

Chapter One

1. Introduction and Literature review

1.1: Nickel Chemistry

1.1.1 : History of nickel

Nickel had been in use for centuries before its actual discovery and isolation. As far back as 3500 BC Syrian bronzes contained a small amount of the element. In China 235 BC, coins were made from nickel. However there was no real documentation of the element until thousands of years later. In the 17th century, German miners discovered a red colored ore they believed to contain copper. They discovered upon analysis that there was no copper but that a useless, smelly material was actually present. Thinking the ore was evil they dubbed it "Kupfernickel" or Old Nick's Copper, which meant false or bad copper. Swedish scientist Baron Axel Frederich Cronstedt in 1751 finally isolated nickel from an ore closely resembling kupfernickel. Hence, he named this new element after the traditional mineral. At the time of its discovery nickel was thought to be useless but as its valuable properties came to light the demand for the metal increased dramatically. The usefulness of nickel as a material in alloys was eventually discovered as the strength, corrosion resistance and hardness it adds to other metals came to be appreciated. In the 1800s, the technique of silver plating was developed with a nickel-copper-zinc alloy being utilized in the process. Today, stainless steel, another nickel containing alloy, is one of the most valuable materials of the 20th century. (Lancashire, 2006)

1.1.2: Occurrence of nickel

Nickel is the earth's 22nd most abundant element and the 7th most abundant transition metal. It is a silver white crystalline metal that occurs in meteors or combined with other elements in ores. Two important groups of ores are: Laterites: oxide or silicate ores such as garnierite, $(\text{Ni, Mg})_6 \text{Si}_4\text{O}_{10} (\text{OH})_8$ which are predominantly found in tropical areas such as New Caledonia, Cuba and Queensland.

1. Sulphides: these are ores such as pentlandite, which contain about 1.5%, nickel associated with copper, cobalt and other metals. They are predominant in more temperate regions such as Canada, Russia and South Africa.

2. Canada is the world's leading nickel producer and the Sudbury Basin of Ontario contains one of the largest nickel deposits in the world. (**Lancashire, 2006**)

1.1.3: Extraction of Nickel

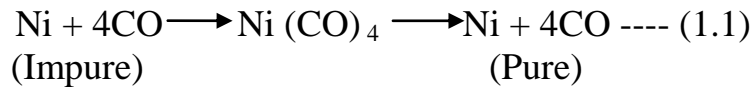
In 1899 Ludwig Mond developed a process for extracting and purifying nickel. The so-called "Mond Process" involves the conversion of nickel oxides to pure nickel metal. The oxide is obtained from nickel ores by a series of treatments including concentration, roasting and smelting of the minerals. (**Lancashire, 2006**)

In the first step of the process, nickel oxide is reacted with water gas, a mixture of H_2 and CO , at atmospheric pressure and a temperature of $50\text{ }^\circ\text{C}$. The oxide is thus reduced to impure nickel. Reaction of this impure material with residual carbon monoxide gives the toxic and volatile compound, nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$. This compound decomposes on heating $230\text{ }^\circ\text{C}$ to give pure nickel metal and CO , which can then be recycled. The actual temperatures

and pressures used in this process may vary slightly from one processing plant to the next. However the basic process as outlined is common to all. **(Lancashire, 2006)**

The process can be summarized as follows:-

50°C 230°C



1.1.4: Properties of nickel

Nickel is a hard silver white metal, which occurs as cubic crystals. It is malleable, ductile and has superior strength and corrosion resistance. The metal is a fair conductor of heat and electricity and exhibits magnetic properties below 345°C. Five isotopes of nickel are known. In its metallic form nickel is chemically unreactive. It is insoluble in cold and hot water and ammonia and is unaffected by concentrated nitric acid and alkalis. It is however soluble in dilute nitric acid and sparingly soluble in dilute hydrochloric and sulphuric acids. **(Lancashire, 2006)**

Nickel has a unique combination of properties:

- High melting point, 1453°C
- Adherent oxide film
- Resists alkalis
- Ductile
- Alloys readily - as solute and solvent
- Magnetic at room temperature
- Deposited by electroplating
- Catalytic

Nickel - the versatile metal:

- >60% used in stainless steel
- high-nickel corrosion- and heat-resisting alloys
- other alloys - strength, corrosion resistance, special physical and magnetic properties
- plating - decorative and engineering uses

- Batteries
- chemicals

1.1.5: Nickel Compounds

Nickel is known primarily for its divalent compounds since the most important oxidation state of the element is +2. However, certain compounds in which the oxidation state of the metal is between -1 to +4. Blue and green are the characteristic colours of nickel compounds and they are often, hydrated. Nickel hydroxide usually occurs as green crystals that precipitate when aqueous alkali is added to a solution of a nickel (II) salt. It is insoluble in water but dissolves readily in acids and ammonium hydroxide. Nickel oxide is a powdery green solid that becomes yellow on heating. It is difficult to prepare this compound by simply heating nickel in oxygen and it is more conveniently, obtained by heating nickel hydroxide, carbonate or nitrate. Nickel oxide is readily soluble in acids but insoluble in cold or hot water.

Nickel dihalides are yellow to dark brown in colour. They can be prepared the element except NiF_2 which is best prepared from reaction of F_2 on NiCl_2 at 350°C . They are water soluble and crystallize as the hexahydrate $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ However, NiF_2 is only slightly soluble in water from which the trihydrate

crystallizes. The only nickel trihalide known to exist is an impure specimen of NiF_3 . (Lancashire, 2006)

Table: 1.1: Properties of nickel halide compound

Formula	Colour	Melting Point	Conductivity (BM)	Structure
NiF_2	Yellow	1450	2.85	tetragonal rutile
NiCl_2	Yellow	1001	3.32	CdCl_2
NiBr_2	Yellow	965	3.0	CdCl_2
NiI_2	Black	780	3.25	CdCl_2

1.1.6: Nickel complexes

Nickel (II) ions form many stable complexes as predicted by the Irving Williams series. Whilst there are no other important oxidation states to consider, Ni (II) ion exists in a wide variety of cyanide (CN's) which complicates its coordination chemistry. For example, for CN=4 both tetrahedral and square planar complexes can be found. For CN=5 both square pyramid and trigonalbipyramid complexes are formed. The phrase "anomalous nickel" has been used to describe this behavior and the fact that equilibria often exist between these forms.(Lancashire, 2006)

Some examples include:

- (a) Addition of ligands to square planar complexes to give 5 or 6 coordinates species
- (b) monomer/polymer equilibria

(C) square-planar/ tetrahedron equilibria

(d) trigonal-bipyramid/ square pyramid equilibria.

(a) Substituted acetate(acacs) reacts with Ni^{2+} to give green dihydrates (6 coordinate). On heating, the two coordinated water groups are generally, removed to give tetrahedral species. The unsubstituted acac complex, $\text{Ni}(\text{acac})_2$ normally exists as a trimers. Lifschitz salts containing substituted 1,2-diaminoethanes can be isolated as either 4 or 6 coordinate species depending on the presence of coordinated solvent.

(b) $\text{Ni}(\text{acac})_2$ is only found to be monomeric at temperatures around 200°C in non-coordinating solvents such as n-decane. 6-coordinate monomeric species are formed at room temperature in solvents such as pyridine, but in the solid state $\text{Ni}(\text{acac})_2$ is a trimer, where each Ni atom is 6-coordinate. Note that $\text{Co}(\text{acac})_2$ actually exists as a tetramer.

(c) Complexes of the type NiL_2X_2 , where L are phosphines, can give rise to either tetrahedral or square planar complexes. It has been found that: $\text{L}=\text{P}(\text{aryl})_3$ are tetrahedral $\text{L}=\text{P}(\text{alkyl})_3$ are square planar for $\text{L}=\text{mixed aryl and alkyl phosphines}$, both stereochemistries can occur in the same crystalline substance. The energy of activation for conversion of one form to the other has been found to be around 50kJ mol.

Ni^{2+} reacts with cyanide(CN^-) to give $\text{Ni}(\text{CN})_2 \cdot n\text{H}_2\text{O}$ (blue-green) which is dehydrated on heating at $180\text{-}200^\circ\text{C}$ to yield $\text{Ni}(\text{CN})_2$. Reaction with excess KCN gives $\text{K}_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (orange crystals) which can be dehydrated at 100°C . Addition of strong concentrations of KCN produces red solutions of $\text{Ni}(\text{CN})^-$. The crystal structure of the double salt prepared by addition of $\text{Cr}(\text{en})^{3+}$ to $\text{Ni}(\text{CN})^-$

showed that two types of Ni stereochemistry were present in the crystals in approximately equal proportions. (**Lancashire, 2006**)

1.1.7: Uses of Nickel and its Compounds

The primary use of nickel is in the preparation of alloys such as stainless steel, which accounts for approximately 67% of all nickel industrial use. The greatest application of stainless steel is in the manufacturing of kitchen sinks but it has numerous other uses as well. Other nickel alloys also have important applications. An alloy of nickel and copper for example is a component of the tubing used in the desalination of sea water. Nickel steel is used in the manufacture of armour plates and burglar proof vaults. Nickel alloys are especially, valued for their strength, resistance to corrosion as in the case of stainless steel. Electroplating is another major use of the metal. Nickel plating is used in protective coating of other metals. In wire form, nickel is used in pins, staples, jewellery and surgical wire. Finely divided nickel catalyses the hydrogenation of vegetable oils. Nickel is also used in the colouring of glass to which it gives a green hue. (**Lancashire, 2006**)

1.1.8: Other applications of nickel:

- Coinage
- Transportation and construction
- Petroleum industry
- Machinery and household appliances
- Chemical industry.

Nickel compounds also have useful applications. Ceramics, paints and dyes, electroplating and preparation of other nickel compounds are all applications of these compounds. Nickel oxide for example is used in porcelain painting and in electrodes for fuel cells. Nickel acetate is used as a mordant in the textiles industry. Nickel carbonate finds use in ceramic colours and glazes.

1.1.9: Nickel Applications and uses:

Today, nickel-containing materials are used in buildings, water supply systems, energy industry, chemical industry, transport industry, electronic components, and medical equipment.(**Bradley, 2011**)

1.1.10: Nickel Advantage

a) Nickel in Stainless Steels:

- Versatility
- Reliability
- Corrosion resistance
- Hygienic
- High quality of 18/8 and 18/10 grades
- Formability
- Weldability
- Availability
- Many finishes
- Non-magnetic
- Lasting value and high intrinsic value as scrap
- Recyclability

b) Nickel as an alloying element:

- Tough low alloy steels
- Ductile and wear-resistant cast irons
- Stainless steels
- Corrosion resistant, high nickel alloys
- Superalloys for gas turbines
- Copper-nickel alloys for marine applications
- Magnetic and controlled expansion alloys
- Shape memory alloys

c) Nickel Plating:

- An early application of nickel
- Electrolytic and chemical deposition
- Provides luster, uniformity and corrosion protection
- Substrate for decorative coatings
- Engineering coatings e.g. for wear resistance
- Electroforming

1.2: Electro Chemical Deposition

1.2.1: What is Electro deposition?

Electro deposition (E.D) is the process of coating a thin layer of one metal on top of a different metal to modify its surface properties.

The process is conducted to achieve the desired electrical and corrosion resistance, reduce wear & friction, improve heat tolerance and for decoration. E.D is a surface coating method that forms an adherent layer of one metal on another. **(Dini, 1993)**

1.2.2: Electroplating Applications:

- Printed circuitry and electrical contacts
- General engineering components
- Gold-Silver wares and Jewelry
- Musical Instruments and Trophies
- Soft metal gaskets
- Anti-seize bearings
- Decorative door, light & bathroom fittings
- Production of micro parts for MEMS

Understanding the relationships between microstructure and mechanical properties is one of the main goals of metallurgy and materials science.

This allowed the tailoring of materials properties by varying the composition and the structure. The fascinating field of electro deposition allows one to tailor the surface properties of a material or to form the entire part by electroforming.

1.2.3: Faraday's Law:

The amount of electrochemical reaction that occurs at an electrode is proportional to the quantity of electric charge (Q) passed through the cell.

The weight of a product of electrolysis is W,

Then

$$W = ZQ \text{ (Z is the electrochemical equivalent)}$$

$$\text{Since } Q = It,$$

$$\text{It follows that } W = Zit$$

Where:

- $W \equiv$ weight of product in grams
- $Z \equiv$ electrochemical equivalent
- $Q \equiv$ the quantity of electric charge in Coulombs
- $I \equiv$ electric current in ampere
- $T \equiv$ time in min
- Production of one gram equivalent of a product at the electrode (W_{eq}) in a cell needs 96487 Coulombs
- The electrochemical equivalent of a metal $Z(M)$ is the weight in grams produced or consumed by one coulomb of charge. **(Dini, 1993)**

1.2.4: Influencing factors in Electro deposition:

Factor that influence E.D are:

1. Current density
2. The nature of the anions or cations in the solution
3. Bath composition and temperature
4. Solution concentration
5. The presence of impurities
6. Physical and chemical nature of substrate surface

- **Current Efficiency:**

Current efficiency (C.E) is the ratio between the actual amounts of metal depositing (or dissolved) M_a to that calculated theoretically from Faraday's law M_t in %.

$$\text{C.E.} = (M_a / M_t) \times 100$$

C.E. indicates the fraction of total current that generates desired products.

The overall amount of chemical change produced by a given quantity of

electricity can be determined. Cathode & anode efficiencies - In an ideal situation, cathode efficiency will be equal to anode efficiency.(Dini, 1993)

- **Cathodic Efficiency:**

The ratio of the weight of metal actually deposited to the weight that would have resulted if all the current had been used for depositing it is called the cathode efficiency.(Dini,1993)

1.2.5: Electrodeposition of nickel

Nickel electroplating is a commercially important and versatile surface-finishing process. Its commercial importance may be judged from the amount of nickel in the form of metal and salts consumed annually for electroplating, now roughly 100, 000 metric tons worldwide, as well as its versatility from its many current applications (DiBari 1996). The applications of nickel electroplating fall into three main categories: decorative, functional, and electroforming.

In decorative applications, electroplated nickel is most often applied in combination with electrodeposited chromium. The thin layer of chromium was first specified to prevent the nickel from tarnishing. It was originally deposited on top of a relatively thick, single layer of nickel that had been polished and buffed to a mirror-bright finish. Today decorative nickel coatings are mirror bright as deposited and do not require polishing prior to chromium plating. Multilayered nickel coatings outperform single-layer ones of equal thickness and are widely specified to protect materials exposed to severely, corrosive conditions. The corrosion performance of decorative, electroplated nickel plus chromium coatings has been further improved by the development of processes by which the porosity of chromium can be varied and controlled on a microscopic scale (micro discontinuous chromium). Modern multilayered nickel coatings in combination

with micro discontinuous chromium are capable of protecting steel, zinc, copper, aluminum, and many other materials from corrosion for extended periods of time. The complexity of modern-day nickel plus chromium coatings is more than offset by the greatly, improved corrosion resistance that has been achieved without significantly, increasing coating thickness and cost.

There are many functional applications where decoration is not the issue. Instead, nickel and nickel alloys with matt or dull finishes are deposited on surfaces to prevent corrosion resistance and wear resistance or modify magnetic and other properties. The properties of nickel electrodeposits produced under different conditions of operation are of particular interest in this connection.

The many current applications of nickel electroplating are the result of developments and improvements that have been made almost since the day the process was discovered. This is evident in the following retrospective on the development of nickel electroplating solutions as well as in subsequent sections that deal with basics, decorative electroplating, functional applications and deposit properties, nickel electroforming, nickel anode materials, quality control, and pollution prevention.**(Philos.1837);(Shore, 1844)**

1.2.6: Retrospective on nickel Electroplating Solutions:

Bottger (1843) developed the first practical formulation for nickel plating, an aqueous solution of nickel and ammonium sulfates, but earlier references to nickel plating can be found. Bird(1837) apparently deposited nickel on a platinum electrode from a solution of nickel chloride or sulfate, and Shore(1844) patented a nickel nitrate solution**(Philos.1837) (Shore, 1844)**. The solution developed by Bottger remained in commercial use for 70 years, however, and he is acknowledged to be the originator of nickel plating.

Dr. Isaac Adams, Jr., a medical doctor educated at Harvard University and at the École de Médecine in Paris, was one of the first to commercialize nickel plating in the United States, and his patented process gave his company a virtual monopoly in commercial nickel plating from 1869 to 1886. His patent covered the use of pure nickel ammonium sulfate. Although Adams's solution was similar to Bottger's, his emphasis on operating the bath at neutral pH was undoubtedly vital for controlling the quality of the nickel deposited, since excessive amounts of ammonia would tend to lower cathode efficiency and embrittle the deposit. Largely as a result of the publicity generated by Adams, nickel plating became known worldwide, and by 1886, the annual consumption of nickel for plating had grown to about 135 metric tons. **(Dubpernel, 1959; Dennis and Such, 1993)**

Remington (1868), an American residing in Boston, attempted to market a nickel ammonium chloride electroplating solution, but perhaps of greater significance, in view of subsequent developments, were his attempts to use small pieces of electrolytic nickel as an anode material in a platinum anode basket.

Weston (1878) introduced the use of boric acid and Bancroft (1906) was one of the first to realize that chlorides were essential to ensure efficient dissolution of nickel anode materials.

Professor Oliver P. Watts (1916) at the University of Wisconsin, aware of most of these developments, formulated an electrolyte in 1916 that combined nickel sulfate, nickel chloride, and boric acid and optimized the composition of the nickel electroplating solution. The advantages of his hot, high-speed formula became recognized and, eventually, led to the elimination of nickel ammonium sulfate and other proprietary solutions. Today, the Watts solution is widely applied,

and its impact on the development of modern nickel electroplating technology cannot be overstated.

1.2.7: Basics of nickel electroplating:

Nickel electroplating is similar to other electro deposition processes that employ soluble metal anodes; that is, direct current is made to flow between two electrodes immersed in a conductive, aqueous solution of nickel salts. The flow of direct current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with nickel. The nickel in solution is present in the form of divalent, positively charged ions (Ni^{2+}). When current flows, the positive ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni^0) at the cathode surface. The reverse occurs at the anode where metallic nickel is dissolved to form divalent, positively charged ions which enter the solution. The nickel ions discharged at the cathode are thus replenished by those formed at the anode. **(Crouch and Hendricksen, 1983)**

1.2.8: Decorative electroplating:

The technology of decorative nickel electroplating has been improved, continually, over the years due to the development of bright and semibright nickel plating solutions, multi layer nickel coatings, and micro discontinuous chromium. The major effect has been an increase in the corrosion resistance of decorative, electroplated nickel plus chromium coatings. In addition new and improved techniques for plating on plastics, aluminum alloys, and stainless steel have broadened the scope of decorative applications. **(Weil, 1981 ;Jousellin and Wiar, 1979)**

1.2.9: Bright Nickel Solutions

Modern bright nickel electroplating solutions employ combinations of additives, carefully formulated to produce bright deposits over a wide range of current density. The deposit have excellent leveling or scratch-filling characteristics, fair ductility, and low internal stress. Modern processes produce bright deposits in areas of low current density, permit use of high average current densities and bath temperatures, are less sensitive to metallic contaminants than some of the solutions first commercialized, permit continuous purification of the plating solution by filtering through activated carbon, and produce breakdown products that can also be removed by activated carbon treatment and are not sensitive to anode effects. Bright nickel electroplating solutions have similar compositions as the Watts nickel electrolyte included in Table 3.4. Because the exact formulations of commercial processes are proprietary, the recommendations of the suppliers of decorative nickel plating processes should be followed. **(Weil, 1981 ; Jousellin and Wiar, 1979)**

1.3: Quality control:

Process quality control involves maintaining the concentrations of the main constituents within specified limits; controlling pH, temperature, and current density; and maintaining the purity of nickel electroplating solutions. Product quality control includes eliminating coating defects, properly preparing substrates prior to electroplating, as well as conducting tests to verify that specified product requirements have been met. The basic nickel electroplating facts can be summarized in the following points:-

1.3.1: Process Control

Controlling the composition of the plating bath is one of the most important factors contributing to the quality of electrodeposited nickel. At the outset, the bath must be prepared to the specified composition, adjusted to the proper pH, and purified before use. Thereafter the composition and pH of the solution must be controlled within specified limits, and contamination by metallic, organic, and gaseous substances must be prevented.

Main Constituents The basic constituents of nickel electroplating solutions that are, regularly, controlled are the nickel metal content, the chloride concentration, pH, and the concentration of all additives. Nickel metal concentration is maintained between 60 and 80 g/L in most commercial applications. It is desirable to have a minimum of 25 g/L nickel chloride in the solution to promote anode corrosion except when sulfur-activated electrolytic nickel anode materials are used. Boric acid is the most commonly used buffer ingredient for nickel plating baths. Boric acid is effective in stabilizing the pH in the cathode film within the ranges normally required for best plating performance. It is available in a purified form and is inexpensive. Organic additives must be controlled within the limits specified by the suppliers of proprietary processes, and they must be replenished due to losses from drag-out, electrolytic consumption, and the effects of carbon filtration. **(Dini, 1993; Rosenstein and Hirsch, 1996)**

1.3.2: Controlling pH, Temperature, Current Density, and Water

Quality the pH of the nickel plating solution will rise during normal operation of the bath, necessitating regular additions of acid to maintain the pH within the prescribed limits. (A decrease in pH accompanied by a decrease in nickel ion concentration indicates that the process is not functioning properly.) In

Watts's solutions, sulfuric acid is added for pH adjustment; sulfamic acid is added to control the pH of nickel sulfamate solutions. The pH of nickel plating solutions should be measured frequently, and it is most of tendone by an electrometric method employing a glass electrode and a saturated calomel reference electrode.

The operating temperature has a significant effect on the properties of the deposits and should be maintained within specified limits ($\pm 2^{\circ}\text{C}$) of the recommended value. In general, most commercial nickel plating baths are operated between 40°C and 60°C . Inorganic, organic, and gaseous impurities, (Table 1.2) may be introduced into nickel plating solutions during normal operations. Continuing efforts to eliminate the sources of these impurities improve the quality of the deposits as well as productivity and profitability. Inorganic contaminants arise from numerous sources, including nickel salts of technical grade, hard water, carry-over from acid dip tanks, airborne dust, bipolar attack of metallic immersion heaters, corrosion of the tank material through cracks in the lining, corrosion of anode bars, dirt from structures above the tank, and parts that fall into the solution and are not removed.

Table 1.2: Maximum limits for inorganic, metallic impurities in nickel plating baths

Contaminant	Maximum Concentration (ppm)
Aluminum	60
Chromium	10
Copper	30
Iron	50
Lead	2
Zinc	20

Note: The limits are different when several contaminants are present at the same time when complexing agents are part of the solution formulation.

The degree of contamination by many inorganic materials may be controlled by continuous filtration and low-current-density electrolysis at (0.2–0.5 Adm^{-2}). This may be accomplished on a batch basis or continuously by installing a compartment and over flowdam at one end of the electroplating tank. Solution from the filter is pumped into the bottom of the compartment, up past corrugated cathode sheets, over the dam, into the electroplating section of the tank, out through a bottom outlet at the far end of the tank, and back to the filter. Solid particles and soluble metallic impurities (e.g., copper, zinc, and lead) are removed simultaneously by this procedure. The effects of chromium, copper, iron, zinc, and lead impurities on some properties of nickel deposits were evaluated, (**American Electroplaters, 1966**)

1.4: Functions of electroplating and deposit Properties:

Electrodeposited nickel coatings are applied in functional applications to modify or improve corrosion resistance, hardness, wear, magnetic, and other properties. Although the appearance of the coating is important and the plated surface should be defect free, the lustrous mirror like deposits described in the previous section are not required.

Typical formulations for Watts baths and sulfamate solutions, the two most popular ones for functional applications, have been included in table 1.3 with recommended operating conditions and representative mechanical properties of deposits from each solution. Although the table indicates that the maximum current density for depositing nickel from Watts solution is (11A dm^{-2}), higher deposition rates can be achieved with increased agitation and solution flow rates. Other nickel

electroplating solutions have been applied in functional applications, and deposits from those solutions have useful properties. **(Zentner, 1952)**

1.4.1: Deposit Properties:

The main constituents in Watts's solutions affect the properties of electrodeposited nickel. Nickel sulfate improves conductivity and metal distribution and determines the limiting cathode current density for producing sound nickel deposits.

Nickel chloride improves anode corrosion but also increases conductivity, throwing power, and uniformity of coating thickness distribution. In addition chlorides increase the internal stress of the deposits, and they tend to refine size and minimize formation of nodules and trees. Boric acid is added for buffering purposes and affects the appearance of the deposits. Deposits may be cracked and burnt at low boric acid concentrations. Anionic wetting agents or surfactant that lower the surface tension of the plating solution so that air and hydrogen bubbles do not cling to the parts being plated are almost always added to control pitting and, by eliminating porosity, have an indirect effect on corrosion performance.

Operating conditions, such as pH, temperature, current density and chloride content, affect the properties of deposits from Watts solutions. **(Zentner, 1952)** In a Watts solution, hardness, tensile strength, and internal stress increase above pH 5.0 while the elongation percentage decreases. The hardness increases rapidly at low values of current density increasing the temperature of the plating solution causes hardness and tensile strength to reach minimum values at 55°C, while the elongation percentage is a maximum at that temperature. Increasing the chloride ion concentration affects the properties of deposits from Watts's solutions; for example, the elongation percentage is at a maximum, and hardness and tensile

strength are at minimum values when the solution contains 25% by weight nickel chloride. In general, conditions that increase the hardness of a nickel deposit will increase its tensile strength and lower its ductility. Close control of the main constituents and the operating conditions is thus required to produce nickel electrodeposits with consistent and known properties. (Sanborn, 1972)

Table 1.3: Nickel Plating solutions and some deposit properties

Type	Composition g/L	pH	Temperature (°C)	Cathode Current Density (A dm ⁻²)	Vickers Hardness, (100g load)	Tensile Strength (MPa)	Elongation (%)	Internal Stress (MPa)
Fluborate	Nickel fluoborate, 225–300 Nickel chloride, 0–15 Boric acid, 15–30	2.5– 4	38–70	3–30	125–300	380–600	5–30	90–200
Hard nickel	Nickel sulfate, 180 Ammonium chloride, 25 Boric acid, 30	5.6– 5.9	43–60	2–10	350–500	990–1100	5–8	300
All chloride	Nickel chloride, 225–300 Boric acid, 30–35	1–4	50–70	2.5–10	230–260	620–930	4–20	275– 340
All sulfate	Nickel sulfate, 225–410 Boric acid, 30–45	1.5– 4	38–70	1–10	180–275	410–480	20	120
Sulfate/c hloride	Nickel sulfate, 150– 225 Nickel chloride, 150 225 Boric acid, 30–45	1.5– 2.5	43–52	2.5–15	150–280	480–720	5–25	210– 280

Type	Composition g/L	pH	Temperature (°C)	Cathode Current Density (A dm ⁻²)	Vickers Hardness, (100g load)	Tensile Strength (MPa)	Elongation (%)	Internal Stress (MPa)
High sulfate	Nickel sulfate, 75–110 Sodium sulfate, 75–110 Ammonium chloride, 15–35 Boric acid, 15	5.3– 5.8	20–32	0.5–2.5				
Black nickel (sulfate bath)	Nickel sulfate, 75 Zinc sulfate, 30 Ammonium sulfate, 35 Sodium thiocyanate, 15	5.6	24–32	0.15				
Black nickel (chloride bath)	Nickel sulfate, 75 Zinc sulfate, 30 Ammonium sulfate, 35 Sodium thiocyanate, 15	5.0	24–32	0.15–0.6				
Nickel Phospho- us	Nickel sulfate, 170 or 330 Nickel chloride, 35–55 Boric acid, 0 or 4 Phosphoric acid, 50 or 0 Phosphorus acid, 2–40	0.5– 3.0	60–95	2–5				

1.4.2: Glycine bath

To deposit nickel coatings with a diversity of useful functional properties, the modern electroplating techniques widely, use solutions of complex salt 1967, N.T. Kudryavtsev proposed the use α -aminoacetic acid (glycine, HGly). In addition to its complexing properties, it exhibits high buffer properties, that maintain the pH, near the cathode layer, at a relatively constant level. Several studies were devoted to specific features of nickel deposition from glycine containing baths. However, the contemporary opinions on the mechanism of this process substantially disagree with one another. Some authors believe that complexes of any composition formed in solutions are discharged simultaneously on both, solid nickel and dropping mercury electrodes. Other show that among glycinates complex $[\text{Ni}(\text{H}_2\text{O})_4\text{Gly}]^+$ is the electro-active species and the discharge of complexes with different compositions necessarily includes a preliminary chemical dissociation stage. The notions on the nature of the limiting stage are also controversial. It was found that the limiting current is of the diffusion nature, whereas in certain kinetic difficulties that arise in the presence of small amino acid concentrations were mentioned. Such deviations in the views on this process were first of all caused by the complex composition of the studied electrolyte for which the comparison of literature data is complicated due to the different experimental conditions used. The studies were carried out for different ratios of main solution components (their concentrations could differ by an order of magnitude) in the presence or absence of supporting baths; for the constant ionic strength or supporting bath concentration. In practice, in conventional nickel-plating baths, the Ni (II) concentration is often maintained constant by correcting procedures; while the glycine concentration and the solution pH vary in wide ranges during the electrolysis.

1.4.3: Citrate bath

Citric acid and citrate are the reagents used chiefly, as pH buffer agent and a complexing agent for electroless nickel plating and electroplating iron-alloy, Ni-W alloy, Cu-Ni alloy baths. Citrate ions in the citrate bath react with nickel ions to form nickel citrate complexes, the complexes are adsorbed on the surface of the cathode. This contributes to the electrodeposition of nickel and the crystallization of the deposits. Citrate ion is also adsorbed on the surface of the cathode, resulting in the inhibition of the hydrogen evolution reaction. So citric acid and citrate are possible substitutes for boric acid. The compositions of the plating baths of nickel electrodeposition in the industrial concentration levels from citrate bath was investigated under different operating conditions, such as bath composition, pH, plating current density, temperature and plating time to find the optimum conditions for producing sound and satisfactory deposits. In all cases, the results produced by the citrate bath were compared with those produced by traditional Watts Bath under the same plating conditions. (**Bradley, 2011**)

1.5: Objective of the research

The objectives are as the follows:-

- To electrodeposited nickel from glycine and acetate baths.
- To optimize the conditions of deposition by varying different parameters such as: current density, temperature, pH and concentration of nickel ions and glycine .
- To determine the obtained coating thickness, deposition rate and nickel content in some samples.

Chapter Two

2. Materials and Methods

2.1: Materials

2.1.1: Chemicals:-

All chemical used in this research were of analytical grade type and include:-

- Nickel chloride (NiCl_2).
- Sodium acetate (CH_3COONa).
- Glycine ($\text{C}_2\text{H}_5\text{NO}_2$).
- Sodium sulphate (Na_2SO_4).
- Ammonium chloride (NH_4Cl).
- Sodium chloride (NaCl).
- Hydrochloric acid (HCl).
- Sodium hydroxide (NaOH).
- Distilled water

2.1.2: Equipment:

- DC power supply(GP-4303D, Japan)
- Ammeter
- Reostate
- Water bath (GFL 1083)
- Thermometer (ACCU-SAFE N16B-Germany)
- pH meter
- Nickel electrode (high pure).
- Copper plate
- Sensitive balance (Sartorius AG Germany- CPA124S)
- Beaker (Schott Duran – Germany)
- Glass rode
- Spatula (Hommoehher- WHN130-15 –Germany)

2.2: Methods:

Preparation of solutions:

23.76g of nickel chloride were weighed and dissolved by distilled water and the volume was completed to 200ml; the final concentration prepared was (0.5M).

5.68g of sodium sulphate were weighed and dissolved by distilled water into 200ml the final concentration prepared was (0.2M)

2.14g of ammonium chloride were weighed and dissolved by distilled water into 200ml the final concentration prepared was (0.2M)

3.5g of sodium chloride were weighed and dissolved by distilled water to 100ml the final concentration prepared was (3.5%)

2.2.1: Electroplating method:

Preparation of copper cathode:

A copper cathode obtained from local market, was cut in to $2 \times 2 \text{ Cm}^2$ and polished using emery paper, rinsed with distilled water and after that it was immersed in HCl for 20second and then rinsed with distilled water dried and weighted.

Electrical circuits and equipment's of nickel electrodeposition:

Pure nickel sheet (each of it was $2 \times 2 \text{ cm}^2$) was used as an anode, copper sheet as a cathode figure (2.1), D.C power supply unit (GP-4303D, Japan), The pH adjusted by adding NaOH 20 % or H_2SO_4 20 % solution, temperature controlled using water bath .

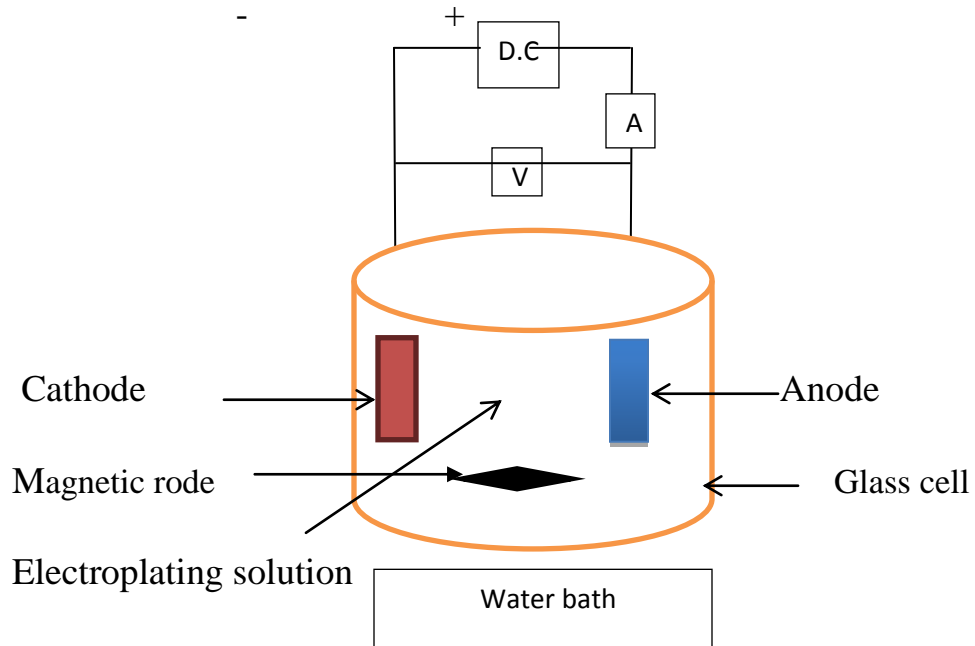


Fig (2.1) Electrical circuit of nickel electrodeposition

A: Ammeter.

V: Voltmeter.

Anode: Ni anode.

Cathode: Copper cathode.

Bath composition of Nickel electrodeposition:

The plating bath composition and operating conditions of nickel electrodeposition are shown in **Table (2.1)** below:

Nickel chloride	0.10-1.00 mole/L
Sodium sulfate	0.2 mole/L
Ammonium chloride	0.2 mole/L
Glycine	0.066-0.199 mole/L
Sodium acetate	0.03-0.18 mole/L
Current	0.10-0.90 A/cm ²
Temperature	25 -100 ⁰ C
pH	1 – 12
Time	10-60 min

Using the data in Table (2.1) systematic studies were carried out to investigate the following parameters:

1. The effect of nickel ions concentration on the CCE% and the thickness of the formed deposits.
2. The effect of glycine, sodium acetate concentration on the CCE% and the thickness of surface.
3. The effect of operating conditions: current density, temperature, pH, and deposition time on the CCE% and (deposits) surface thickness.

2.2.2: Corrosion method:

3.5% of sodium chloride was prepared then plate of weighted copper and electroplated copper plate were immersed into previous solution for 7 days then both plates were weighed and the loss of plate weight was recorded.

Chapter Three

3. Results and Discussion

3.1: Electroplating results:

Table (3.1): The effect of glycine concentration

Concentration of Glycine (M)	Weight(mg)
0.066	64.8
0.099	70
0.133	77.6
0.166	86.7
0.199	88.7

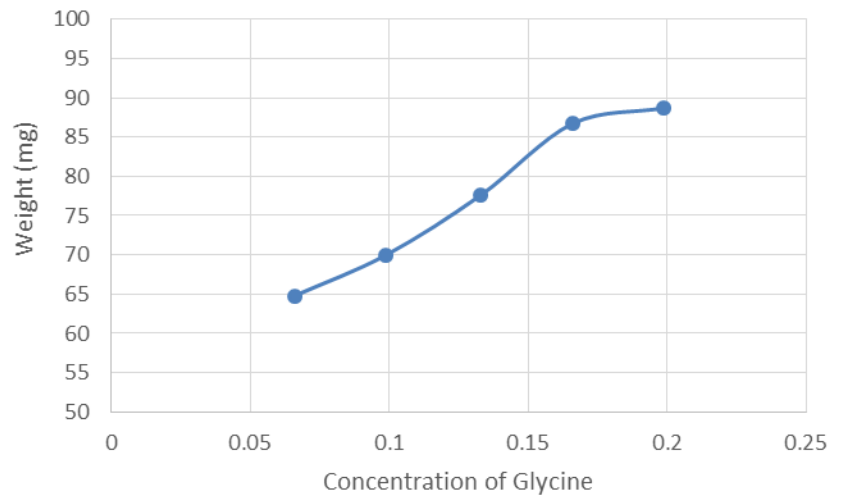


Fig (3.1):The effect of deffrent Concentration of Glycine

Fig (3.1): electrodeposition of nickel from bath containing nickel chloride (0.5M), sodiumsulphate (0.2M), pH=5, temperature=30°C, current=0.5A/cm², time=10min and the concentration of glycine (0.066-0.199mole/L)

It clearly from Table (3.1) and Fig (3.1) is that the weight of plate increased as glycine concentration increasing and is good agreement with (**Bradley, 2011**) that the complex ion $[\text{Ni}(\text{H}_2\text{O})_4\text{Gly}]^+$ was involved on deposition process also every complexing agent has inhibiting effect after the maximum deposition rate.

Table (3.2): The effect of sodium Acetate concentration

Concentration of sodium Acetate (M)	Weight(mg)
0.03	67.0
0.06	82.2
0.09	83.5
0.12	92.7
0.15	94.4
0.18	97.1

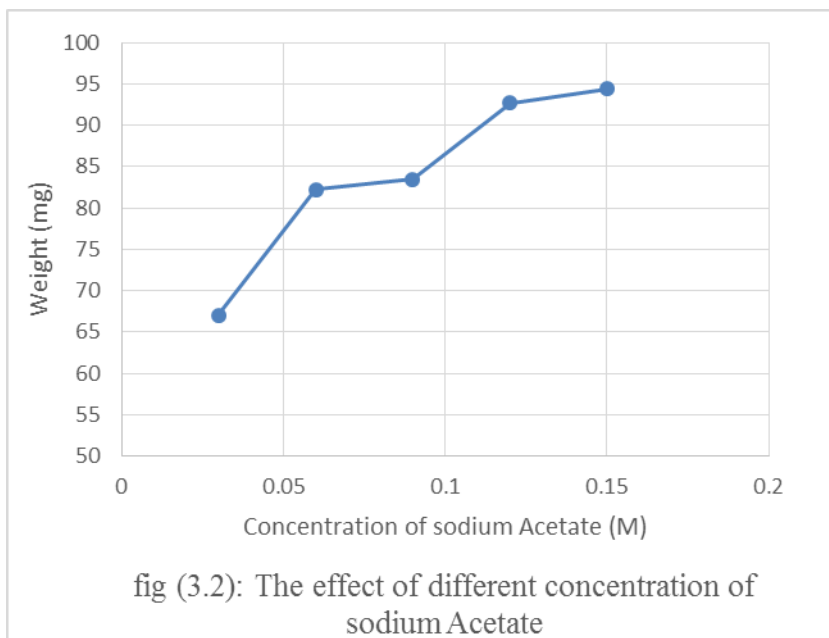


Fig (3.2) electrodeposition of nickel from bath containing nickel chloride (0.5M), sodium sulphate (0.2M), pH=5, temperature=30°C, current=0.5A/cm², time=10min and the concentration of sodium acetate (0.03-0.18mole/L)

Acetate ions consider being strong electrolyte so that increasing of sodium acetate concentration increasing the quantity of electric charge due to present of acetate ion and so then the weight of plate increase according to Faraday's law.

Table (3.3): The effect of current density or weight deposited

Current (A)	Weight (mg)
0.2	28.2
0.3	63.9
0.4	68.2
0.5	112.2
0.6	81.4

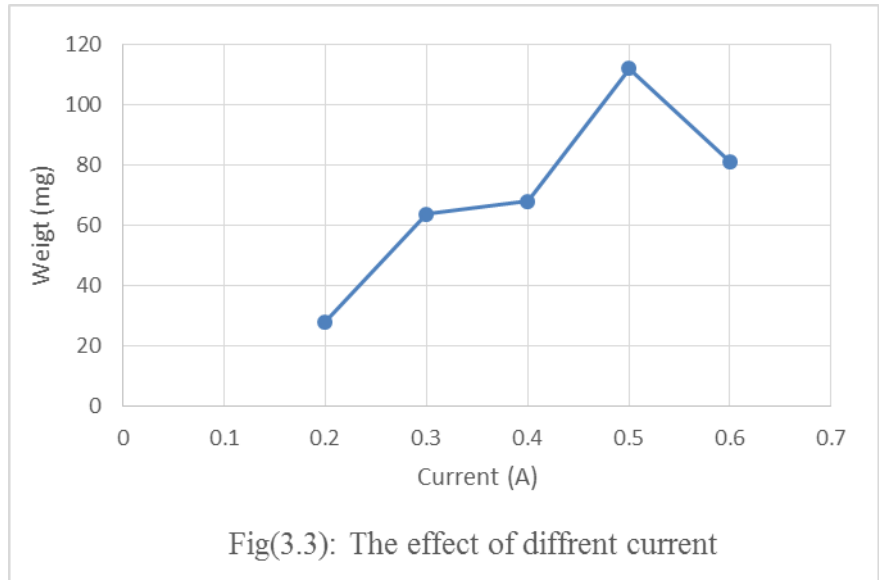


Fig (3.3) electrodeposition of nickel from bath containing nickel chloride (0.5M), sodium sulphate (0.2M), pH=5, temperature=30°C,time=10min and the current (0.2-0.6A/cm²)

From Table (3.3) and Fig (3.3) the weight of copper plate increased as current increasing but up to (0.5A) and after that it was decreased due to polarization effect which causes evolution of hydrogen gases which block the active site on the cathode surface.

Table (3.4): The effect of nickel chloride concentration

Concentration (M)	Weight (mg)
0.3	54.7
0.5	91.3
0.7	89.9
0.9	88.6
1.0	81.6

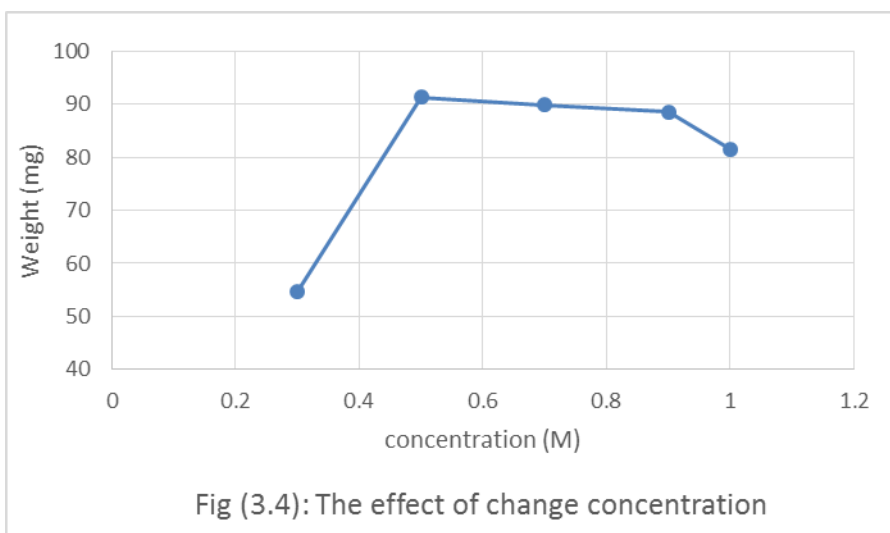


Fig (3.4) electrodeposition of nickel from bath containing nickel chloride (0.3-1.0 mole/L), sodium sulphate (0.2M), pH =5, temperature=30°C, current=0.5A/cm², time=10min

No doubt that increasing ion concentration in the electrolytic solution leads to increasing of electrodeposition rate according to Faraday law's also from Nernst equation the potential follow the concentration of nickel ion as indicated from Table (3.4) and Fig (3.4) up to (0.5M) and after that it decrease due to polarization effect.

Table (3.5): The effect of pH

pH	Weight (mg)
1	72.1
2	77.1
5	117.6
7	81.3
10	99.7
12	64.3

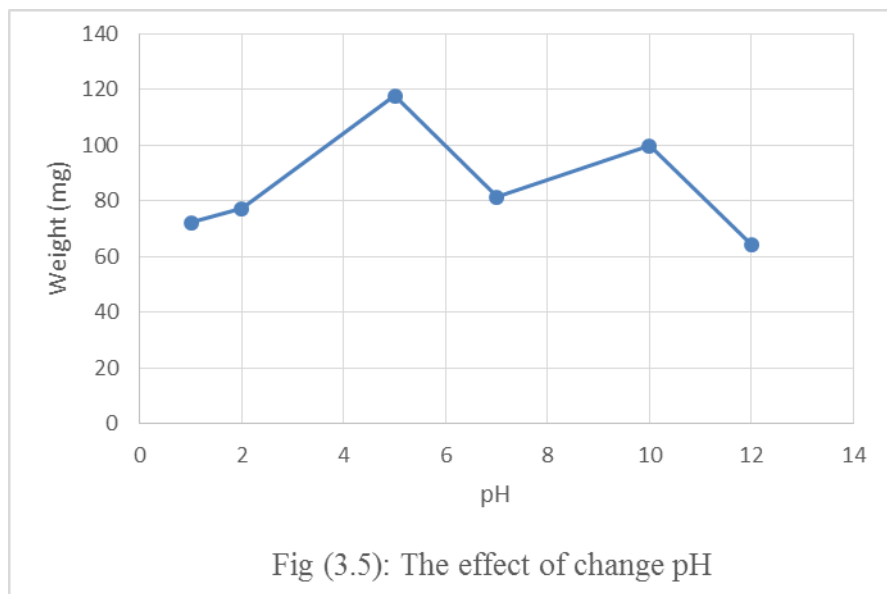


Fig (3.5)electrodeposition of nickel from bath containing pH = (1-12), temperature=30°C, current=0.5A/cm², concentration of nickel chloride=0.5M,sodium sulphate (0.2M) and time=10min

From Table (3.5) and Fig (3.5) the pH is clearly effect on the deposited weight on the plate, in acidic solution produced hydronium ion which transport proton to anode and create free metal particle this charge are deposit onto cathode so that the weight of plate decrease at higher acidic medium, a basic medium form hydroxide ion and if the pH of solution is very higher Ni (OH)₂will produced and being precipitating this reducing the efficiency of electroplating process.

Table (3.6): The effect of time

Time (min)	Weight (mg)
10	62.4
20	133.7
30	319.4
40	473.2
50	523.2
60	711.2

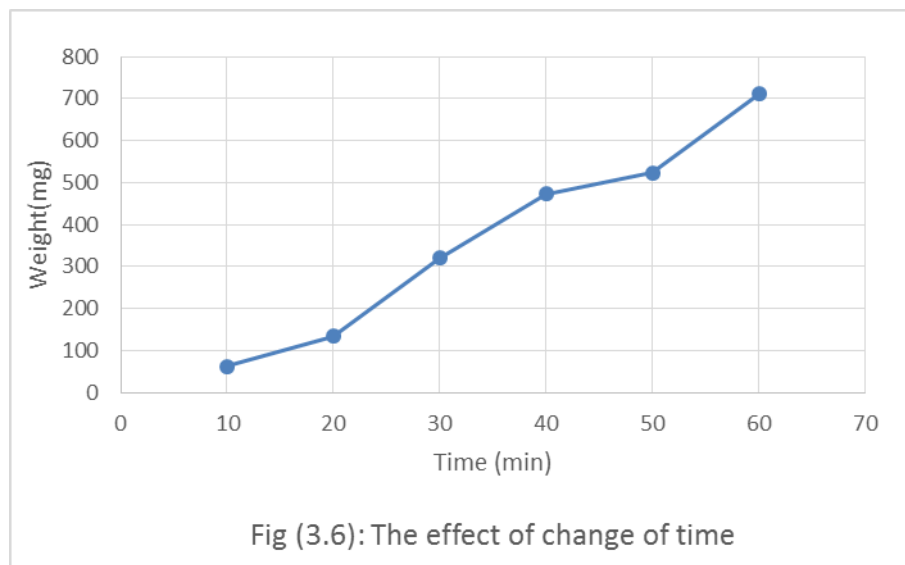


Fig (3.6)electrodeposition of nickel from bath containingpH = 5, temperature=30°C, current=0.5A/cm², concentration of nickel chloride=0.5M, sodium sulphate (0.2M) and time= (10-60min)

Time effect on electroplating was shown in Table (3.6) and Fig (3.6) the plate weight increased with time as in Faraday's law.

Table (3.7): The effect of temperature

Temperature (°C)	Weight (mg)
40	92.9
50	99
60	109.3
70	110.9
80	170.3
90	182.1

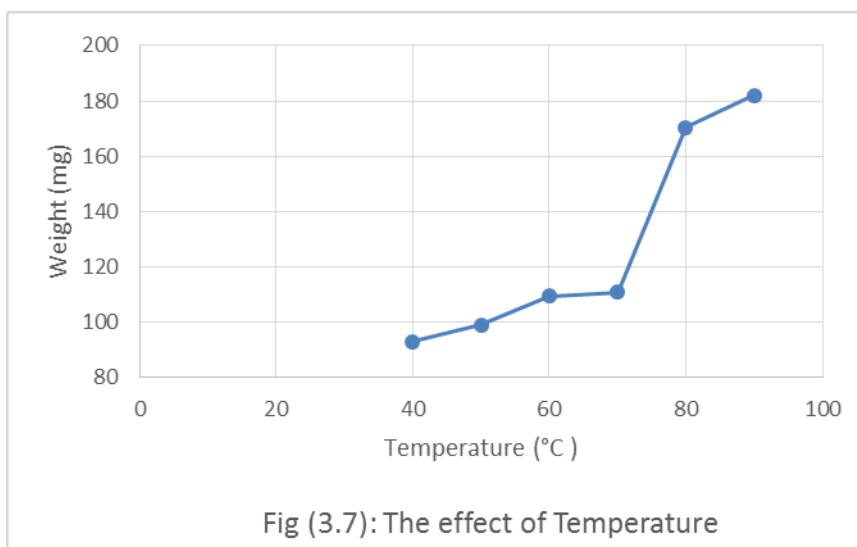


Fig (3.7)electrodeposition of nickel from bath containing pH = 5, current=0.5A/cm², temperature= (25-100°C), concentration of nickel chloride=0.5M,sodium sulphate (0.2M) and time=10min

Most chemical reaction go faster at higher temperature so that more nickel ion will deposit from warm nickel chloride solution than cooler one all other things being equal, furthermore according to Nernst equation the cathode potential is affect by temperature so the weight of plate increasing follow to it as shown as in Table (3.7) and Fig (3.7).

3.2: corrosion result:

Table (3.8) the result of corrosion test applied at room temperature for 7 days in sodium chloride solution (3.5%)

Copper plate	Weight of plate before corrosion(g)	Weight of plate after corrosion(g)	Net weight (g)
Before electroplating	2.8836	2.7698	0.1138
After electroplating	2.9763	2.894	0.0823

From Table (3.8) the plated copper substrate resists the corrosion process more than copper substrate alone and this can be explained by the fact that the nickel layer created a barrier between the copper substrate and the corroding medium.

3.3: Conclusions

The aim of the present research was to electroplate nickel from glycine and sodium acetate baths

1. The optimum concentration of nickel chloride solution was found to be (0.5M) and it used on all electroplating process.
2. The optimum current was found to be (0.5A).
3. The pH used in practical was (5).
4. The optimum time was used in practical (10min) because it gave beautiful shape and made decorative plating and it was used in all electroplating process.
5. The temperature effect studied was found to be the controllable temperature in this research.

The corrosion test was applied on electroplated copper sheet and the result was found to be best than copper sheet that mean the electroplating was help us to increase the resistance against corrosion of electroplated copper sheet.

3.4: References

- **C. B. Sanborn, (1972),** “*Electroforming Applications—Why They Exist,*” Symp. Electrodeposited Metals as Materials for Selected Applications. Metals and Ceramics Information Center, Battelle Columbus Laboratories, Columbus, OH, MCIC Report/Jan, p. 65.
- **C. Rosenstein and S. Hirsch,(1996)** “*Chemical Analysis of Plating Solutions,*” in Metal Finishing Guidebook and Directory Issue, Elsevier Science, New York, , p. 479.
- **E. Weston, (1878)** U.S. Patent 211,071.
- **G. A. Di Bari, (1996)** “*Nickel Electroplating Applications and Trends,*”*Plating Surf. Finish.*,83(10), 10.
- **G. Bird, Philos, (1837).** *Trans.*, 127, 37.
- **G. Dubpernell, (1959).** *The Story of Nickel Plating,*”*Plating*,46, 599.
- **G. J. Greenall and C. M. Whittington,** *Plating*, 40, 1391 (1953);37, 1157 (1950);39, 1343 (1952);39, 1033 (1952);41, 1307 (1954);, 53, 217 (1966). “*Metallic Impurities in Nickel Plating Solutions,*” *Plating “Reports of American Electroplaters’ Society Research Project Number 5,”*
- **J. K. Dennis and T. E. Such, (1993),** *Nickel and Chromium Plating*, 3rd ed., Wood head Publ., Cambridge, England.
- **J. Shore, (1840),** U.K. Patent 8407.
- **J. W. Dini, (1993),** *Electrodeposition— The Materials Science of Coatings and Substrates*, Noyes, Park Ridge, NJ, Ch. 7, pp. 195–248.
- **Kevin Bradley,(2011),** *Nickel Applications & Uses.*
- **M. Jousellin and R. Wiart, (1981),** “*Anion Dependence of Nickel Electrodeposition in Acidic Electrolytes,*” in Proc. Symp. On Electro crystallization, R. Weil, Ed., *Electrochemical Society*, Pennington, NJ, p. 111.
- **O. P. Watts, (1916).** *Trans. Am. Electrochem. Soc.*, 29, 395.
- **P. C. Crouch and H. V. Hendricksen, (1983).** *Trans.Inst. Metal Finish*, 61, 133.
- **P. Zentner, A. Brenner, and C. W. Jennings, (1952),** *Plating*,39, 365, 1229.

- R. Bottger, (1843), “*Investigation of Nickel Plating on Metals,*” Erdmann’s J. Praktische Chemie, 30, 267.
- **R. Weil, (1981),** “*Epitaxial Electro crystallization under Inhibited Growth Conditions,*” in Proc. Symp. On Electro crystallization, R. Weil, Ed., Electrochemical Society, Pennington, NJ, p. 134.
- **Robert J. Lancashire,(2006),***nickel chemistry,*.
- **W. D. Bancroft, (1906),** *Trans. Am. Electrochem. Soc,*9 , 218.
- **W. H. Remington, (1868),** U.S. Patent 82,877.