are recommended.

Conclusion:

The addition of chemicals and life of bath wholly depend on the volume of production taken out and the careful maintenance of the bath after chemical analyses with at most care of freedom from dust and dirt falling in the bath leading to unwanted “seeding” phenomenon.

When the bath is not in use, reduce the working pH, and keep it covered with lid.

This formulation is much useful for large scale production of eNi plating of automobile, electrical, electronic and mechanical parts and components.

Tiny components- washers, screws etc., may easily be eNi plated by barrel plating and bigger components-bumpers, mechanical parts of machnes by rack plating.

About Author:

Dr. Krishna Ram Thoguluva Seshadri is an expert with 4 decades of experience in Electroplating, Metal Finishing, Anodizing, Surface finishing, Electro less Copper, Electro less Nickel Plating, ENIG for PCBs, Immersion Tin, Immersion Silver etc. He is presently engaged as specialist consultant in PCB, Plating and Surface Finishing in India and South Africa.

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