ELECTROLESS NICKEL PLATING
ON
ALUMINIUM

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1998

To,

Shri Bhumika Mata,

My Mother,

and

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STATEMENT

I hereby state that this thesis for the Ph.D. degree on " ELECTROLESS NICKEL PLATING ON ALUMINIUM " is my original work and that it has not previously formed the basis for the award of any degree, associateship and fellowship or any other similar title to the best of my knowledge and information.

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CERTIFICATE

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ABSTRACT

Although, the growing demand of metals in the world is largely met with increase in production, the destruction of these metals is equally on the rise due to alarming increase in atmospheric pollution. Surface technology, therefore acquires greater importance in its role to overcome such destruction. In this, the simple method of protection of highly corrosive metals has been the use of paints or the protective coating of less corrosive metals or alloy.

Conventional electroplating or galvanic plating is a well established technique in metal coatings wherein cathodic reduction of metals to be deposited is carried out under applied electrical current. Chemical or electroless plating is another fast developing plating method in which metal ions from aqueous medium are reduced and deposited on the substrate material in the presence of a chemical reducing agent. Electroless deposition has an advantage over electroplating since the former has better throwing power or uniform deposition on complicated shapes. Also deposition on non-conductors is possible by this method.

Nickel (E^{o} = -0.25 v) metal is comparatively less susceptible to corrosion when compared to aluminium (E^{o} = -1.66 v) or iron (E^{o} =-0.44 v) and hence it is widely used either singly or in alloy form to give protective coating to corrosive metals in general. Other applications of electroless plating include decorative, steel grey coloured matt finish and production of black selective solar absorber surfaces.

Complexing agent plays an important role in electroless plating since it controls the concentration of free metal ions and restrains their precipitation. The present work deals with electroless plating of nickel on aluminium by using nitrilotriacetic acid, $N(CH_2COOH)_3$, as complexing agent. Major objective of the work is to standardize the optimum condition for parameters like temperature, pH, and metal ion concentration to obtain a good metal coating. In addition to this, it also aims at studying the corrosion resistance of the coated metal in various environments.

Another important constituent of the electroless plating bath is the reducing agent. Whereas exhaustive literature is available on the use of sodium hypophosphite as reducing agent, not much work has been done on hydrazine. Interestingly 98-99% pure metal can be deposited as against 92% in the case of the former (with 6-7% P). An attempt is therefore made in this investigation to study the reduction of nickel ions by hydrazine in electroless plating.

A general introduction to the theory and technique of electroless plating, with special emphasis on the role of hydrazine as a reducing agent, is given in **Chapter I.** A review of literature on electroless plating of nickel on aluminium in the presence of various complexing and reducing agents is also included in this chapter.

In **Chapter II** the experimental procedures followed in the present study for carrying out electroless plating of nickel on aluminium, are described. The various methods adopted to monitor the deposition of nickel on the substrate are also given here. The analytical and the instrumental techniques used to evaluate the corrosion resistance of plated metal in various media or environments are briefly explained in this chapter. These techniques include IR Spectroscopy, X-Ray diffraction, Salt spray analysis, Potentiostat-Galvanostat, SEM and High Resolution Power Photography.

Several factors influence the electroless deposition process and important among these are: the temperature, the pH, the nature and the concentration of (i) metal ion, (ii) complexing agent, (iii) the reducing agent. Optimization of each of these factors is essential in standardization of electroless bath. This study is presented in **Chapter III**. It is observed that a good matt finish deposit of nickel is obtained at the temperature 348 K and at pH = 10.75 and that the pretreatment process of the substrate material plays a vital role in the nature of the coating.

Chapter IV deals with corrosion studies of plated substrates under various corrosive environments. Coated sample plates are exposed to vigourous saline and acidic media and corrosion resistance is monitored by simple and electrochemical techniques. Corrosion rates are found to be as low as 0.0245 mpy for plating obtained under standardized conditions as mentioned in the preceeding para. However, the corrosion rate increases marginally with the increase in the curing temperature of the coated material.

The final discussion and conclusion of this study is given in **Chapter V**. The duration of zincating in the pretreatment of substrate material affects both the nature and the corrosion resistance of the plated surface. Electroless plating of nickel on aluminium, obtained with new bath formulation ,is found to exhibit very good adhesion and resistance to abrasive wear. Its resistance to corrosion, especially in acidic medium is encouraging.

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CHAPTER
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CHAPTER ONE

LITERATURE SURVEY

1. INTRODUCTION

Corrosion can be defined as the destructive and unintentional attack of metal, as a result of which there is material loss which lowers the load bearing capability of the component. Corrosion is usually an electrochemical phenomenon and begins at the surface. About 4% of the GNP is spent on preventive measures and replacement for the components. Although corrosion cannot be stopped permanently, it can be minimized by proper choice of material, environment and *suitable protective coating*. Surface technology, therefore, acquires importance in present day scientific research.

Modern surface technology addresses itself not only to the menace of corrosion and wear but also to the other functionalities of the coated surface. In these, it provides surface properties which the substrate materials do not intrinsically possess. Protection of metals against corrosion and abrasive wear are the two important functions of the surface coatings. Corrosion and wear invariably occur at the surface, hence they can be reduced or eliminated only by surface treatments. Whereas, emulsion paints may partially protect metal substrate only from corrosion, it is the metal or alloy coating which can perform both the functions. Metals or alloys are deposited on a substrate usually from an aqueous solutions by electrolysis or chemical *(electroless)* process.

In electro-deposition, the substrate to be coated is made cathode in the circuit and dipped in a solution containing the ion(s) of the metal(s) to be deposited. The electroless process, as its name implies, uses no external current source and the reduction of metal ions to the metal results from the presence of chemical reducing agents in solutions.

1.1 ELECTRODEPOSITION

The electrolytic deposition of metals is based on the cathodic discharge of metal ions. In this the metal ions are reduced to metal at the cathode, which acts as a source of electrons. Electrons are generated at the "sacrificial" anode, which acts as sink. The reactions occurring at the two electrodes are as follows:

Anode........ $Me \rightarrow Me^{+z} + ze^-$

Cathode...... $Me^{+z} + ze^- \rightarrow Me$

This conventional plating, normally designated as 'electroplating' or Galvanic metal plating is accomplished when metal ions are reduced to the metallic state and deposited as such at the cathode by using proper current density. This Galvanic/electroplating have been refined to such an extent by the variation of basic electrolytes, conditions of depositions and by ever new additives that now a days it is considered as the most used and versatile process of modern surface technology. Exhaustive literature is available on electro-deposition[1] technique and practice.

However, Galvanic metal plating has certain disadvantages, such as,(a)coating for components subjected to great wear are not sufficiently hard, (b) it exhibits unevenness in the thickness, (c) difficulties in producing uniform coating on complicated shapes, (d)use being limited to conventional metal components and direct coating of non-conductors, dielectrics and semiconductors is not possible. The overcoming of this technological impass and the solution with new technique became possible due to the invention of chemical (electroless) nickel plating

1.2 ELECTROLESS DEPOSITION - "CHEMICAL PLATING"

An auto-catalytic process of depositing a metal, in presence of a chemical reducing agent, but in the absence of an external source of electric current, is termed as 'Electroless ' metal deposition or chemical plating[2]. In this process, the deposited metal itself acts as a catalyst for further deposition of the metal. Hence the thickness of the depositing metal layer continue to increase even after the substrate is completely covered by the deposited metal.

Although Wurtz[3] was first to discover the reducing property of hypophosphites, credit for the discovery and first use of the term electroless/chemical nickel plating goes to A. Brenner and G. Riddell[2,4]. Their work in developing a process for plating inner walls of tubes with nickel tungsten alloy, using an insoluble anode had accidently brought out the unusual reducing properties of the hypophosphites.

However, a literature survey shows that the term "electroless plating" has been used to describe not only the auto-catalytic processes, but also two other, fundamentally different processes of metal deposition which are performed in the absence of an external electric current. They are:

(i) metal deposition by galvanic displacement and

(ii) metal deposition by substrate catalysis

In both these processes, deposition of metal ceases once the substrate is covered completely with a thin layer of deposited metal. The following discussions and the present investigation concentrate on **auto-catalytic** "electroless plating" process. Initially, acceptance of the chemically deposited coating was slow, but subsequently due to the fast development of the process achieved through the improvements of both bath composition and techniques, it has increased manyfolds with industrial utilization. Several articles and books[5-17] are available on the principles and practice of "elctroless plating" or '*chemical plating*' or '*autocatalytic plating*'

Electroless deposition provides several advantages over electro-deposition process, Some of these are listed below

i) It produces a more uniform coating particularly when applied to complex shaped parts

ii) It produces dense and non-porous coating.

iii) The process is applicable to a greater variety of substrates ranging from metals and semi conductors to non-conductors like plastics, ceramics etc.

iv) Electrical contact is eliminated.

v) The resulting deposits have unique chemical, mechanical and magnetic properties

vi) They offer particular advantages for coating of inner surfaces of vessels, pipes, bored holes, etc. where galvanic process fail completely. Chemical plating has its place in the metallization of various insulators as well as of semi conductors.

1.3 COMPOSITION OF ELECTROLESS PLATING BATHS

The electroless plating bath contains (Table-1.1) an aqueous solution of metal ions, reducing agents, complexing agents, bath stabilizers and the pH regulators. They form the coating at a particular temperature and pH.

The metals which can be plated by this method are Nickel, Cobalt, Palladium, Copper, Platinum, Gold, Silver, and their alloys. The most common metal which is widely plated by the use of the electroless method is Nickel, particularly deposits containing Nickel-Phosphorous or Nickel-Boron and *pure metal.*

By proper choice of solution composition, pH, and the operating temperature the rates of deposition can be as high as 20- 25 μm / hr, sufficiently fast for industrial applications. Here, depending upon the application, the substrate material is subjected to appropriate pre-treatment before the actual electroless plating is carried out. In brief, electroless plating processes have found a wide spread use in various industry.

Table-1.1

The Function of Various Components in Electroless plating

Component	**Function**
Metal salt	Provides metal ions to be plated
Reducing agent	Provides reducing power at a catalytic heterogeneous interface
Complexing agent	Complexing of metal ions and prevents bulk decomposition
Stabilizer	Ensures homogeneous stability against bulk decomposition
pH adjuster	Ensures optimum pH for plating rate and deposit composition
Wetting agents	Increases the wetting properties of the surface to be plated
Exaultants	Accelerates the rate of deposition.

1.4 PRETREATMENT OF THE SUBSTRATE MATERIAL

Proper preparation of the surface of the substrate or base material, prior to the plating, is an important step in the electroless plating. This pre-plate process[42-45] depends on the nature of the substrate. Non-conductor substrates like plastics or ceramics are required to be sensitized and activated before actual plating is carried out. Whereas, in the case of mild steel or aluminium substrate the pre-plate process is different.

Degreasing and removal of the oily matter before plating is prerequisite for a good adhesion of coating and the aluminium metal is no exception to this requirement. Further, in the case of this metal, to obtain a good adhesive coating of nickel, a thin layer of zinc in the form of zincating solution is developed[46-53] before electroless plating is carried out. The details of this zincating process are discussed in Chapter – II.

1.5 MECHANISM OF ELECTROLESS PLATING OF NICKEL

Mechanism of the electroless plating of nickel depends on the reducing agents used in the process. There are different reducing agents which are commonly employed for the purpose. Common among them are sodium hypophosphite, hydrazine and sodium boron hydride.

1.5.1 SODIUM HYPOPHOSPHITE AS REDUCING AGENT

Metal deposition in the presence of sodium hypophosphite as a reducing agent can be represented[7] by the following sequence of equations:

$$[H_2PO_2]^- + H_2O \rightarrow [HPO_3]^{-2} + H^+ + 2H\,(cat) \ldots\ldots\ldots\ldots (i)$$

$$M^{2+} + 2H\,(cat) \rightarrow M^0 + 2H^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (ii)$$

$$[H_2PO_2]^- + H\,(cat) \rightarrow H_2O + OH^- + P \ldots\ldots\ldots\ldots\ldots (iii)$$

$$[H_2PO_2]^- + H_2O \rightarrow [HPO_3]^{-2} + H^+ + H_2 \ldots\ldots\ldots\ldots\ldots (iv)$$

Metal ions are reduced to metal by H (cat) species adsorbed on the catalytic surface of the substrate material. As is seen above, one of the side reaction, given in equation (iii), and occurring simultaneously, liberates phosphorus which contributes to the deposition of Ni-P alloy. The last reaction given above not only makes the bath unstable but also reduces its efficiency. Nickel is precipitated as insoluble phosphite compound due to orthophosphite ion, $[HPO_3]^{-2}$, thus reducing the efficiency of the hypophosphite based bath (about 38 %). Since H^+ ions are continuously generated during these reactions, the pH of the bath decreases during the reduction and therefore it is essential to maintain the optimum value of pH by the addition of base.

Electroless deposition, thus obtained, invariably contain Ni-P alloy with about 91- 94 % metal. Typical electroless plating bath for nickel-phosphorus deposition is given in Table-1.2. Although attempts are made to control the phosphorus content in the deposited Ni-P alloy by adjusting the hypophosphite concentration in the plating bath, the deposition of pure nickel metal cannot be achieved by using this bath.

Table-1.2
Typical electroless plating bath with hypophosphite reducing agent

Nickel sulphate, $NiSO_4.7H_20$	19-23 g/l
Sodium hypophosphite, $NaH_2PO_2.H_2O$	23-30 g/l
Complexing agent	30-50 g/l
pH	4.2 - 4.8
Temperature	about 368K

1.5.2 HYDRAZINE AS REDUCING AGENT

More than 99% pure nickel metal can be deposited [1.0 to 100 um thick] with hydrazine as a reducing agent in an alkaline solution of pH above 9.0. The reduction of the metal by hydrazine can be represented[18-20] as:

$$2Ni^{++} + N_2H_4 + 4OH^- \rightarrow 2Ni^0 + N_2\uparrow + 4H_2O$$

Table -1.3

Typical electroless plating bath with hydrazine[21-41] reducing agent

Nickel Chloride , $NiCl_2.6H_2O$	5 g/l
Hydrazine N_2H_4	30 g/l
Sodium tartarate, $NaC_4O_6.H_2O$	7 g/l
pH (with NaOH)	10
Temperature	368K

Here OH^- ions are continuously consumed during the reduction, as a result of which the pH of the bath decreases. It is therefore important to replenish these ions and also maintain the pH of the bath solution to the optimum value by the addition of a suitable base. Since hydrazine is also used up continuously during the reduction of the metal ions, the periodic addition of this reducing agent is also essential for continuous deposition of the metal. Many hydrazine based electroless plating baths have been developed since it was first used. One such hydrazine based electroless plating bath is given in Table 1.3.

1.6 COMPLEXING AGENTS IN ELECTROLESS HYPOPHOSPHITE BATH

Nature and the concentration of the complexing agent plays an important role, alon with the other factors in determining the speed of separation and the stability of electroless bath.

Complexing agents added in an electroless plating bath with hypophosphite reducing agent are usually organic additives (Table 1.4), which play a vital role in the stabilisation of the process, increase in the speed of separation, and suitability of components. It is known that, complexing agent form various metal complexes and in this manner reduce the concentration of free metal ions. Consequently the solution is stabilized and the precipitation of metal phosphite or metal hydroxide is restrained.

Solution which were originally investigated contained a salt of glycolic acid, citric acid or acetic acid, and preferably glycolate. In 1953, G. Gutzeit and E.J.Ramiraj patented the use of dicarboxylic acid[62] eg. Succinic acid, malonic acid, and glutaric acid. It was shown that the speed of separation had a maximum value at a certain concentration of acid.

Together with the simplest hydroxy – carboxylic acid, the glycolic acid[63] (oxy-acetic acid) lactic acid[57,58,64,65] became very popular as one could reach maximum speed. Lactic acid is the rare example of an organic additive playing multiple role in which at the same time it has the effect of a complexing agent as well as having a significant capacity as a buffer, and at optimum concentration it also has an accelerating effect.

The first members of the homologue series of the saturated carbonic acids ($H.COOH$ and CH_3COOH) are poor complexing agents. Combinations of carboxylic and hydroxy carboxylic acids e.g. propionic acid/ lactic acid [58,66] are also used for complexing. G . Gutzeit has examined the complex forming action of the amino acids[67], namely amino acetic acid (Glycine), ∝- amino propionic acid (∝ - alanine), β - amino propionic acid (β - alanine), ∝ - amino butyric acid, amino succinic acid (aspartic acid) imino di, and tri-acetic acid as well as EDTE[68].

The formation of complexes is not only limited to the use of organic additives. In certain cases, there are some inorganic salts such as ammonium salts[60,69] and fluorine borates[61,70], which are also used even if only to a limited extent.

A complexing agent has to be added for Ni^{+2} alkaline solution in order to avoid the precipitation of hydroxides or of basic salts. Ammonia is one such unavoidable additive which complexes a large part of the nickel ions. The number of complexing agent used in this context is modest. Foremost in use is citrate anion (sodium citrate, ammonium citrate, citric acid) and the ammonium cation (NH_4OH, NH_4Cl). Their most important task is the formation of nickel complexes,, and thus to stabilise the bath solution. M.Schwartz established the use of pyrophosphate ion with $K_2P_4O_7$, $Na_2P_4O_7$[73] as complexing agents.

1.7 COMPLEXING AGENTS IN ELECTROLESS HYDRAZINE BATH

Complexing agent has the same role to play whether it is a hypophosphite or hydrazine that is used in the reduction. Many of these complexing agents are therefore commonly used with both the reducing agents. One difference between hypophosphite and hydrazine based baths is that, in the case of the latter the complexing is stronger and more stable. Hydrazine is itself a wellknown[83] ligand which forms variety of complexes with metal salts in aqueous medium.

In addition to those mentioned in the table for hypophosphite bath, there are other complexing agents reported[84-102] in the literature (Table- 1.5) which are also used in hydrazine based baths.

1.8 NITRILOTRIACETATE AS COMPLEXING AGENT IN PLATING BATH

Nitrilotriacetic acid[103], $H_3[N(CH_2COO)_3]$, is a tri-basic acid known to form a variety[104-106] of salts with metal ions. Although the acid itself is sparingly soluble in water, with solubility[107] equal to 1.28 g in one litre at 298K, most of its salts are highly soluble. Being tri-protic acid, it has three dissociation constants, having pK values[108] as 1.89, 2.49 and 9.73. This acid is used in detergents[109], dyes[110], softening of boiler water, electro-deposition processes etc.

Nitrilotriacetate salts are extensively[111-134] used in the electro-deposition processes. It is used as a constituent in electro-cleaners[135-136] in the pre-plate treatment and also as a complexing agent in the plating bath.

Nickel forms nickel nitrilotriacetate salt with nitrilotriacetic acid. The equilibrium constant value[137,138] (with $\log K = 11.26$) of this metal chelate indicates that the complex salt is very stable. Hence, nitrilotriacetic acid can be conveniently used as a complexing agent in controlled reduction of the nickel ions from the aqueous solution.

Table - 1.4

Complexing agents used in various electroless plating baths.

Complexing agent	Reducing agent	References
Lactic acid/Lactate Propionate	$Na_2H_2PO_2$ (A)	57,58
Glycolic acid	$Na_2H_2PO_2$ (A)	54
Acetic acid	$Na_2H_2PO_2$ (A)	59
Sodium acetate	$Na_2H_2PO_2$ (A)	59
Ammonium acetate	$Na_2H_2PO_2$ (A)	59
Fluoroboric acid	$Na_2H_2PO_2$ (A)	61
Fluoride	$Na_2H_2PO_2$ (A)	60
Tartaric acid.	$Na_2H_2PO_2$ (A)	64
Succinic acid	$Na_2H_2PO_2$ (A)	64
Salycylic acid	$Na_2H_2PO_2$ (A)	63
Phthalic acid	$Na_2H_2PO_2$ (A)	63
Glycine	$Na_2H_2PO_2$ (A)	65
Amino acids	$Na_2H_2PO_2$ (A)	67
Sodium Citrate	NaH_2PO_2 (Ak)	54
Ammonium Citrate	NaH_2PO_2 (Ak)	71
Sodium Pyrophosphate	NaH_2PO_2 (Ak)	73
Potassium	NaH_2PO_2 (Ak)	73
Ammonium Chloride	NaH_2PO_2 (Ak)	71
Sodium tetra Borate	NaH_2PO_2 (Ak)	72
Ammonium Oxalate	NaH_2PO_2 (Ak)	74
Ammonium Sulphate	NaH_2PO_2 (Ak)	74
Glycolic acid.	NaH_2PO_2 (Ak)	76
EDTA – Sodium salt.	NaH_2PO_2 (Ak)	76
Sodium Potassium tartarate	$NaBH_4$	78
EDTE	$NaBH_4$	55
Sodium Fluoride	$NaBH_4$	77
Sodium Citrate	*DEAB*	55
Sodium Succinate	*DEAB*	55
Sodium Acetate	*DMAB*	81
Sodium Pyrophosphate	*DMAB*	82
Lactic acid	*DMAB*	79
Boric acid	*DMAB*	80
Malonate	*DMAB*	56
Malein Glycine	*DMAB*	56
Pyrophosphate	*DMAB*	56

Key: A = Acidic Bath, AK = Alkaline Bath.
DMAB – Dimethyl Amino Borane DEAB – Diethyl Amino Borane.
$NaBH_4$ – Sodium boron hydride

TABLE - 1.5

Complexing agents used in various electroless plating baths with *Hydrazine* as reducing agent

Complexing agent	**References**
Tartaric acid	83,84
Sodium sulphite	85
Sodium Tartarate	83,87,93
Ammonia	86,88,90,94
Amine	88
Di sodium salt of EDTA	88
Amylamine	88
Ethanolamine	88
Monoethanolamine	88
Sodium citrate	91,98
Citric acid	93,98,102
Potasium cyanide	90,95
Glycine	101

1.9 CHARACTERISTICS OF EN PLATING

Characteristics of electroless nickel plating on any metal substrate can be summarized as follows.

a] The aqueous separating solution contains the compound which delivers the nickel ions as well as reducing medium, the solution is stabilized so that both components do not react with one another under the working conditions which are recommended. A low concentration of nickel of approximately 0.05 to 0.2 mol/l is characteristic.

b] The metal separation starts and is kept going by a catalyst.

c] The surface to be coated acts as a catalyst; although its materials itself has catalytic properties or it has been activated by a catalyst.

d] The speed of separation is in the first instance dependent upon the temperature of the solution. The added buffers, complexing agents, accelerators and stabilizers ensure optimum speed of separation and stability of the solution.

e] The reduction of nickel is accompanied by liberation of hydrogen or nitrogen - the mol proportion of the separated nickel to the gases formed lies between 1:1.76 and 1:1.93.

f] Coating formed as a result of reactions which have taken place are of either pure metal or of alloy.

g] The chemicals which are used for metal separation are added continuously or from time to time as soon as the concentration has fallen below certain minimum value.

1.10 APPLICATIONS OF ELECTROLESS NICKEL DEPOSITS

Electroless Nickel (EN) is primarily used for engineering applications[139-158] where uniform thickness, high degree of hardness and wear resistance of the surface and improved corrosion resistance are required. Thus, EN process is used to deposit on complex shapes, large surfaces especially large interior surfaces which are subjected to wear. It is also used to replace expensive stainless steel vessels in some processing industries and to repair or salvage nickel plated machine parts. Electroless method can be conveniently employed for in situ nickel depositions where electrical power is not available, for improving the adhesion of enamels on steels, for printed circuit boards and electronic industries for corrosion resistance and solderability

Inner surfaces of pumps, driers, tubes, gasoline, containers and tanks, valves screws, nuts, fasteners etc, are coated with Electroless Nickel for improved corrosion resistance and uniformity of deposition. Cylinders, cranks, bearing surfaces, rotating shafts, printed press parts, motor blades etc. are coated with EN for improved corrosion resistance and uniformity of deposition. Cylinders for hydraulic pumps, piston rings, piston cylinders, cranks, bearing surfaces, rotating shafts, printed parts, motor blocks etc. are coated with EN for improved wear & abrasion resistance under lubricating conditions.

Aluminium and aluminium parts used in aircrafts or space crafts are coated with electroless nickel for improved wear resistance and corrosion resistance. Nuclear reactor parts, light alloy dies, radar wave guides, printed circuit boards are also coated with EN. EN used on rollers and crippling tracks in textile industries provides a uniform highly wear resistant and corrosion resistant surface.

All parts coated with electroless nickel and precision turned to an accuracy between 0.05 and 1.0 micron smoothness are used in parabolloid mirrors in space vehicles. Electroless methods[159-162]are also used for "metallization" of plastics of non-conductors. With proper surface preparation, metals can be deposited having good adhesion.

One of the major applications of electroless plating, in recent times, has been in the trapping of the solar energy. Solar collector technology involves conversion of solar radiation into heat. A good solar absorber surface is essential to perform such a function. Black metallic or emulsion coated surface is useful for this purpose. However, the former is more durable than the emulsion method. In black metallic surface electro-plated black chromium[163-173] , nickel[174-183],copper[184]and aluminium[185-187]are known Recently electroless black nickel[188-189], from hypophosphite bath, has been tried for such an application.

1.11 SCOPE OF PRESENT INVESTIGATION

As is already discussed in the beginning of this chapter, the main thrust of the modern surface technology is to increase the life of functional metallic material with the help of suitable metal coating. Pure nickel with reduction potential of -0.25 volt is less susceptible to corrosion,compared to aluminium which has reduction potential of -1.66 volts It is therefore envisaged that a thin layer, uniform deposition of nickel on aluminium would serve as a protective film against corrosion of the base metal. Although hypophosphite-reduction based electroless plating bath is more convenient and well developed, major disadvantage with this bath has been the low efficiency and a lower stability. Similarly, this EN bath is not suitable for use where specific functions with pure nickel coated surface are envisaged. Due to high purity of nickel metal deposits obtained from hydrazine-reduction based electroless bath, it was thought interesting to investigate and develop this bath with a new complexing agent namely nitrilotriacetic acid.

Another important application of the electroless deposition methods has been in solar absorption. From the literature survey it was found that hydrazine-reduction based electroless-nickel has not been investigated for such an application. Since the hydrazine based baths operate at pH of more than 9.0, in such an alkaline medium a different nature and texture of nickel deposit can be visualized. It is therefore necessary to study this aspect of the method of plating adopted in the present investigation.

Table 1.6
Various applications of Electroless Nickel

[References:139 to 158]

AUTOMOTIVE	AIRCRAFT	CHEMICAL
Heat Sinks *Pistons* *Engine Bearings* *Hose Couplings* *Gears* *Bushing* *Brake Cylinders* *Brake Pad Holders* *Shock Absorbers* *Exhaust Manifolds* *Cams* *Carburetors*	*Engine Overhaul* *Landing Gear* *Hydraulics* *Propellers* *Engine Mounts* *Turbine Parts* *Gyro Parts* *Compressor Stators* *Compressor Spaces* *Compressor Blades, Case* *Laser Mirrors* *Engine Pistons, Fuel Lines*	*Tants, Vessels* *Pumps* *Filters* *Heat Exchangers* *Control Valves* *Spray Nozzles* *Centrifugal Screens* *Stirrers / Blenders* *Extruders*
ELECTRIC MOTORS	PRINTING	MINING
Motor Shafts *Roter Blades* *Starters*	*Printing Rolls* *Impact Print Cylinders* *Rollers (Copiers)*	*Drills* *Hydraulics* *Bearings*
ELECTRONICS	TEXTILE	POWER GENERATION
Heat Sinks, Chassis *Transistors, Headers* *Printed Circuit Boards* *Memory Disks, Filters* *Terminals, Lead wires* *Hermetic Seals* *Packaging IC's*	*Feed Rolls* *Drop wires* *Heddles* *Spinneretts* *Bobbins* *Thread Guides* *Spools, Combs*	*Reactor Head (nuclear)* *Steam Turbine Parts* *Gas Turbine Parts*
OIL AND GAS	*PULP & PAPER*	*RAIL ROADS*
Safety Valves, Collars *Fire Tubes, Tubulars,* *Mud Pumps, Chokes* *Couplings, Packers* *Flow Control Valves* *Pump Impellers*	*Rollers*	*Diesel Shafts* *Trunions*

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CHAPTER TWO

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CHAPTER TWO

EXPERIMENTAL

2. INTRODUCTION

The experimental procedures, analytical methods and physico-chemical techniques employed in the present investigation are described in this chapter. These include pretreatment of base metal substrate, preparation of various electroless bath solutions, electroless plating, monitoring and control of different bath parameters during deposition, characterization of plated materials using different analytical techniques and various structural properties studied during the course of investigation.

2.1 MATERIALS USED

Commercially available chemicals, analar or equivalent grade are used in the investigation. All the solutions were prepared from analar grade reagent / chemicals.

i) Sodium potassium tartarate

ii) Trichloroethylene

iii) Carbon tetrachloride(CCl_4)

iv) Sodium Hydroxide, NaOH, Qualigen

v) Zinc Oxide, ZnO, E.Merck

vi) Nickel carbonate basic , $NiCO_3$, $2Ni(OH)_2$, $4H_2O$ - Loba-chem

vii) Nitrilotriacetic acid ,$H_3[N(CH_2COO)_3]$ - Loba – chem

viii) Hydrazine Hydrate ,$N_2H_4.H_2O$ (99-100%) Qualigen

ix) Liquor Ammonia , Analar – Qualigens

x) Ethylenediaminetetraacetic acid - disodium salt, EDTA , Qualigen

xi) Nitric acid , Qualigen

xii)Hydrochloric acid , Qualigen

xiii) Sulphuric acid , Qualigen

xiv) Sodium Chloride

xv) Sodium Hypophosphite

xvi) Zinc Sulphate, Loba -chem

xvii) Murexide indicator

xviii) Eriochrome Black -T indictor

xix) Solochrome Black indicator

2.2 CHEMICAL ANALYSIS

Estimation of metal or metal ions was carried out by using volumetric methods.

2.2.1 ESTIMATION OF ALUMINIUM

Aluminium panels used as substrate material for plating in this investigation was chemically analysed for its purity by known analytical method[1-2] . In this method, known quantity of Al (0.100 g) metal was dissolved in 5.0 cm^3 conc. HCl and heated to dryness. The residue was extracted with about 50 cm^3 of H_2O to which, known excess of 0.01 M EDTA solution was added.The pH of the solution was then adjusted to 7-8 with ammonia and boiled to ensure complete complexation. On cooling this mixture,the pH was again adjusted to 7-8. After addition of 0.05 g Solochrome Black / KNO_3 mixture, the solution was then titrated with 0.01 $ZnSO_4$ solution until colour changes from blue to wine red. Volume of 0.01 EDTA used by Al ions for complexation was determined by method of difference.

1.0 cm^3 of 0.01 M EDTA used by Al = 0.0002698 g Al

2.2.2 ESTIMATION OF NICKEL

Nickel solution containing nitrilotriacetate complexing agent was first decomposed with 1.0 cm^3 conc. HNO_3 and 3.0 cm^3 H_2O_2 by heating and then used for estimation. The Ni^{2+} solution was mixed with 0.05 g Murexide / KNO_3 indicator and 10 cm^3 1.0 M ammonium chloride and the pH of the solution was adjusted to 10 with ammonia. This mixture was then titrated with 0.01 M EDTA until colour changes from yellow to violet[1].

1.0 cm^3 0.01 M EDTA = 0.0005871 g Ni.

2.3 PREPARATION OF ALUMINIUM ELECTRODES

Aluminum panels (0.04-0.1 cm thick) were used as electrodes or substrate materials. Electrodes were cut to a suitable size (7cm x 2cm) and mechanically polished. These specimen sample plates were then cleaned with carbon tetrachloride and degreased by using trichloroethylene. The washed specimen were then used for appropriate pre-plate treatment before plating.

2.3.1 CLEANING

The elementary step of the plating process on aluminium has been the cleaning sequence which has been designed to remove soils, lubricants, polishing compounds, etc. from the surface. For heavily soiled surface this may involve both pre-cleaning and then soak cleaning. Soak cleaners, in general remove superficial contaminants, both organic and inorganic, from the aluminium surface. Non-silicated soak cleaners have been specified in many cases to avoid silicate contamination of the aluminium surface. In the present investigation non silicated alkaline soak cleaners were used. A good rinsing with demineralised (DM) water is recommended following this alkaline soak cleaner.

2.3.2 RINSING

Adequate rinsing of the aluminium has been an essential part of successful electroless nickel plating. Rinses need to be included between each step in the pre-plate sequence. Double rinses have been especially recommended after the desmut to ensure an alkali/acid free surface as possible,prior to entering the next step. Spray rinses have been particularly important in that they achieve mechanical impregement on the surface and allow contamination to be removed with greater consistency.

2.3.3 ETCHING

One of the most critical step in the pre-plate process for electroless nickel plating of aluminium has been the etching[3] step. The primary purpose of the etchant step, is the removal of various metal impurities to provide a uniformly aluminium rich surface for plating. There are two categories of etchants namely acidic and alkaline. The use of acidic etchant has been recommended,since it is more effective in the preparation of the surface for a broader range of aluminium alloys without significantly attacking the aluminium itself. This not only helps to retain the surface finish and dimensional tolerance, but it also reduces the amount of smut developed on the surface.

Alkaline etchant have certain advantages for plating aluminium as well. One important example is the electroless nickel plating on threaded and machined parts which need to satisfy certain corrosion tests and services in corrosive environment. Alkaline etchant have been used to mitigate, to some extent, the effects of surface condition on corrosion protection. Finally, casting which are heavily oxidized, are processed in many cases through alkaline etchant to help, to provide a thiner and more uniformly deoxidised surface . This in turn can help adhesion on the final plate. In the present investigation alkaline etchant have been used.

2.3.4 DESMUTTING

The desmutting process involves acidic cleaning of Al.-substrate to remove insoluble residues after the etching operation. Alkaline etchant always form a smut which must be removed prior to zincating. This smut can be removed by immersion into a dilute solution of nitric acid. The addition of sulphuric acid to the dilute nitric acid solution has been found useful in removal of magnesium and aluminium oxide. Therefore desmuting solution composed of nitric acid (50%) and sulphuric acid (10%) and combination thereof has been commonly recommended . In the present investigation, above desmuting solution have been used. The desmut step leaves a uniformly thin oxided aluminium rich surface on which the zincate layer can be developed through zincating process.

2.3.5 ZINCATING : ZINC AS A CONVENTIONAL BARRIER DEPOSIT

Aluminium surface rapidly forms a tenacious oxide, therefore, to ensure an oxide free surface for plating it is customary to deposit an immersion coating of zinc on to previously cleaned aluminium surface. This immersion process is commonly known[4,5] as zincating process, since dissolved zinc exists in a caustic solution as zincate ion, $Zn(OH)^{4-}$.This process continues to be the most important requirement for consistently adherent deposit of electroless nickel on aluminium. The functions of the zincating solution are (Fig. 2.1) :

(i) to further conditions of the aluminium substrate,

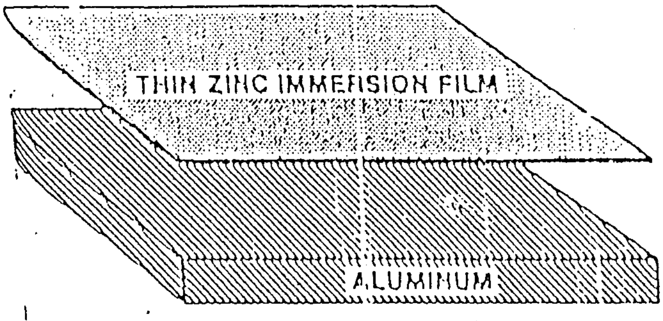
(ii) to provide a thin coating, to act as a barrier against reoxidation, and

(iii) to act as a barrier between electroless solution and aluminium substrate.

The amount of zinc deposited is governed by its own equilibrium to deposit and dissolve in the strong caustic zincating solution. Although much of zinc from substrate surface is known to dissolve[6] in the electroless nickel solution during deposition, the retention of some zinc on substrate surface is necessary for adherent deposit. This has also been described as zinc rich zone by Mallory[7]. Zincating solutions employed in pre-plate treatment are strongly alkaline, although they may vary significantly in zinc and caustic contents.

Various additives including other metals are used[8] to promote better surface conditioning and receptability to electroless deposition. The more dilute version with small amount of heavy metal additives eg. Fe, Cu, Ni and combinations thereof are generally preferred, because of the ability to deposit a more durable and uniform coating. The amount of zinc deposited is limited by its own equilibrium to deposit and dissolve in the strong caustic zincating solution. In the present investigation various formulations of zincating solutions available in the literature were selected (Table-2.1) and used to get desired matt finish EN coating. Such zincating solution was then standardised with respect to immersion time and concentration of ingredients in solutions.

Fig. 2.1: Zincating as pre-plate process for the deposition of Ni on Aluminium



DOUBLE BARRIER ACTIVATION
OF ALUMINUM

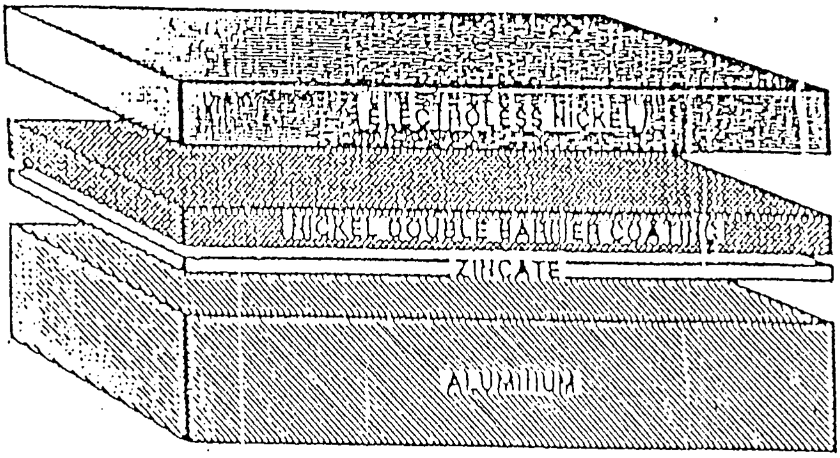


Table – 2.1

Composition of the aqueous zincating solutions used in the pre-plate treatment of the aluminium substrate

Code	ZnO (g)	NaOH (g)	Na-K tartarate	$ZnSO_4$(g)	Volume	Reference
ZNCT - 1	93	425	-	-	1lit	7
ZNCT -2	14	94	-	-	1lit	7
ZNCT -3	529	97.5	-	-	1lit	4
ZNCT -4	-	30	40	20	1lit	-

Besides the composition of the zincating solution, another important factor in this pre-plate treatment is the immersion time for the substrate. Regardless of the type of the zincating solution employed, immersion times are relatively short i.e. 15 - 16 seconds. Adhesion properties of EN deposits are greatly improved by employing a double zincating process[9] whereby first zinc deposit is removed in a dilute nitric acid solution and a second shorter immersion in the same zincate solution is repeated . The incomplete coverage obtained from the first zincate treatment allows potential sites for the non-adherent , blistered electroless nickel deposit. Nitric acid treatment after the first zincating operation is important, because it further purifies the aluminium alloy substrate by the removing exposed inclusions from the previous aggressions of the zincating solution. The Al rich surface is now less vulnerable to second zincating operation and a thinner, yet more uniform and dense zinc deposit is produced. From the literature [8,9] it has been found that for most of the applications, immersion time of 30 - 40 seconds in the first zincating and 15 - 20 seconds in the second zincating produces reasonably consistent results. In the present investigation we have also employed double zincating treatment with a standardized zincating solution and standardised immersion time.

Aluminium plates of desired size and area were cleaned and degreased. They were then etched in an alkaline etchant solution followed by rinsing with demineralised water. They were dipped in a zincating solution for barrier coating for about 10 to 15 seconds , followed by DM-water rinse. The sequence of the processes is given in Table-2.2.

Table-2.2 Pre-plate processing scheme for Al substrate used in the present investigation

Process	Chemical type	Immersion time	Temperature
Precleaning	Clorinated solvent	5 min. or less	Room temp
Soak cleaning	Non silicated alkaline soak cleaner	1-5 min.	Room temp
Etching	Alkaline type	5-20 sec.	Room temp
Desmutting	Nitric acid + Sulphuric acid	15 –20 sec	Room temp
Zincating	Dilute (New Formulation)	15 –20 sec	Room temp
Zincate stripping	Dilute nitric acid	5-10 sec.	Room temp
Zincating	Dilute (New Formulation)	10-12 sec.	Room temp
EN plating	As necessary	As necessary	348K

Each of the above step in the process /scheme was followed by a demineralised water rinse. EN-Plating for ½, 1, 2, 3, 4, 5, and 6 hours have been carried out similarly, for determining the rate of deposition and also to study the stability of the bath.

2.4 PRE-PLATE PROCESS FOR DEPOSITION ON COPPER SUBSTRATE

Electroless plating of Nickel on copper substrate was also studied with novel bath. Copper plates of desired shape and dimensions (7.0 cm x 2.0cm x 0.1cm) were cut and cleaned in carbon tetrachloride and degreased by using trichloroethylene. After DM-water wash, plates were etched or cleaned in dilute HCl followed by DM-water rinse. These copper plates were then sensitized with dilute $SnCl_2$ solution (0.1 g + 0.5 cm^3 HCl in 100 cm^3 solution) for about 1 to 2 minutes and then activated in dilute $PdCl_2$ solution (0.1 g $PdCl_2$ + 0.5 cm^3 HCl in 100 cm^3 solution) for 1 minute. After DM-water rinse , again they were then dipped in the bath solution for electroless plating of nickel.

Table- 2.3
Pre-plate processing scheme for Cu substrate used in the present investigation

Cleaning and degreasing

Washing
Demineralised water

Etching
Dilute HCl

Rinsing
Demineralised water

Sensitisation
$SnCl_2$ Solution

Rinsing
Demineralised water

Activation
$PdCl_2$

Rinsing
Demineralised Water

Electroless Plating

Rinsing
Demineralised water

2.5 PREPARATION OF EN BATH SOLUTION

An electroless plating bath solution essentially consists of a metal ion source, a complexing agent, a reducing agent and a pH regulating substance. Calculated amount of all the above components are dissolved in pure water to obtain aqueous bath solution. Although the quality of the deposition can be improved by the addition of other agents like wetting agent, stabilizer, brightner, exaulants etc., in the present investigation, only essential constituents (Table-2.4) were used for standardisation of the bath.

Table-2.4 Chemicals used as essential agents in this investigation

FUNCTION	CHEMICALS
Nickel ion source	$NiCO_3.2Ni(OH)_2.4H_2O$ Basic nickel carbonate
Complexing agent	$N(CH_2COOH)_3$ Nitrilotriacetic acid (NTA)
Reducing agent	$N_2H_4.H_2O$ Hydrazine hydrate
pH regulator	NH_3 Liquor ammonia

Three different methods were used for the preparation of the bath solution.These methods essentially contain nickel nitrilotriacetate as a source of both nickel ion and the complexing agent.

2.5.1 METHOD-I

Aqueous suspension of basic nickel carbonate and NTA, mixed in a required molar ratio of Ni^{+2} and NTA was warmed to about 55 - 60 °C in a water bath. The clear solution was then filtered through Whatman paper 41 and treated with the calculated amount of hydrazine hydrate and diluted with distilled water to the required volume. The pH of the bath solution was then adjusted to a required value by the addition of liquor ammonia. This solution was then used as such for plating.

$NiCO_3.2Ni(OH)_2.4H_2O + 3N(CH_2COOH)_3 \rightarrow 3[N(CH_2COO)_3]HNi + CO_2 + 9H_2O$

2.5.2 Method-II

Nickel nitrilotriacetate salt in solid form was first synthesised in situ[10] by using the method given elsewhere. Calculated amount of this salt was then dissolved in a definite volume of distilled water, followed by addition of hydrazine hydrate and liquor ammonia as mentained in Method-I above.

2.5.3 Method-III

Nickel hydrazinium nitrilotriacetate salt, $[N(CH_2COO)_3](N_2H_5)Ni$, was prepared in situ[11] by using the method given elsewhere. In this method, aqueous Ni-NTA salt was treated with $N_2H_4.H_2O$ (or N_2H_5OH), such that molar ratio Ni:NTA:N_2H_4 equal to 1:1:1 .

$$[N(CH_2COO)_3]HNi + N_2H_5OH \rightarrow [N(CH_2COO)_3](N_2H_5)Ni + H_2O$$

and then nickel hydrazinium nitrilotriacetate salt was isolated in solid form. It was then dissolved in warm water to obtain the bath solution which contains in it metal ion, ligand and a reducing agent. pH of the solution was then adjusted by adding liquor NH_3.

Table-2.5 Selected Composition of EN plating bath solutions

CHEMICALS	BATH-1 ($g\ L^{-1}$)	BATH-2 ($g\ L^{-1}$)	BATH-3 ($g\ L^{-1}$)	BATH-4 ($g\ L^{-1}$)	BATH-5 ($g\ L^{-1}$)
$NiCO_3.2Ni(OH)_2.4H_2O$	1.2536	2.5072	3.7608	5.0144	1.2536
$N(CH_2COOH)_3$ [NTA]	1.9114	3.8228	5.7342	7.6456	1.9114
$N_2H_4.H_2O$	0.5	1.0	1.5	2.5	0.5
$NaH_2PO_2.H_2O$	-	-	-	-	10.601
pH [with NH_3]	As required	As required	As required	As required	As required

Total volume of solution with water is one litre.

2.6 MONITORING THE QUALITY OF THE DEPOSITION : *ADHESION*

For technical applications of the chemically (electroless) deposited nickel, it is important that the coatings should have a good adhesion on the substrate material. A metal-to-metal bonding between deposit and the substrate metal is envisaged in electroless plating. The following tests are commonly used for qualitative determination of adhesion in electroless plating.

2.6.1 PEEL-OFF TEST

A strong adhesive tape was fixed on the plated surface and then removed. A good adhesion is indicated[12] by non removal of plated metal (nickel).

2.6.2 BENDING TEST

In this test, the coated plate is bent through 180^0 . A good adhesion will not exhibit[13] lifting of the coating on bending.

2.6.3 QUENCHING TEST

This is a simple, common and reliable method[14] of qualitative determination of adhesion of coated nickel in electroless plating. Here, the coated plate is heated to about 473-500K, and then, this hot plate is quenched by dipping in water at room temperature. A weak adhesion is indicated by lifting off the coating. It is customary to use peel-off method after quenching for better assessment.

All the three tests mentioned above were used in this study.

2.7 MONITORING OF THE RATE AND THICKNESS OF DEPOSITION

Rate of deposition of Nickel on Aluminium was evaluated peroidically or otherwise by using weight gain method. In this method the weight of dry plate was found out (i) before pre-plate process (ii) after pre-plate process (iii) after EN plating at the end of the experimental period. The difference in weight or the gain in weight on plating,the area of the plated surface and density of Nickel was then used to calculate[15], the rate of deposition by employing the following equation:

$$\textbf{Rate of deposition} = \frac{W}{A\ d\ t} \times 10^{4}\ \mu m / hr$$

Where W= weight of nickel deposited in g

A= area of the coated surface in cm^2

t = plating time in hours

d =density of Ni (8.5 g / cm^3)

Thickness of plating = Rate of deposition X Time.

2.8 X-RAY POWDER DIFFRACTION

The X-ray diffraction patterns[16] were obtained using Phillips X-ray Diffractometer model PW 1840 using Cu Kα radiation with nickel filter.

2.9 INFRARED SPECTROSCOPY

Every molecule has a number of fundamental vibrational frequencies and each fundamental frequency may be associated with absorption of radiation of its own frequency. This absorption of frequencies[17-18] appears as a spectrum in the infrared spectroscopy.

The infrared spectra of samples in solid form were recorded by using Shimadzu FTIR-8101A Infrared Spectrophotometer.

2.10 CORROSION STUDIES

The corrosion susceptibility of the coated material was monitored and evaluated by using both electrochemical and non-electrochemical methods.

2.10.1 NON-ELECTROCHEMICAL METHOD

Most common non-electrochemical methods widely used in the corrosion studies are the weight loss method and the Gasometric method. In the present investigation the weight loss method was employed for monitoring the corrosion resistance of the plated material.

2.10.1.1 WEIGHT LOSS METHOD

In this method the corrosion current was expressed in terms of the variation in weight / unit surface and per unit time or penetration of the corrosive process into the metallic material per unit time. Different specimens (size mentioned above) coated with nickel were obtained and, if required, lacquer was applied on its four sides . Initial weight of all the plates or panel specimen were noted . The panels were then separately dipped in 100 cm^3 beaker containing 3.5 % NaCl solution. After 24 hours the specimens were separately removed , washed, dried and weighed . The panels were then dipped in a fresh 3.5 % NaCl solution . The experiment was repeated for one week and the weight loss was calculated .

$$\text{Corrosion Rate} = \frac{534\ W}{D\,A\,T}$$

where W = weight loss in g

D = density of specimen,

A = area of specimen

T = Time in seconds.

2.10.1.2 SALT SPRAY METHOD

Salt spray testing : The ASTM-B117 (DIN 50021) 3.5% neutral salt spray method for evaluating the corrosion performance of coating has been used extensively. This test method was performed on the plated flat panels with mask off edges. The panels were placed in a chamber at a specific angle and the effect of the salt environment was evaluated . Specimen panels were kept in the salt spray chamber from 8 hours to 8 days and experimental data was collected. Electrolyte used was 3.5 % NaCl neutral solution.

2.10.2 ELECTROCHEMICAL METHOD

The electrochemical methods can be divided into two major classes namely Direct Current and Alternate Current Techniques. The methods employed in this study are given below.

2.10.2.1 DIRECT CURRENT TECHNIQUES

1. Tafel polarisation method
2. Galvanostatic method
3. Potentiostatic method
4. Potentiodynamic method

Corrosion process, occurring in the aqueous media are electrochemical in nature. The overall reaction is the combination of anodic reaction in the dissolution of the metal as under:

$$M \rightarrow M^{2+} + ne^-$$

And the cathodic reaction is the evolution of hydrogen or reduction of O_2 gas.

$2H^+ + 2e^- \rightarrow H_2$ (acidic medium)
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (neutral /alkaline medium)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (acidic medium)
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (neutral medium)

Since the corrosion process is electrochemical in nature. Various electrochemical techniques have been widely used for the determination of corrosion rates.

2.10.2.1.1 TAFEL POLARISATION METHOD

This method involves the measurement of potential of an electrode for various current densities using a galvanostatic set up. The current was increased either at regular interval or continuously and the resultant electrode potential was measured after it reaches a steady value. The plot of potential Vs logarithmic current was obtained and an extrapolation of linear region to corrosion potential ($\eta = O$) was used to evaluate[19] the corrosion current.

2.10.2.1.2 GALVANOSTATIC METHOD

A constant current was applied to the electrode and the potential of this electrode was measured against a suitable reference electrode. The constant current was obtained from a current regulator. The applied current has to remain constant, despite the changes with time of the over voltage of the reaction at the test electrode and the corresponding changes of the cell voltage. The main disadvantage of the galvanostatic technique is the fact that the polarization behaviour of the metal to be tested has to be known previously in order to determine the range of current to be applied for polarization studies.

2.10.2.1.3 POTENTIOSTATIC METHOD

A constant potential was applied to the test electrode and the current flowing between the counter electrodes and working electrode was recorded. The advantage here is the fact that the polarization behaviour of the test electrode need not be known. Starting from the corrosion potential (CRP) the potential was changed in steps and the current measured and recorded when it had reached a constant value. The potential was applied between working electrode and reference electrode and the output i.e. current between working electrode and Counter Electrode (CE) was measured. By increasing area of CE, polarization at the counter electrode could be minimised.

2.10.2.1.4 POTENTIODYNAMIC METHOD

Applied potential was changed at a constant rate using a voltage scan generator, starting at the corrosion potential i.e. OCP. This technique leads to less scatter in the experimental results and further due to the fast scan the surface change occurring at the electrode is minimised.

2.10.2.1.5 LINEAR POLARIZATION OR POLARIZATION RESISTANCE METHOD

Stern and Geary have shown that there was a linear relationship between the current and the potential at those values which are very close to the corrosion potential (η=10 mV). Stern and Geary[20] considered this relationship to be especially important. From this 'low current polarization' measurements combined with corrosion rate data per unit area calculation for one of the Tafel slopes is possible if the other is known. They also pointed out that since the measurement were made out close to the corrosion potential, any surface changes which may result from high current polarisation were eliminated.

$$i_{corr} = \frac{\beta a \ \beta c}{2.303 \ (\beta a + \beta c) \ R p}$$

Where βa = Anodic Tafel slope

βc = Cathodic Tafel slope

R p = Polarization resistance

This equation was called as Stern - Geary equation.

$$I_{corr} = \beta / Rp$$

The value of β can be calculated by two methods.

i) By assuming the value of βa and βc, β[21] can be calculated.

Rp is calculated from a plot of η vs i

slope $d\eta / di = Rp$

When Rp changed with scan rate, the value of Rp was made scan independent by extrapolating to zero scan following the method due to Macdonald[22].

2.10.2.1.6 GALVANOSTATIC POLARIZATION TECHNIQUE

Polarization measurements were carried out galvanostatically by exposing 1 cm^2 area of the plated specimen using constant current regulator. Platinum was used as an auxillary electrode and saturated calomel electrode as reference electrode. Current was varied from 0 to 1000 mA and the corresponding change in potential was measured against SCE ,using Elico make Galvanostat / potentiostat model and also EG & G make Potentiostat / Galvanostat model .

The electrolytes used in the study were 3.5% NaCl , 2N H_2SO_4 and 1N HCl . Both anodic and cathodic polarization were carried out in all electrolytes. Graph were drawn against potential and current density (C.D.) by using Tafel extrapolation method .Corrosion current and corrosion potentials were determined. The instrument used in the study is shown in Fig . 2.2

2.10.2.2 ALTERNATE CURRENT TECHNIQUES

The following methods are normally used in the study of corrosion in metals

1. Impedance method
2. Faradaic rectification method
3. Faradic distribution method
4. Small amplitude cyclic voltametry. These methods were not used in the study.

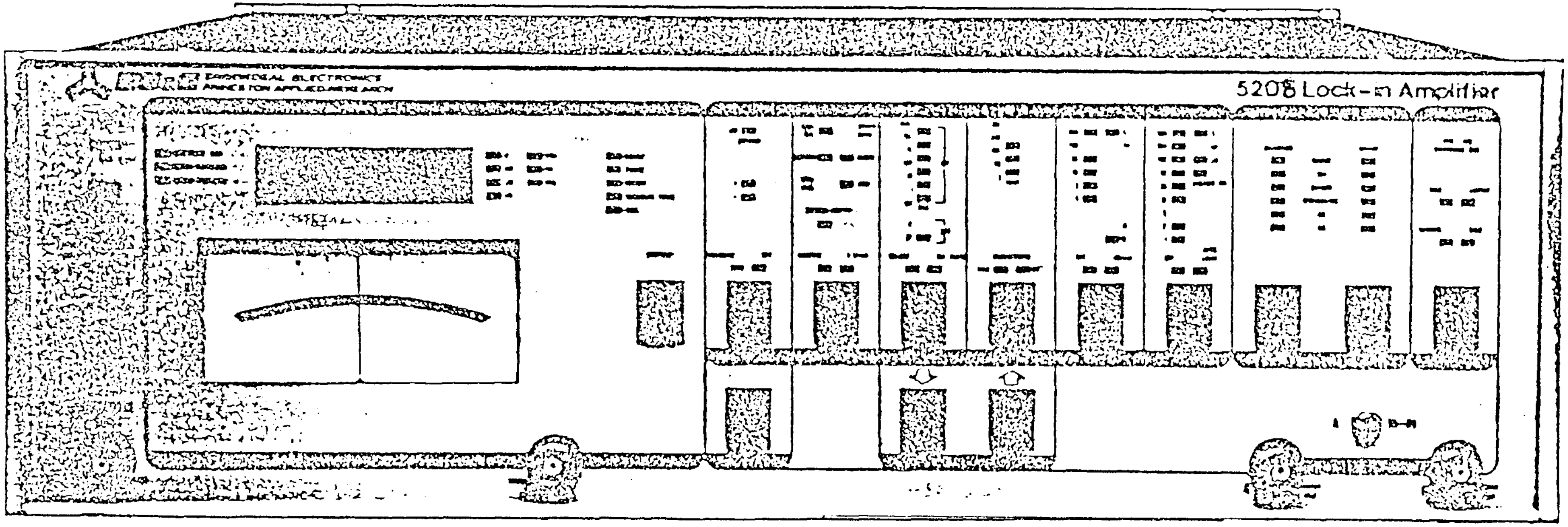


Figure 2.2: Instrument used in the corrosion studies.

2.11 SURFACE MORPHOLOGY

Surface morphology of the plated material was investigated by using High Resolution Photography with Leica - Orthoplan Pole Microscope at the magnification of 650 times. This microscope is used to obtain micrographs of the covered surface to assess damage caused by corrosion. Scanning Electron Microscope.(SEM) was also used for this purpose to scan some coated surfaces. The SEM uses the secondary electron produced by the scanning beam to give a life-like , almost three dimensional image of the surface of the specimen being scanned. The magnification range of the SEM is more than 100,000.

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CHAPTER THREE

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CHAPTER THREE

ELECTROLESS DEPOSITION OF NICKEL ON ALUMINIUM:

STANDARDISATION OF BATH COMPOSITION

3. INTRODUCTION

Electroless deposition as one of the surface treating techniques[1] is emerging as a major branch of the deposition methods for surface modification. The impending demand[2] for newer and better processes has made the electroless industry blossom into a promising field of metal finishing. This method has become indispensable in the deposition of thin films where high precision and fine quality are of foremost important. Efforts have been made to deposit various types[3] of metals or alloys on substrate material having the most useful characteristics to meet the requirement of the users. Of these, electroless nickel (EN) process has increased enormously, because of its wide range of applications[2]. The vast patented literature available in the field shows that EN has emerged into a much wanted industry in the world-market today.

Preparation of an electroless nickel bath is usually based on one or two solutions. These are mixed with de-ionised water to give the correct dilution for plating. The bath is raised to the required temperature, and its pH is adjusted to the appropriate value with suitable acid or base and is thus made ready for use. Important constituents in electroless bath, besides metal ion source, are the complexing and reducing agents.

Like ethylene diamine tetra acetic acid (EDTA), the nitrilotriacetic acid (NTA) is also a welknown[4] complexing agent. However, although reports[3,5] are available in the literature on the use of the EDTA as a complexing agent in the electroless bath formulations, not much work[6] has been done with NTA. In the present study, therefore, an attempt is made to establish the role and the use of the NTA in EN deposition on aluminium substrate.

3.1 SETTING UP OF ELECTROLESS NICKEL BATH

Deposition of nickel by the electroless technique is influenced by various important factors[3] such as:

1. pre-plate treatment of the surface,
2. bath composition,
3. bath temperature,
4. pH of the medium, and
5. other factors viz. Surface/volume ratio, etc.

To obtain the optimum operating parameters for desired good quality coatings, experiments aimed at the standardization of essential parameters in plating bath for desired applications are conducted with the bath ingredients.

3.2 BATH COMPOSITION

The various compositions of the electroless bath tried during this study are given in Table 2.5. In these EN baths, hydrazine[7,8], in the form of hydrazine hydrate [$N_2H_4.H_2O$], and nitrilotriacetic acid [$N(CH_2COOH)_3$], are the reducing and complexing agents respectively. Liquor ammonia is used to regulate the pH of the solution. The methods of the preparation of these solutions have been already discussed in Section 2.5. The pH of the solution was monitored electrometrically and the rate of the deposition and the thickness of the plated layer was calculated by using the weight gain method described in Chapter 2.

3.3 STANDARDIZATION OF NICKEL ION CONCENTRATION

During the experiments carried out at a pH = 9 and a temperature of 348K, it is observed that, at lower concentrations of the Ni^{2+} ions (0.01M), a good steel grey colour deposit is obtained from a stable bath. The texture of the coating and the stability of the bath deteriorates at higher concentrations of the metal ion (Table – 3.1). Here, although the rate of deposition improves marginally (Fig.3.1) at higher concentrations of the nickel ions, the nature of the deposition is not of desired quality. Similar pattern of behaviour is observed (Table-3.2 and 3.3) for various concentrations of both reducing and complexing agents.

Table – 3.1

Variation of the thickness , rate and quality of deposition with concentration of Nickel ions at 348 K

Area of the plate: 33.6 cm^2	pH of EN bath : 9.0
Bath composition : 1:1:1	Zincating time : 10 – 12 sec
Zincating type : ZNCT- 4 (single)	Surface to volume ratio : 1:20
Density of Ni : 8.5 g / cm^3	Plating time : 1 hour

Plate code No.	Concentration of Ni^{+2} moles/lit.	Weight gain g	Thickness µ m	Deposition rate µm / hr	Surface finish	Stability of bath
C-1	0.005	0.0025	0.08753	0.08753	dull	Stable
C-2	0.01	0.0060	0.21009	0.21009	Matt. Bright	Stable
C-3	0.02	0.0063	0.22059	0.22059	Matt.	Stable
C-4	0.025	0.0070	0.245107	0.245107	Matt. Grey	Stable
C-5	0.03	0.0075	0. 262612	0. 262612	Matt. Grey	Stable
C-6	0.04	0.0091	0.318639	0.318639	Matt. dull	Unstable
C-7	0.05	0.0099 .	0.34664	0.34664	Matt. dull	Unstable
C-8	0.10	0.0131	0.45870	0.45870	Matt.Black	Turbid

Fig.3.1:Variation of the rate of deposition with the concentration of Ni ions.

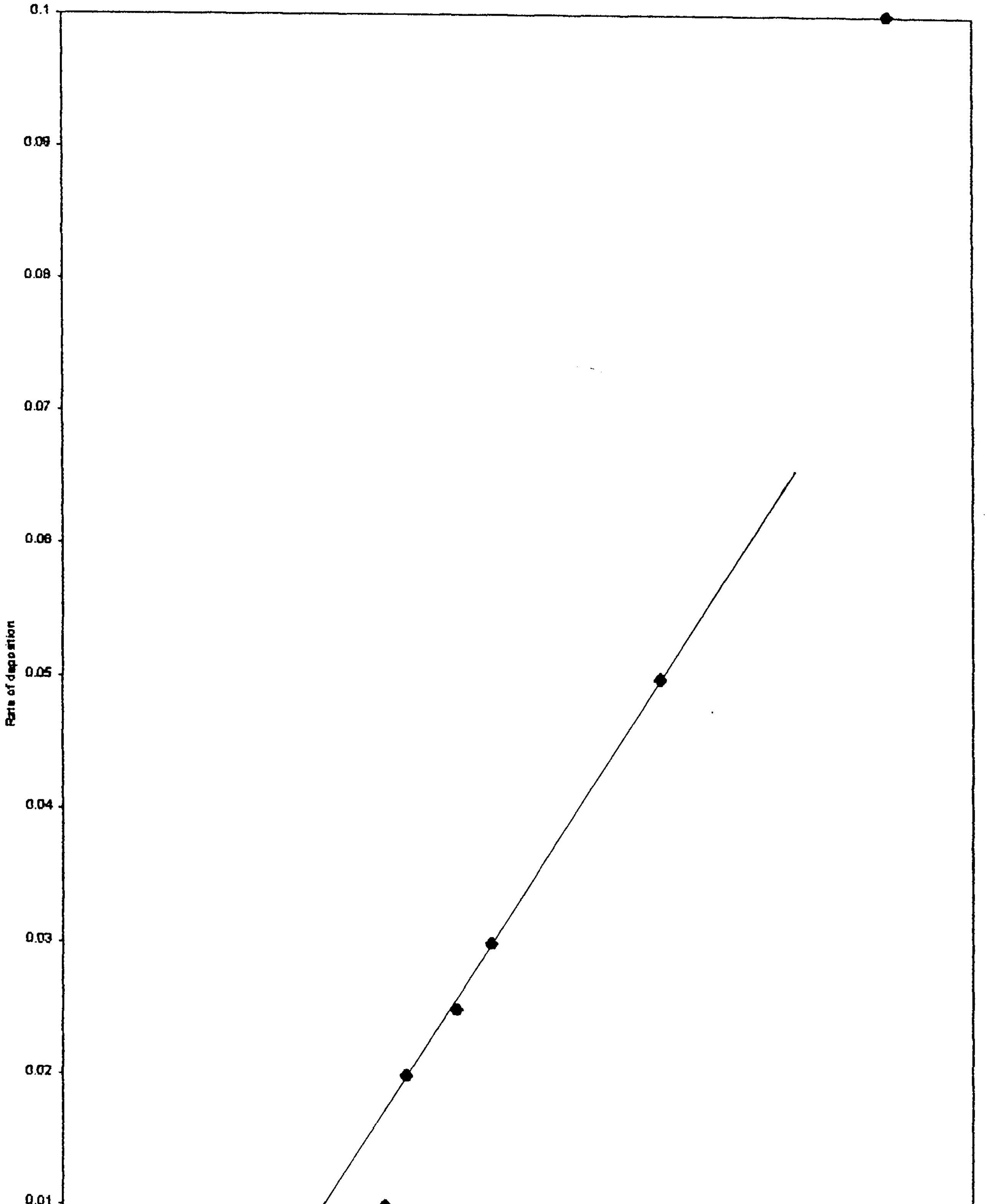


Table – 3.2

Effect of the bath constituents on the rate of deposition at various temperatures

Zincating time : 10 – 12 sec

pH of EN bath : 9.0

Zincating type : ZNCT- 4 (single)

Surface to volume ratio : 1:20

Density of Ni : 8.5 g / cm^3

Plating time : 1 hour

Bath Constituents	Basic Nickel Carbonate	N T A	N_2H_4	Rate of deposition in µm / hr at temperatures			
				328K	333K	343K	348K
	1A	1B	1C	0.1200	0.1300	0.1800	0.2200
	2A	1B	1C	0.1250	0.1350	0.1860	0.2300
	3A	1B	1C	0.1300	0.1400	0.1900	0.2400
	1A	2B	1C	0.1300	0.1350	0.1800	0.2300
	1A	3B	1C	0.1300	0.1350	0.1800	0.2350
	1A	1B	2C	0.1250	0.1400	0.2300	0.2400
	1A	1B	3C	0.1400	0.2300	0.2400	0.2500
	1A	1B	Excess	0.2300	0.2450	0.2500	0.3300

A = 1.2536 g $NiCO_3.2Ni(OH)_2.4H_2O$ / litre .

B = 1.9114g Nitrilotriacetic acid [NTA] / litre .

C = 0.5 g N_2H_4 / litre.

Table – 3.3

Effect of the bath constituents on the nature of coating and the bath stability

Zincating time : 10 – 12 sec	pH of EN bath : 9.0
Zincating type : ZNCT- 4 (single)	Surface to volume ratio : 1:20
Density of Ni : 8.5 g / cm^3	Plating time : 1 hour
Temperature : 348 K	

Bath Constituents	Basic Nickel Carbonate	N T A	N_2H_4	Stability of bath	Turbidity	Surface finish
Basic Nickel Carbonate	1A	1B	1C	Very stable	No turbidity	Matt
	2A	1B	1C	stable	slight turbidity	Matt dull
	3A	1B	1C	unstable	ppt.	Matt dull
N T A	1A	2B	1C	unstable	turbidity	Matt
	1A	3B	1C	unstable	More turbidity	Grey matt
N_2H_4	1A	1B	2C	stable	No turbidity	Matt
	1A	1B	3C	stable	No turbidity	Grey matt
	1A	1B	Excess	stable	No turbidity	Grey

A = 1.2536 g $NiCO_3.2Ni(OH)_2.4H_2O$ / litre.

B = 1.9114 g Nitrilotriacetic acid [NTA] / litre.

C = 0.5 g N_2H_4 / litre.

3.4 EFFECT OF THE pH ON THE STABILITY OF THE BATH

Presence of the OH^{-1} ions is essential[3,9] in the reduction of metal ions in a hydrazine based electroless plating bath as discussed in Chapter-I. Hence the pH of the bath solution plays an important role in both the stability and the nature of coating. Studies carried out at various pH values, regulated by the addition of ammonia as indicated in Table –3.4 and 3.5, reveal that a good deposition can be obtained at pH = 10.75. All the subsequent experiments are therefore carried out at standardized pH = 10.75 and 0.01 and 0.02 M Ni^{2+} ion concentrations in the bath solution.

3.5 EFFECT OF VARIOUS TYPES AND CONCENTRATIONS OF ZINCATING SOLUTION IN PRE-PLATE TREATMENT OF THE ALUMINIUM SUBSTRATE

Zincating[10] is an important and essential step in the pre-treatment of the aluminium surface in the plating process. Various zincating solutions have been tried and reported earlier in the literature on pre-plate treatment of aluminium substrate. Most of the zincating solutions are prepared by mixing ZnO and NaOH in an aqueous solution. Known[3,11] zincating solutions ZNCT –1,2 and 3 (Table – 2.1) are found to give a dark grey or black nickel deposition. Excessive presence of Na^{+1} ions in a strongly alkaline zincating solution (Fig. 3.4 and 3.5) probably detracts good quality deposit from equally strong alkaline EN bath. Whereas zincating solution ZNCT – 4 which contain

Table – 3.4
Effect of the Temperature and the pH on EN Plating.

Concentration of Ni $^{2+}$: 0.01M

Bath composition : 1:1:1

Zincating type: ZNCT- 4 (single).

Zincating time: 10 – 12 sec.

Area of the plate: 28 cm^3

Surface to volume ratio : 1:20.

Plating time : 1 hour.

Density of Ni : 8.5 g / cm^3

Plate No.	pH	Weight gain in g and type of coating at various temperatures					
		298K	313K	318K	323K	328K	333K
1	4	Nil	Nil	Nil	Nil	Nil.	Nil.
2	6	Nil	Nil	Nil	Nil	Nil.	Nil.
3	7	Nil	Nil	Nil	Nil	Nil.	Nil.
4	8	Nil	Nil	Nil	Nil	Nil.	Nil.
5	9	Nil	Nil	Nil	Nil	0.0010 (grey)	0.0012 (grey)
6	10	Nil	Nil	Nil	Nil	0.0016 (grey)	0.0018 (grey)
7	11	Nil	Nil	Nil	0.0020 (grey)	0.0025 (grey)	0.0031 (grey)

Table – 3.5

Effect of the pH on the thickness and rate of deposition in EN plating at 328K.

Concentration of Ni^{2+} : 0.01M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single).

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour

Plate code No.	pH	Weight gain g	thickness μm	Deposition rate μm / hr	Surface finish	Stability of bath
P-1	8.5	0.0011	0.046217	0.046217	Grey	Stable
P-2	9.0	0.0013	0.054626	0.054626	Grey	Stable
P-3	9.5	0.0015	0.063027	0.06302	Grey	Stable
P-4	10.0	0.0020	0.084029	0.084029	Grey	Stable
P-5	10.5	0.0028	0.117651	0.117651	Grey	Stable
P-6	10.75	0.0031	0.130248	0.130248	matt	Stable
P-7	11.00	0.0033	0.138660	0.138660	matt	Unstable

tartarate salt (same table) yields a good matt finish nickel deposit. From the experiments carried out with various concentrations of this ZNCT-4 solution (Table - 3.6), it is evident that 0.025 M concentration of this solution is ideal for obtaining deposit of the desired texture. Zincating period is also an important factor which determines the nature of the metal coating. It was noticed during this study with different zincating periods, that the single zincating (Fig.- 3.4, 3.5, 3.12 and 3.13) process of short duration of 10-12 seconds (Table- 3.7) gives the desired nickel deposition.

3.6 EFFECT OF VARIOUS ALKALINE pH REGULATORS ON THE QUALITY OF DEPOSITION

As stated earlier, hydrazine based electroless plating baths operate in an alkaline medium. Hence bases are used in regulating the pH of these baths. Experiments are carried out by using NH_3[3], N_2H_5OH ($N_2H_4.H_2O$), NaOH[12] and K_2CO_3[3] solutions as pH adjusters. A stable bath and a good quality coating is obtained only with NH_3 (Table-3.8) as a pH regulating agent. With the addition of NaOH and K_2CO_3 solution the EN bath becomes unstable due to the disolution of base aluminium metal in this strongly alkaline medium. In the case of N_2H_5OH, since N_2H_4 is a strong ligand, concentration of the free Ni^{+2} ions is decreased thus affecting the bath. In this case, the OH^{-1} ions of this base seems to preferentially attack the substrate metal.

Table – 3.6

Effect of the concentration of zincating ZNCT-4 solution on the thickness and rate of deposition .

Concentration of Ni $^{2+}$: 0.01M

Area of the plate: 28 cm^2

Bath composition : 1:1:1

Temperature :348 K , pH = 10.75

Zincating time : 10 – 12 sec.

Surface to volume ratio : 1:20

Density of Ni : 8.5 g / cm^3

Plating time : 1 hour

Plate code No.	**Concentration of zincating solution**	**Weight gain g**	**thickness μm**	**Deposition rate μm / hr.**	**Surface finish**	**Stability of bath**
Z – 5	0.01	0.0015	0.088235	0.088235	Matt.	Stable
Z – 6	0.025	0.0034	0.20000	0.20000	Matt. Bright.	Stable
Z – 7	0.05	0.0041	0.241176	0.241176	Black Matt.	Stable
Z – 8	0.1	0.0080	0.3360	0.3360	Black	Stable

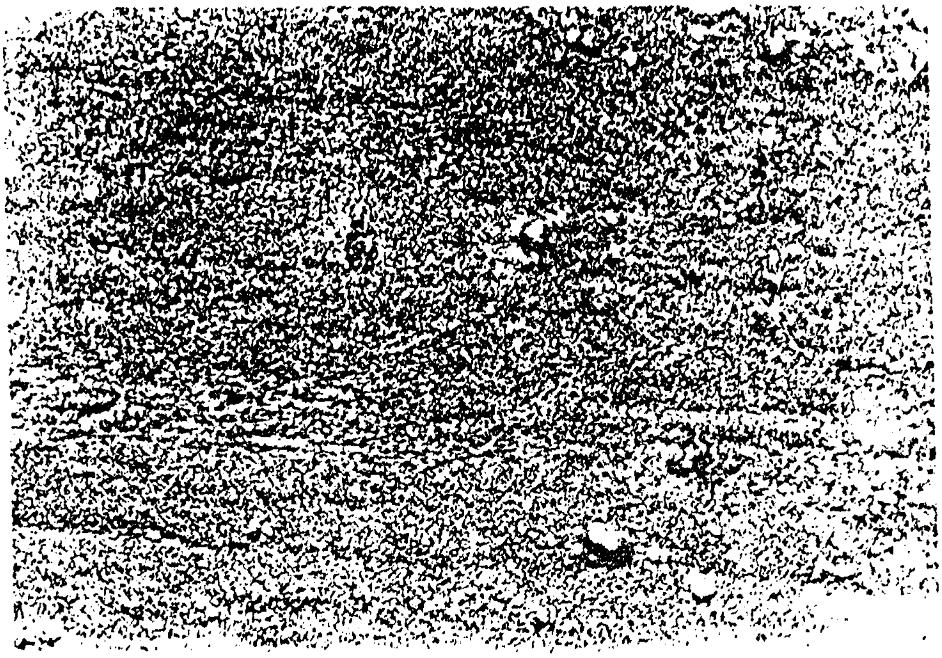


Figure 3.4 : Single Zincated Aluminium Surface - Magnification 650X

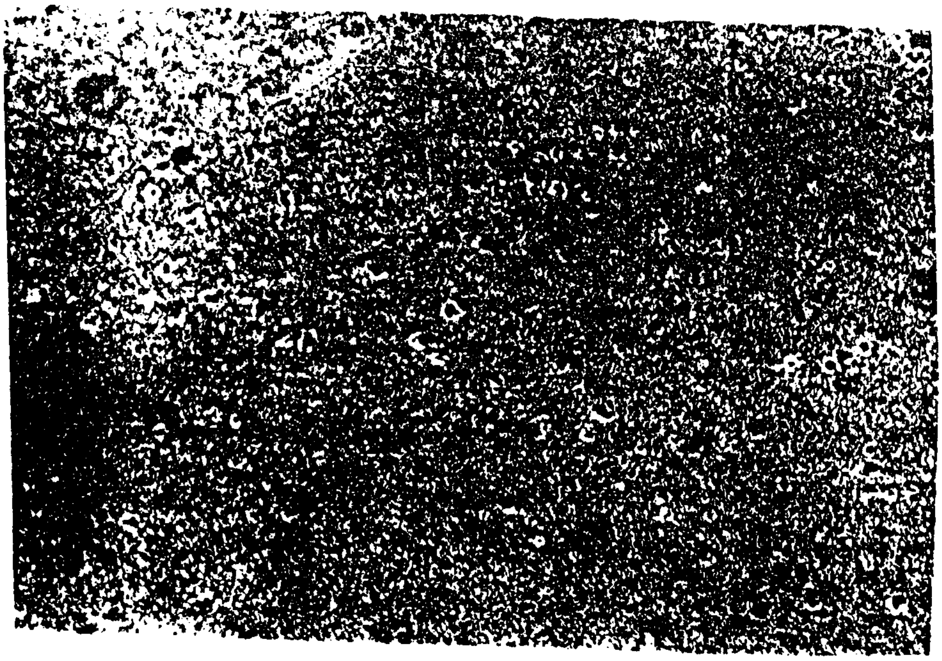


Figure 3.5: Double Zincated Aluminium Surface - Magnification 650X

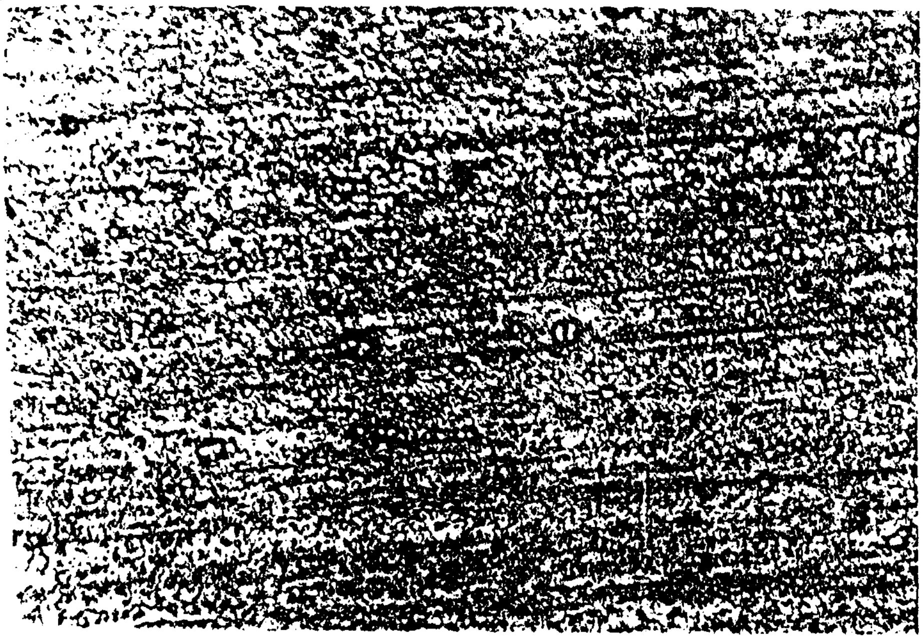


Figure 3.12: Photograph of EN Coated Aluminium Plate with Excess Zincating Magnification 650X

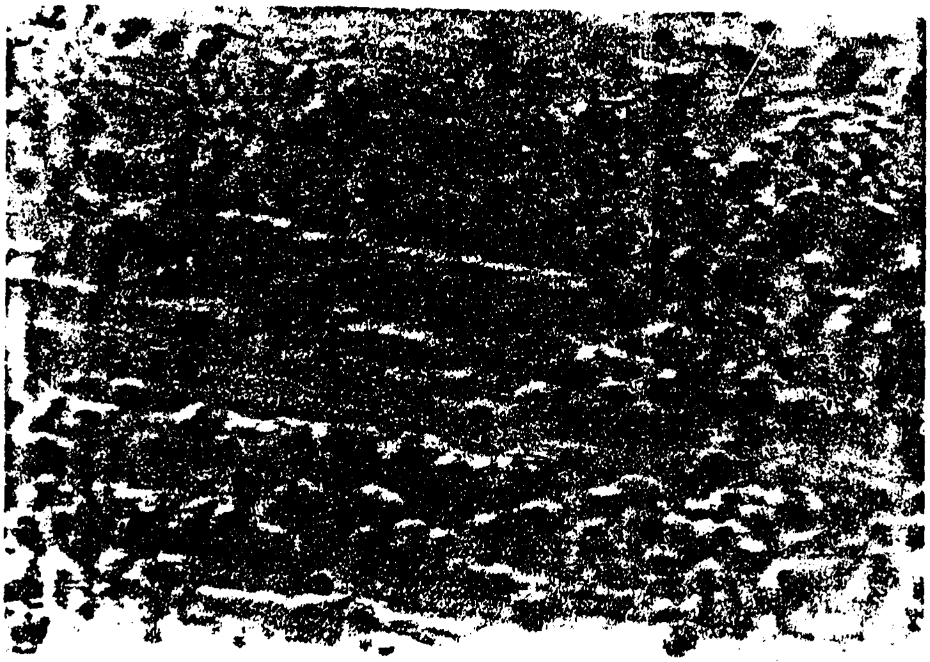


Figure 3.13: Photograph of EN Coated Aluminium Plate with Double Zincating Magnification 650X

Table – 3.7

Effect of the zincating time on the thickness and rate of deposition

Concentration of Ni^{2+} : 0.01M	Area of the plate: 28 cm^2
Bath composition : 1:1:1	Temperature :348 K , pH = 10.75
Zincating type : ZNCT- 4 (single)	Surface to volume ratio : 1:20
Density of Ni : 8.5 g / cm^3	Plating time : 1 hour

Plate code No.	Zincating time in sec	Weight gain g	Thickness µm	Deposition rate µm/ hr.	Surface finish	Stability of bath
Z - 1	10 - 12	0.0050	0.20060	0.2006	Matt.	stable
Z - 4	10 - 12	0.0053	0.21268	0.21268	Matt.	stable
Z - 2	20	0.0076	0.304975	0.304975	Black dull	stable
Z - 3	30	0.0097	0.389245	0.389245	Black Matt.	stable

Table –3.8

Effect of various alkaline pH adjuster on the thickness and quality of deposition

Concentration of Ni^{2+} : 0.01M

Area of the plate: 24 cm^2

Bath composition : 1:1:1

Zincating time : 10 – 12 sec

Zincating type : ZNCT- 4 (single)

Surface to volume ratio : 1:20.

Density of Ni : 8.5 g / cm^3

pH =10.75 ,Temperature :348 K

Plate code No.	**Weight gain g**	**Thickness μm**	**pH adjuster**	**Surface finish**	**Stability of bath**
PA –1	0.0045	0.20098	NH_3	Matt.	Stable
PA –2	0.0067	0.32843	N_2H_4	Dark grey	Stable
PA –3	0.0024	0.11764	NaOH	Grey	turbidity
PA –4	0.0055	0.26960	K_2CO_3	Grey with particles	turbidity

3.7 EFFECT OF TEMPERATURE ON EN PLATING

In an attempt to optimise the temperature for nickel deposition of desired quality by electroless plating from novel bath, experiments were carried out at various temperatures from 333 to 353 K. The results of this investigation, with 0.01 M of Ni^{+2} ion concentration in bath solution, are presented in Tables – 3.9 to 3.14.

Similarly, experiments were also done with 0.02M Ni^{+2} bath solution in the same range of temperatures (Table – 3.16 to 3.22) wherein it is observed that the deposition and the stability of the bath was not of the required nature.

3.8 MECHANISM OF THE Ni^{+2} REDUCTION WITH N_2H_4 IN PRESENCE OF NTA

Mechanism of the reduction of Ni^{+2} ions by the hydrazine in the presence of nitrilotriacetate complexing agent can be explained in the following manner.

Basic nickel carbonate reacts with nitrilotriacetic acid, in an heterogeneous reaction, to give nickel nitrilotriacetate. Aqueous solution of this salt when treated with hydrazine hydrate yields nickel hydrazinium nitrilotriacetate[13,14].

$$NiCO_3.2Ni(OH)_2.4H_2O + 3N(CH_2COOH)_3 \rightarrow 3[N(CH_2COO)_3]HNi + CO_2 + 9\,H_2O \ldots (i)$$

$$N(CH_2COO)_3\,HNi + N_2H_4.H_2O \rightarrow N(CH_2COO)_3\,(N_2H_4)Ni + H_2O \ldots\ldots\ldots\ldots (ii)$$

Nickel hydrazinium nitrilotriacetate ionizes in an aqueus medium, in the following reaction, to give hydrazinium ion which is a source for hydrazine, a strong reducing agent.

$2\,N(CH_2COO)_3(N_2H_5)Ni \rightarrow 2\,[N(CH_2COO)_3Ni]^{-1} + 2\,N_2H_5^{+1}$ ....(iii)

$2\,N_2H_5^{+1} \rightarrow 2\,N_2H_4 + 2\,H^{+1}$ ....(iv)

$N_2H_4 + 4\,OH^{-1} \rightarrow N_2 + 4\,H_2O + 4\,e^{-1}$ ....(v)

The OH^{-1} ions are continuosly consumed during the electroless plating process. This phenomenon results in gradual lowering (Fig.3.2) of the pH of the bath solution as seen in the Table –3.15. It is therefore important to monitor and maintain the pH of the bath at the appropriate value which can be accomplished by intermitant addition of ammonia. Hydrazine is also consumed continuously during the reduction of the metal. It is therefore important to maintain the concentration of hydrazine appropriately at the standardised value for continuous deposition of the metal. This is achieved by timely replenishment of hydrazine, in the bath through the addition of hydrazine hydrate. It is therefore essential to maintain the concentration of hydrazine in the bath solution constant throughout the plating process to build up (Table – 3.23) the deposition since the thickness increases (Fig .3.3) with time.

Nickel from $[N(CH_2COO)_3 Ni]^{-1}$ ion, which is formed during the ionization as given in equation (i), subsequently undergoes reduction to nickel metal in electroless plating.

$$2\,[N(CH_2COO)_3 Ni]^{-1} + 4\,e^{-1} \rightarrow 2\,Ni^{0} + 2\,N(CH_2COO)^{-3} \quad \ldots\ldots\ldots\ldots\ldots(vi)$$

Nitrilotriacetate ion generated during this process combines with H^{+1} ions to give back nitrilotriacetic acid. During the present investigation, this acid was detected as a solid product, separating out after a long use of the electroless plating bath. NTA is also found to separate out from the bath solution when replenishment of hydrazine is stopped. The infrared spectrum of the solid product [residue] separating out is shown in Fig.3.33.

Similar machanism was proposed earlier by Wiese and Weil[5] in electroless copper deposition from bath containing EDTA as a complexing and formaldehyde as reducing agent . The ethylene diamine tetra acetic acid was detected as a product formed in this process.

$$3\,H^{+1} + N(CH_2COO)^{-3} \rightarrow N(CH_2COOH)_3$$

Table – 3.9

Effect of the pH on the thickness and rate of deposition at 333K

Concentration of Ni^{2+} : 0.01M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single).

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour

Plate code No.	pH	Weight gain g	thickness µm	Deposition rate µm/ hr	Surface finish	Stability of bath
P-8	8.5	-	-	-	-	-
P-9	9.0	0.0010	0.042016	0.042016	Grey	Stable
P-10	9.5	0.0015	0.063027	0.063027	Grey	Stable
P-11	100	0.0018	0.075633	0.075633	Grey	Stable
P-12	10.5	0.0026	0.109247	0.109247	Grey matt	Stable
P-13	10.75	0.0032	0.134458	0.134458	matt	Stable
P-14	11.00	0.0035	0.147064	0.147064	matt	unstable

Table – 3.10

Effect of the pH on the thickness and rate of deposition at 338K

Concentration of Ni^{2+} : 0.01M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single)

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour

Plate code No.	pH	Weight gain g	thickness µm	Deposition rate µm / hr.	Surface finish	Stability of bath.
P-15	8.5	0.0011	0.046218	0.046218	Grey	Stable
P-16	9.0	0.0015	0.063027	0.063027	Grey	Stable
P-17	9.5	0.0017	0.071431	0.071431	Grey	Stable
P-18	100	0.0022	0.09244	0.09244	Grey	Stable
P-19	10.5	0.0027	0.113449	0.113449	Grey	Stable
P-20	10.75	0.0033	0.138660	0.138660	matt	Stable
P-21	11.00	0.0035	0.147064	0.147064	matt	unstable

Table –3.11

Effect of the pH on the thickness and rate of deposition at 343K

Concentration of Ni^{2+} : 0.01M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single)

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour.

Plate code No.	pH	Weight gain g	thickness µm	Deposition rate µm / hr.	Surface finish	Stability of bath
P-22	8.5	0.0013	0.054623	0.054623	Grey	Stable
P-23	9.0	0.0017	0.071431	0.071431	Grey	Stable
P-24	9.5	0.0020	0.084036	0.084036	Grey	Stable
P-25	10.0	0.0024	0.100844	0.100844	Grey	Stable
P-26	10.5	0.0030	0.126055	0.126055	Grey	Stable
P-27	10.75	0.0035	0.147064	0.147064	matt	Stable
P-28	11.00	0.0040	0.168074	0.168074	matt	unstable

Table –3. 12

Effect of the pH on the thickness and rate of deposition at 348K

Concentration of Ni^{2+} : 0.01M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single)

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour

Plate code No.	pH	Weight gain grams	thickness µm	Deposition rate µm / hr	Surface finish	Stability of bath
P-29	8.5	0.0019	0.079834	0.079834	Grey	Stable
P-30	9.0	0.0026	0.10924	0.109247	Grey	Stable
P-31	9.5	0.0030	0.126055	0.126055	matt	Stable
P-32	100	0.0035	0.147064	0.147064	matt	Stable
P-33	10.5	0.0042	0.176477	0.176477	matt	Stable
P-34	10.75	0.0053	0.222697	0.222697	matt	Stable
P-35	11.00	0.0063	0.252809	0.252809	matt	unstable

Table – 3.13

Effect of the pH on the thickness and rate of deposition at 353K

Concentration of Ni^{2+} : 0.01M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single)

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour

Plate code No.	pH	Weight gain g	thickness µm	Deposition rate µm / hr	Surface finish	Stability of bath
P-36	8.5	-	-	-	-	-
P-37	9.0	0.0023	0.096636	0.096636	Grey	Stable
P-38	9.5	0.0031	0.130257	0.130257	matt	Stable
P-39	10.0	0.0036	0.151264	0.151264	matt	Stable
P-40	10.5	0.0045	0.189074	0.189074	matt	Stable
P-41	10.75	0.0058	0.243706	0.243706	matt	Stable
P-42	11.00	0.0068	0.285725	0.285725	matt	unstable

Table – 3.14

Effect of the pH and the temperature on the thickness , rate of deposition and stability of bath

Concentration of Ni $^{2+}$: 0.01M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single)

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour.

pH of bath.	Rate of deposition at various temperature in μm / hr.						Stability of bath
	328k	333k	338k	343k	348k	353k	
8.5	0.046217	-	0.046218	-	0.079834	-	stable
9.0	0.054626	0.042016	0.063027	0.071431	0.109247	0.09663	stable
9.5	0.063027	0.063027	0.071431	0.084036	0.126055	0.130257	stable
10.00	0.084029	0.075633	0.09244	0.10084	0.147064	0.151264	stable
10.50	0.107651	0.109297	0.113449	0.126055	0.176477	0.180074	stable
10.75	0.130248	0.134458	0.138660	0.147064	0.222697	0.243706	stable
11.00	0.138640	0.147064	0.147064	0.168074	0.264715	0.285725	unstable

Table 3.16

Effect of the pH on the thickness and rate of deposition at 328K with 0.02M Ni^{2+} ions

Concentration of Ni^{2+} : 0.02M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single)

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour

Plate code No.	pH	Weight gain g	Thickness μm	Deposition rate μm / hr	Surface finish	Stability of bath
-	8.5	-	-	-	-	-
P-43	9.0	0.0018	0.075633	0.075633	Grey	Stable
P- 44	9.5	0.0020	0.084036	0.084036	Grey	Stable
P- 45	100	0.0028	0.117651	0.117651	Grey	Stable
P- 46	10.5	0.0030	0.126055	0.126055	Grey	Stable
P- 47	10.75	0.0035	0.147064	0.126055	matt	Stable
P- 48	11.00	0.0038	0.159669	0.159669	matt	unstable

Table-3.17

Effect of the pH on the thickness and rate of deposition at 333K

Concentration of Ni^{2+} : 0.02M

Area of the plate: 28 cm^2

Bath composition : 1:1:1

Zincating time : 10 – 12 sec

Zincating type : ZNCT- 4 (single)

Surface to volume ratio : 1:20

Density of Ni : 8.5 g / cm^3

Plating time : 1 hour

Plate code No.	pH	Weight gain g	Thickness µm	Deposition rate µm/ hr	Surface finish	Stability of bath
-	8.5	-	-	-	-	-
P-49	9.0	0.0020	0.084029	0.084029	Grey	Stable
P- 50	9.5	0.0022	0.092437	0.092437	Grey	Stable
P- 51	10.0	0.0029	0.127853	0.127853	Grey	Stable
P- 52	10.5	0.0032	0.140791	0.140791	Grey	Stable
P- 53	10.75	0.0038	0.159669	0.159669	matt	Stable
P- 54	11.00	0.0040	0.168073	0.168073	matt	unstable

Table –3.18

Effect of the pH on the thickness and rate of deposition at 338K.

Concentration of Ni^{2+} : 0.02M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single)

Density of Ni : 8.5 g/cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour

Plate code No.	pH	Weight gain g	Thickness μm	Deposition rate μm / hr.	Surface finish	Stability of bath
-	8.5	-	-	-	-	-
P-55	9.0	0.0023	0.096636	0.096636	Grey	Stable
P- 56	9.5	0.0028	0.117651	0.117651	Grey	Stable
P- 57	10.0	0.0031	0.130247	0.130247	Grey	Stable
P- 58	10.5	0.0035	0.147064	0.147064	Grey	Stable
P- 59	10.75	0.0039	0.163871	0.163871	matt	Stable
P- 60	11.00	0.0042	0.176477	0.176477	matt	unstable

Table –3.19

Effect of the pH on the thickness and the rate of deposition at 343K

Concentration of Ni^{2+} : 0.02M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single)

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour

Plate code No.	pH	Weight gain g	Thickness µm	Deposition rate µm / hr.	Surface finish	Stability of bath
-	8.5	-	-	-	-	-
P-61	9.0	0.0026	0.109243	0.109243	Grey	Stable
P- 62	9.5	0.0030	0.126049	0.126049	Grey	Stable
P- 63	10.0	0.0032	0.134458	0.134458	Grey	Stable
P- 64	10.5	0.0036	0.151264	0.151264	Grey	Stable
P- 65	10.75	0.0040	0.168073	0.168073	matt .	Stable
P- 66	11.00	0.0044	0.184812	0.184812	matt .	unstable

Table – 3.20

Effect of the pH on the thickness and rate of deposition at 348K

Concentration of Ni^{2+} : 0.02M

Area of the plate: 28 cm^2

Bath composition : 1:1:1

Zincating time : 10 – 12 sec

Zincating type : ZNCT- 4 (single)

Surface to volume ratio : 1:20

Density of Ni : 8.5 g / cm^3

Plating time : 1 hour

Plate code No.	pH	Weight gain g	Thickness µm	Deposition rate µm / hr.	Surface finish	Stability of bath
-	8.5	-	-	-	-	-
P-67	9.0	0.0027	0.113449	0.113449	Grey	Stable
P- 68	9.5	0.0032	0.134451	0.134451	Grey	Stable
P- 69	10.0	0.0035	0.147057	0.147057	Grey	Stable
P- 70	10.5	0.0040	0.168075	0.168075	matt	Stable
P- 71	10.75	0.0050	0.210074	0.210074	matt	Stable
P- 72	11.00	0.0055	0.231101	0.231101	matt	turbidity

Table –3.21

Effect of the pH on the thickness and rate of deposition at 353K.

Concentration of Ni^{2+} : 0.02M

Area of the plate: 28 cm^2

Bath composition : 1:1:1

Zincating time : 10 – 12 sec

Zincating type : ZNCT- 4 (single)

Surface to volume ratio : 1:20

Density of Ni : 8.5 g / cm^3

Plating time : 1 hour

Plate code No.	pH	Weight gain g	Thickness µm	Deposition rate µm / hr.	Surface finish	Stability of bath.
-	8.5	-	-	-	-	-
P-73	9.0	0.0030	0.126049	0.126049	Grey	Stable
P- 74	9.5	0.0034	0.142855	0.142855	Grey	Stable
P- 75	10.0	0.0037	0.155468	0.155468	Matt	Stable
P- 76	10.5	0.0042	0.176477	0.176477	Matt	Stable
P- 77	10.75	0.0052	0.218495	0.218495	Matt	turbidity
P- 78	11.00	0.0058	0.243737	0.243737	Matt	turbidity

Table-3.22

Effect of the pH and the temperature on the thickness and rate of deposition with 0.02M Ni^{2+} bath.

Concentration of Ni^{2+} : 0.02M

Bath composition : 1:1:1

Zincating type : ZNCT- 4 (single)

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

Plating time : 1 hour

pH of bath.	**Rate of deposition at various temperature in μm / hr.**						Stability of bath
	328k	**333k**	**338k**	**343k**	**348k**	**353k**	
9.0	0.075633	0.084029	0.096636	0.109243	0.113449	0.126049	stable
9.5	0.084036	0.084036	0.092437	0.117651	0.126049	0.134451	stable
10.00	0.117651	0.127853	0.130247	0.134458	0.147057	0.155468	stable
10.50	0.126055	0.140741	0.147064	0.151264	0.168075	0.176477	stable
10.75	0.147064	0.159669	0.163871	0.168073	0.210074	0.218495	stable
11.00	0.159669	0.168073	0.176477	0.184812	0.231101	0.243737	turbidity.

Table –3.15

Variation of the pH of the EN bath with time

Concentration of Ni^{2+} : 0.01M	Area of the plate: 28 cm^2
Bath composition : 1:1:1	Zincating time : 10 – 12 sec
Zincating type, : ZNCT- 4 (single)	Surface to volume ratio : 1:20.
Density of Ni : 8.5 g / cm^3	pH =10.75 ,Temperature :348 K

Plate code No.	Plating time hours	Weight gain g	hickness µm	Change in pH	Surface finish	Stability of bath
R	0.25	0.0002	-	10.3810	grey	Stable
R - 1	0.50	0.0023	0.096638	10.3500	Matt.	Stable
R –2	0.75	0.0035	0.147058	10.3237	Matt.	Stable
R –3	1.00	0.0054	0.226890	10.2999	Matt.	Stable
R –4	1.25	0.0061	0.256302	10.2662	Matt.	Stable
R –5	1.50	0.0075	0.315126	10.1994	Matt.	Stable
R –6	1.75	0.0080	0.33613	10.1459	Matt.	Stable
R –7	2.00	0.0092	0.386554	10.0459	Matt.	Stable
R –8	3.00	0.0100	0.420168	10.0005	Matt.	Stable

Table –3.23

The Rate of deposition and the thickness as a function of time.

Concentration of Ni^{2+} : 0.01M

Bath composition : 1:1:1

Zincating type : ZNCT-4 (single)

Density of Ni : 8.5 g / cm^3

Area of the plate: 28 cm^2

Zincating time : 10 – 12 sec

Surface to volume ratio : 1:20

pH =10.75 ,Temperature :348 K

Plate code No.	Plating time hours	Weight gain g	thickness µm	Deposition rate µm / hr	Surface finish	Stability of bath
R - 1	0.50	0.0023	0.096638	0.193276	Matt	Stable
R –2	0.75	0.0035	0.147058	0.196077	Matt	Stable
R –3	1.00	0.0054	0.226890	0.226890	Matt	Stable
R –4	1.25	0.0061	0.256302	0.205041	Matt	Stable
R –5	1.50	0.0075	0.315126	0.210083	Matt	Stable
R –6	1.75	0.0080	0.33613	0.192074	Matt	Stable
R –7	2.00	0.0092	0.386554	0.193277	Matt	Stable

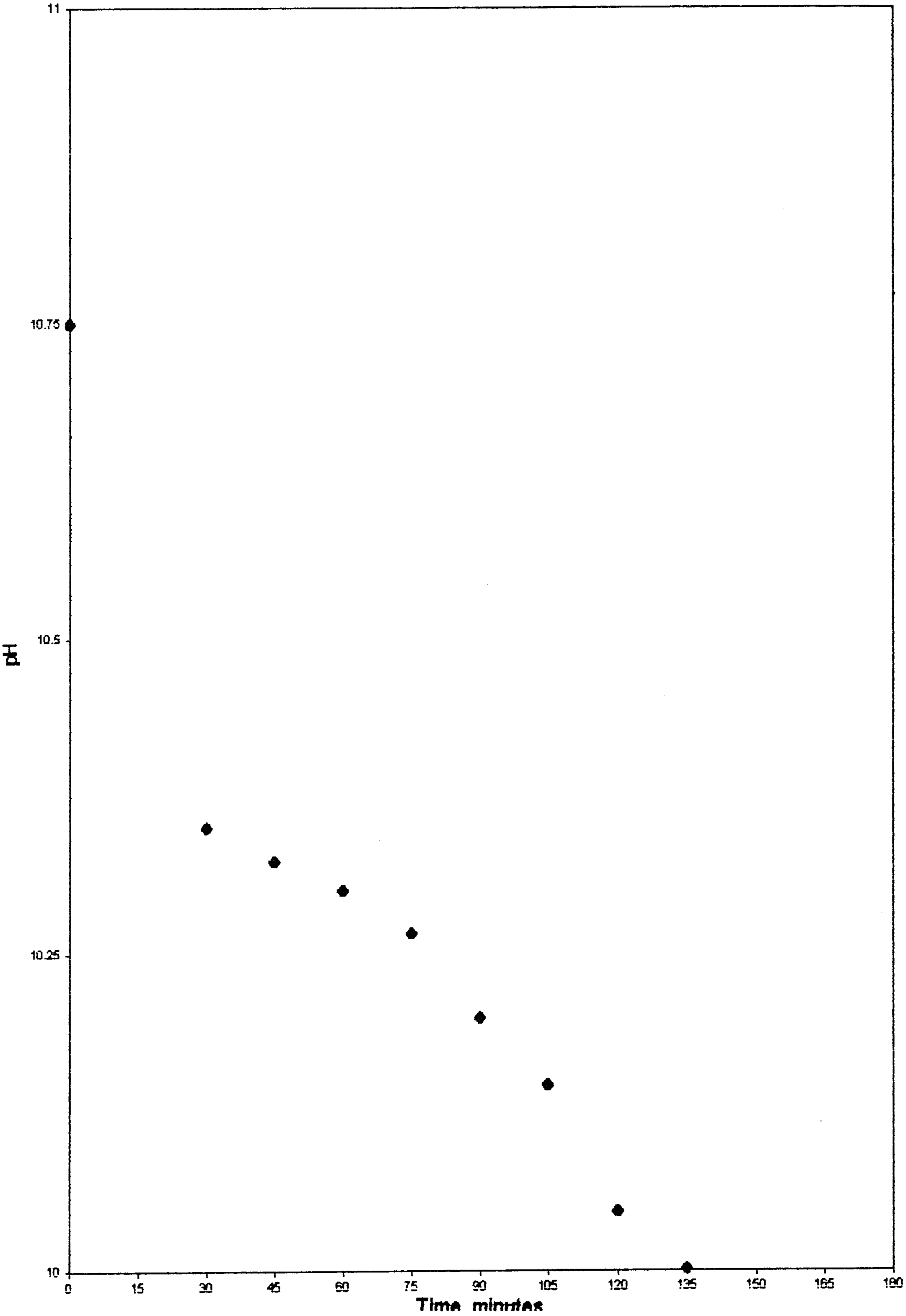
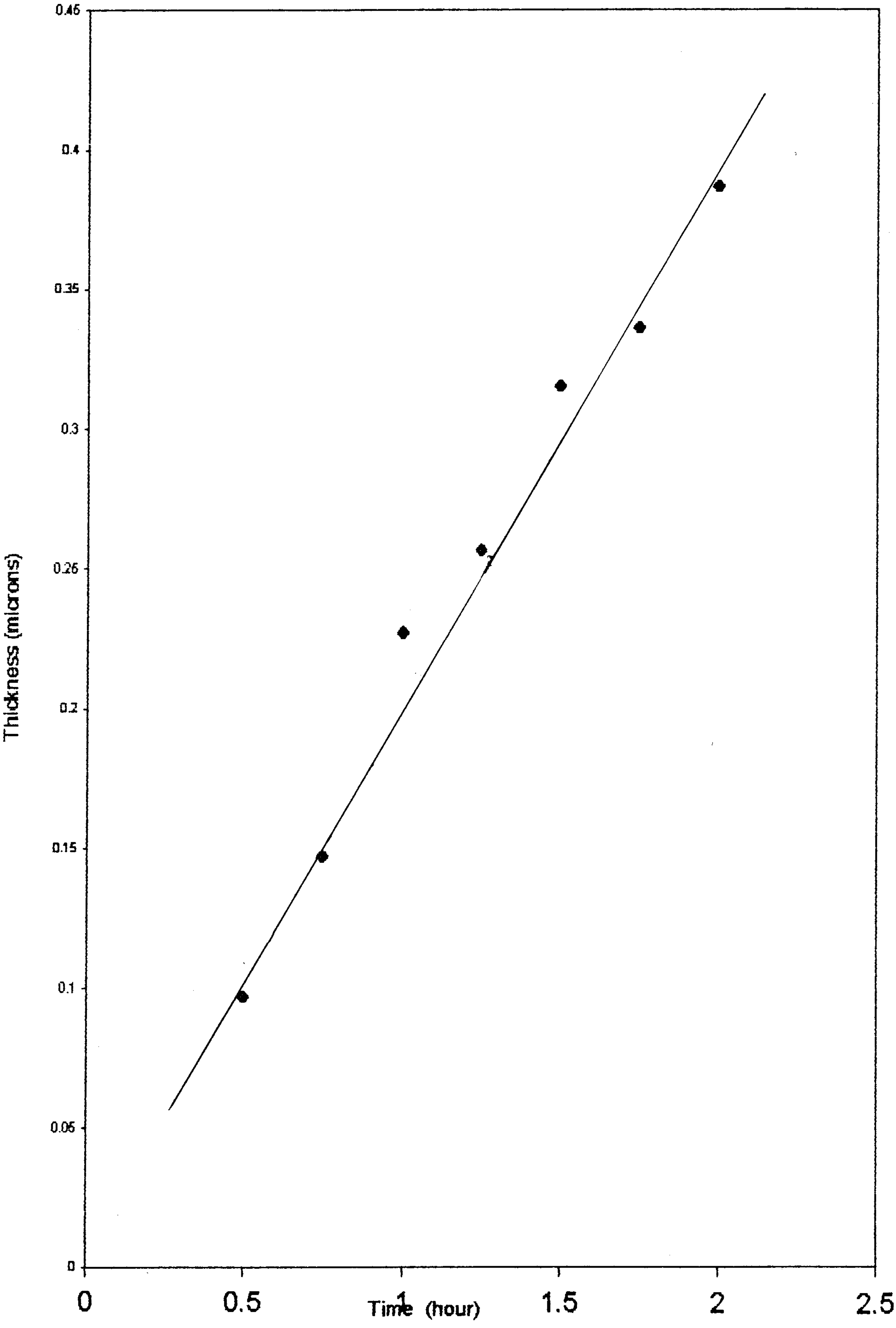


Fig.3.2:Variation of the pH of the EN bath with Time

Fig.3.3: Variation of coating thickness with time



3.9 EFFECT OF ADDITIVES ON THE NATURE OF THE COATING

In addition to a large variety of buffering or complexing agents, that have been used in the electroless plating bath, other substances have also been tried[15] and patented to improve the rate of depositon, the stability of bath and the brightness of the deposit. It has been reported that the brightness of the deposit and the rate of deposition of nickel can be enhanced by the addition of cobalt acetate[15] or zinc sulphate or uranium acetate. Similar pattern is observed (Table – 3.24) during the use of these brightners or accelerators in our study (Fig. 3.14, 3.15 and 3.16). The amount of these agents added is very critical in controlling the rate of deposition as well as the brightness of the coating.

3.10 EFFECT OF POST-PLATE TREATMENT ON THE PROPERTIES OF THE PLATED METAL

The panels, when heated in air, in a temperature controlled oven at various temperatures from 373 to 773 K for one hour, it is observed from the high resolution photographs that the surface remains stable up to a temperature of 673 K without any change in properties. However, beyond this temperature, the metal surface develops cracks although the texture of the deposit remains unaltered. Comparison of the surface texture before and after heating of plates are given in Fig. – 3.6 and 3.7 (0.01M bath); Fig. – 3.8 and 3.9 (0.02M bath); and Fig. – 3.10 and 3.11 (0.05M bath).

Table –3.24

Effect of the additives on the thickness and quality of deposition.

Concentration of Ni^{2+} : 0.01M	Area of the plate: 28 cm^2
Bath composition ; 1:1:1	Zincating time : 10 – 12 sec
Zincating type : ZNCT- 4 (single)	Surface to volume ratio : 1:20
Density of Ni : 8.5 g / cm^3	pH =10.75 ,Temperature :348 K

Plate code No.	Weight gain g	thickness µm	Type of additives	Surface finish	Stability of bath
AD –1	0.0035	0.147058	B. A.*	Matt.	Stable
AD –2	0.0042	0.17647	T.U.*	Matt.(Black)	Stable
AD –3	0.0045	0.18907	N.B.A..*	Matt	Stable
AD –4	0.0056	0.23529	C.A.Z.*	Matt.(Shining)	Stable
AD –5	0.0044	0.18487	C.A.Z.+N.B.A.*	Matt.	Stable
P -34	0.0053	0.22268	Nil.	Matt.	Stable

* Key :

B.A. = 28 mg / litre of Boric acid.

T. U.=0.5 mg / litre of Thiourea.

N.B.A.= 29 mg / litre of NaCl + 28 mg / litre of Boric acid.

C.A.Z.= 15mg / litre of Cobalt acetate + 5 mg / litre of Zinc Sulphate.

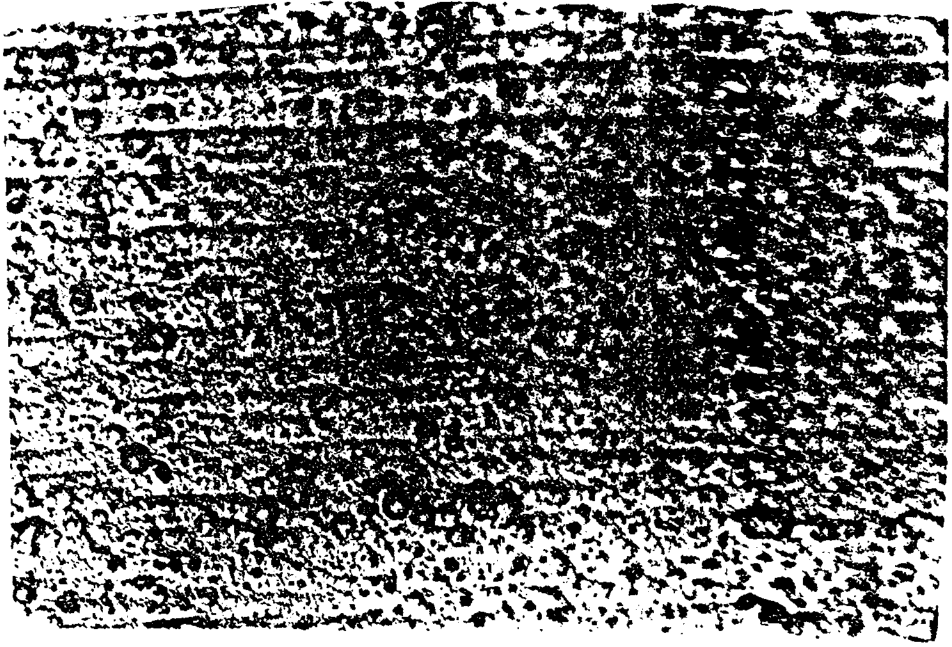


Figure 3.14: Photograph of EN [0.01M Ni^{2+}] Coated Aluminium Plate without additives Magnification 650X

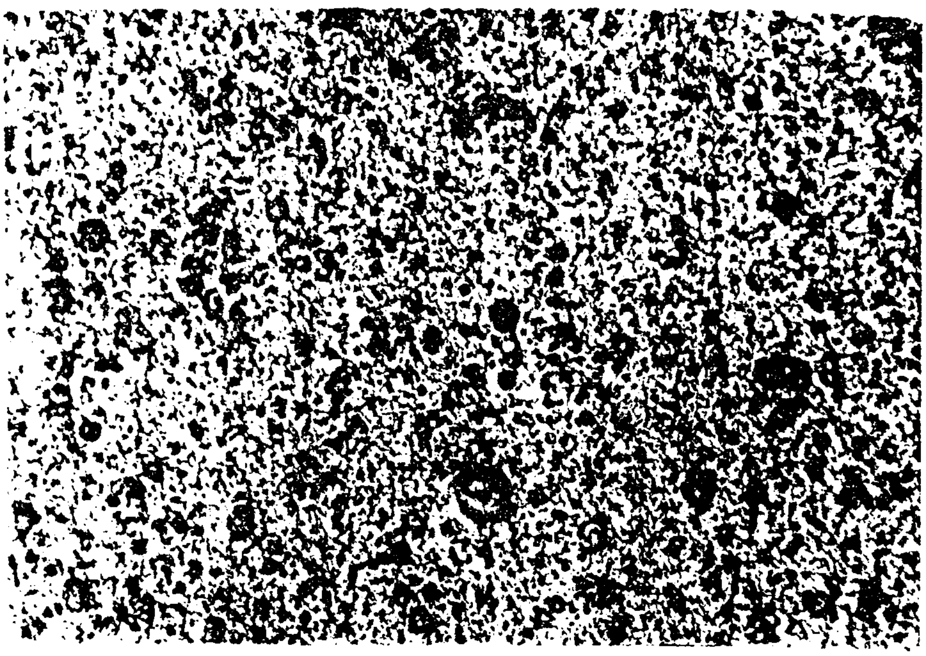


Figure 3.15: Photograph of EN [0.01M Ni^{2+}] Coated Aluminium Plate with additives* Magnification 650X

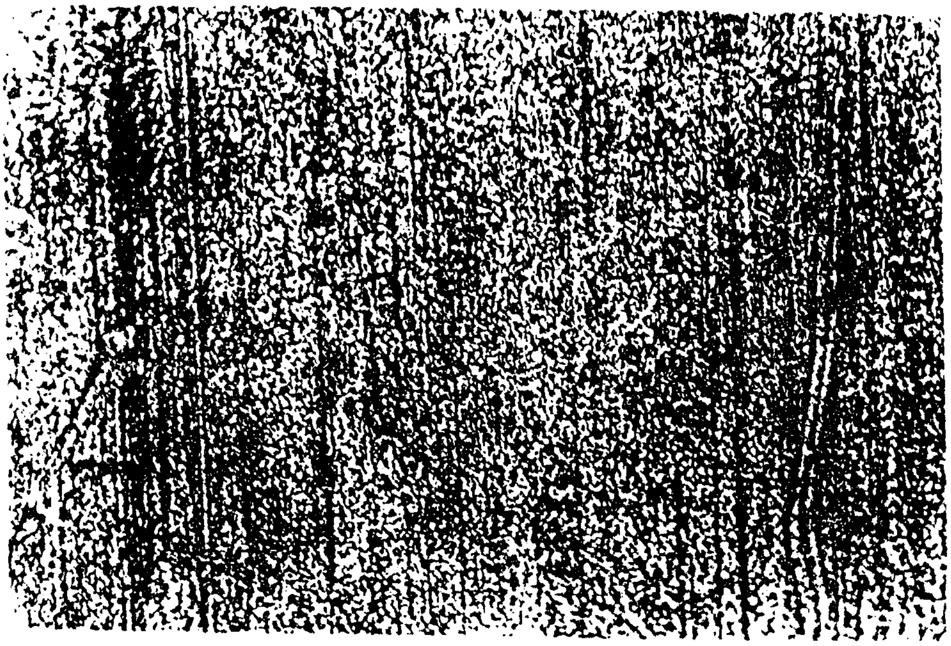


Figure 3.16: Photograph of EN [0.01M Ni^{2+}] Coated Aluminium Plate with additives** Magnification 650X

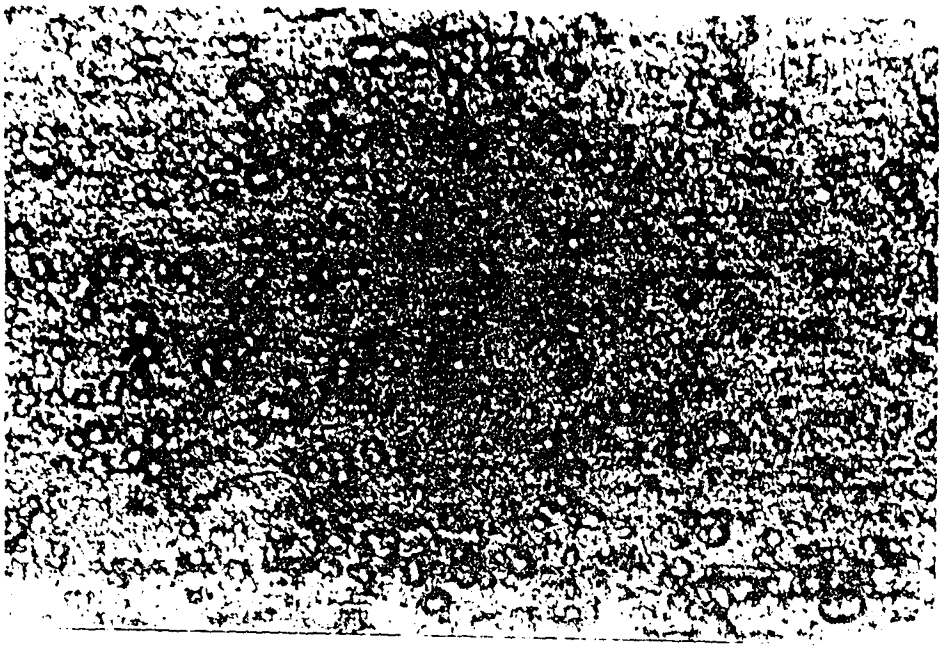


Figure 3.17: Photograph of EN [0.01M Ni^{2+},Sodium hypophosphite bath] Coated Aluminium Plate Magnification 650X

Table – 3.2

Effect of the bath constituents on the rate of deposition at various temperatures

Zincating time : 10 – 12 sec	pH of EN bath : 9.0
Zincating type : ZNCT- 4 (single).	Surface to volume ratio : 1:20
Density of Ni : 8.5 g / cm^3	Plating time : 1 hour

Bath Constituents	Basic Nickel Carbonate	N T A	N_2H_4	Rate of deposition in µm / hr at temperatures			
				328K	333K	343K	348K
[illegible]	1A	1B	1C	0.1200	0.1300	0.1800	0.2200
	2A	1B	1C	0.1250	0.1350	0.1860	0.2300
	3A	1B	1C	0.1300	0.1400	0.1900	0.2400
[illegible]	1A	2B	1C	0.1300	0.1350	0.1800	0.2300
	1A	3B	1C	0.1300	0.1350	0.1800	0.2350
[illegible]	1A	1B	2C	0.1250	0.1400	0.2300	0.2400
	1A	1B	3C	0.1400	0.2300	0.2400	0.2500
	1A	1B	Excess	0.2300	0.2450	0.2500	0.3300

A = 2.1516 g $NiCO_3.2Ni(OH)_2.4H_2O$ / litre .

B = 1.9116 g Nitrilotriacetic acid [NTA] / litre .

C = 0.5 g N_2H_4 / litre.

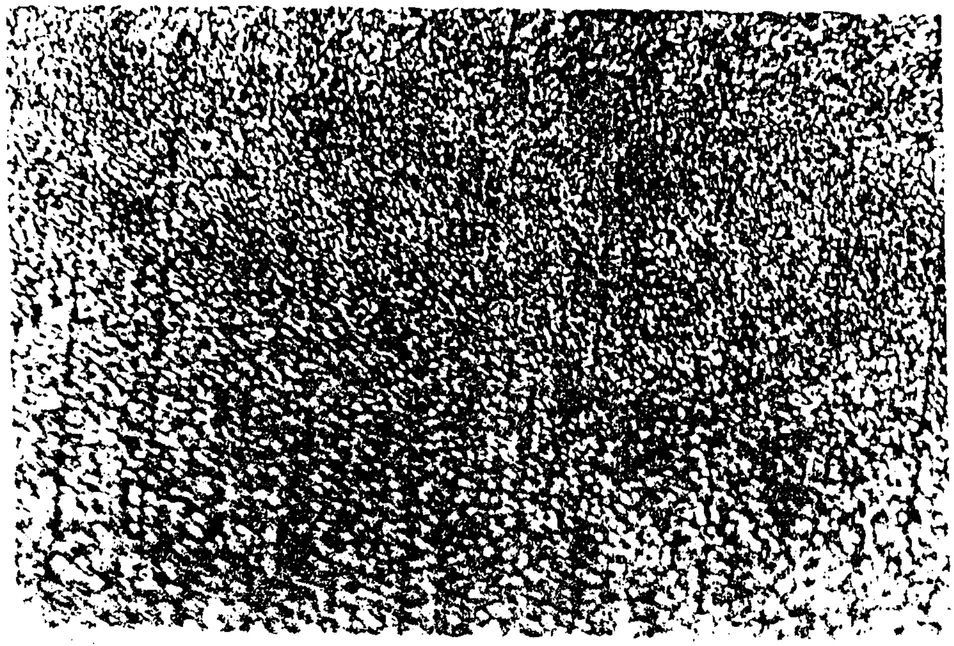


Figure 3.6: Photograph of EN [0.01M Ni $^{2+}$] Coated Aluminium Plate with Magnification 650X

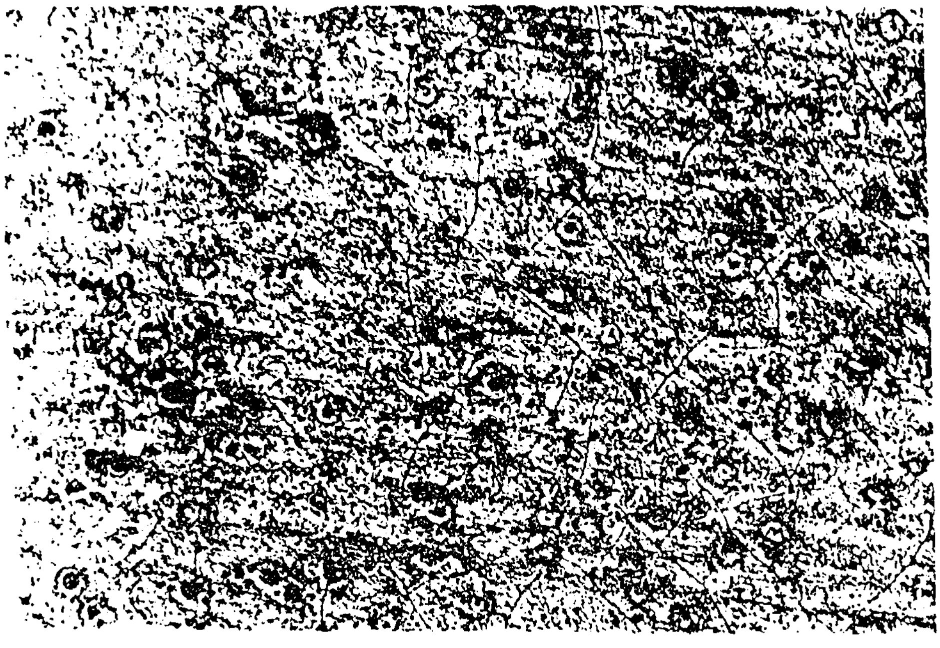


Figure 3.7: Photograph of EN [0.01M Ni $^{2+}$] Coated and Heated Aluminium Plate Magnification 650X.

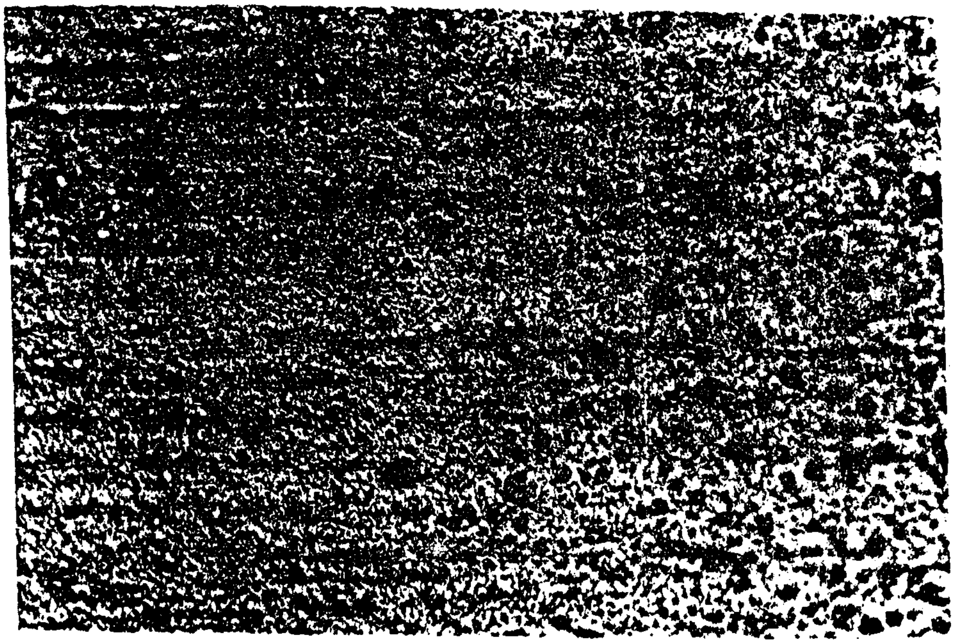


Figure 3.8: Photograph of EN [0.02M Ni $^{2+}$] Coated Aluminium Plate with Magnification 650X.

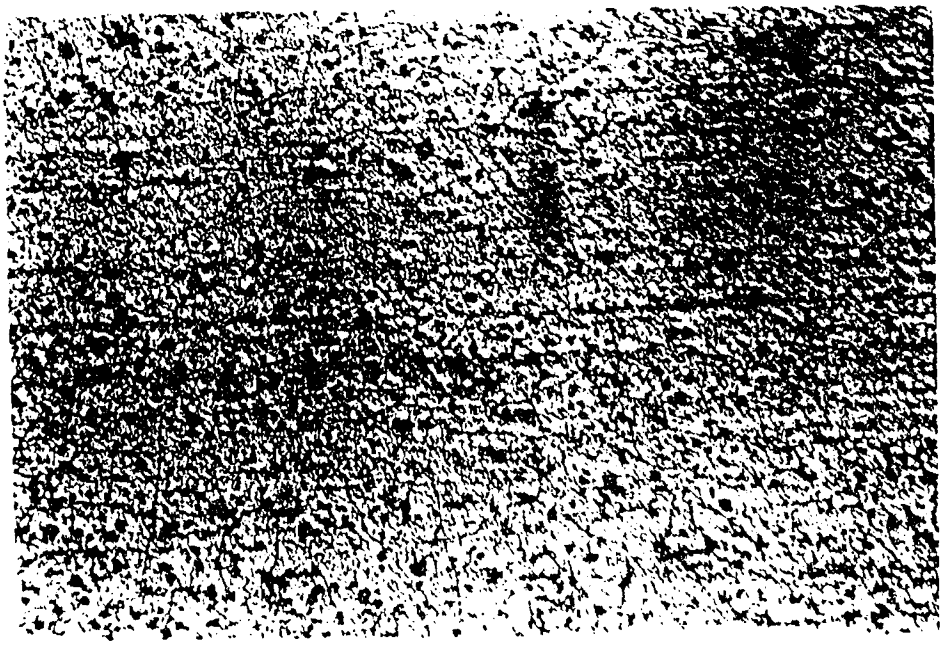


Figure 3.9: Photograph of EN [0.02M Ni $^{2+}$] Coated and Heated Aluminium Plate Magnification 650 X

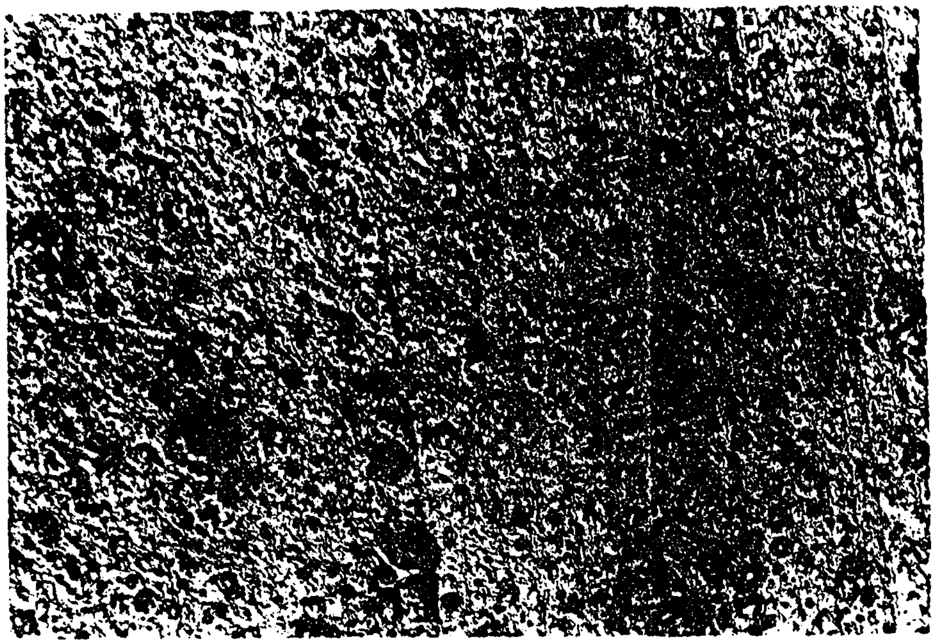


Figure 3.10: Photograph of EN [0.05M Ni $^{2+}$] Coated Aluminium Plate with Magnification 650X

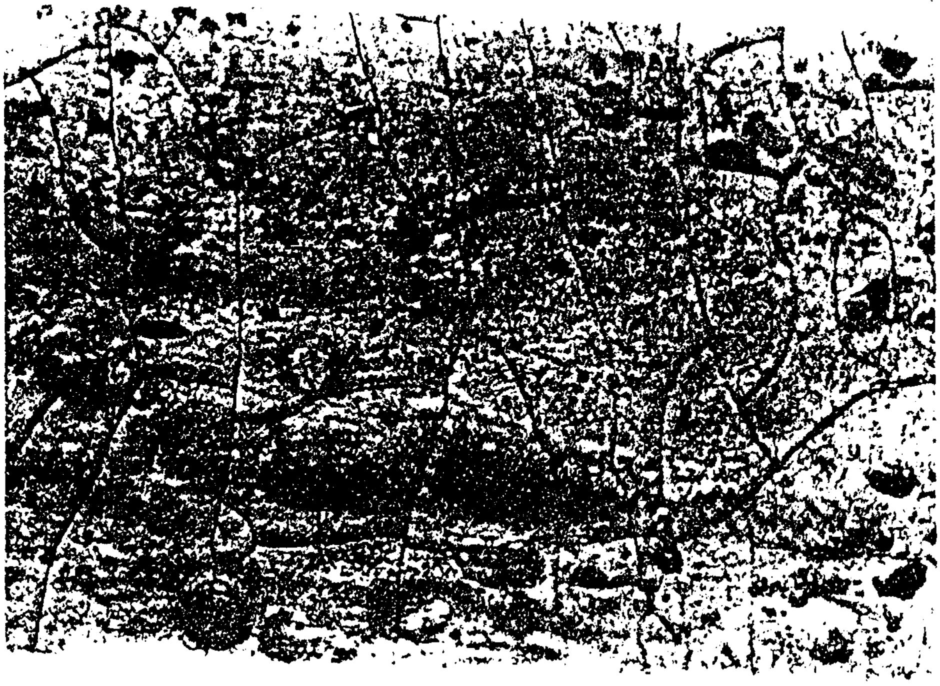


Figure 3.11: Photograph of EN [0.05M Ni $^{2+}$] Coated and Heated Aluminium Plate Magnification 650 X

3.11 SEM STUDIES OF EN COATED ALUMINIUM

Surface morphology of EN coated aluminium plates was studied by using Scanning Electron Microscope with 100 to 35,000 times magnification (Fig. 3.18 – 3.26) . This study reveals uniform deposition of nickel on the substrate .Though pits are seen on the surface of the coated plates , these pits , in patches are observed on the base metal before actual deposition is carried out .

3.12 X – RAY DIFFRACTION OF EN COATED Al PLATES

X – ray diffraction patterns of the base metal and also of the EN coated sample plates were obtained by using the instrument mentioned in the chapter Two.Comparing the patterns for aluminium base metals (Fig 3.26) with those of EN coated aluminium (Fig 3.27-3.29), one can observed additional peaks due to nickel metal ,although predominantly Al patterns are seen . The d –values calculated from this data confirms the presence of nickel metal with the d = 2.0300 in confirmation with (Table-3.25) with those reported earlier [16]. Interestingly , none of the oxides of the nickel are detected in this study with d- values .

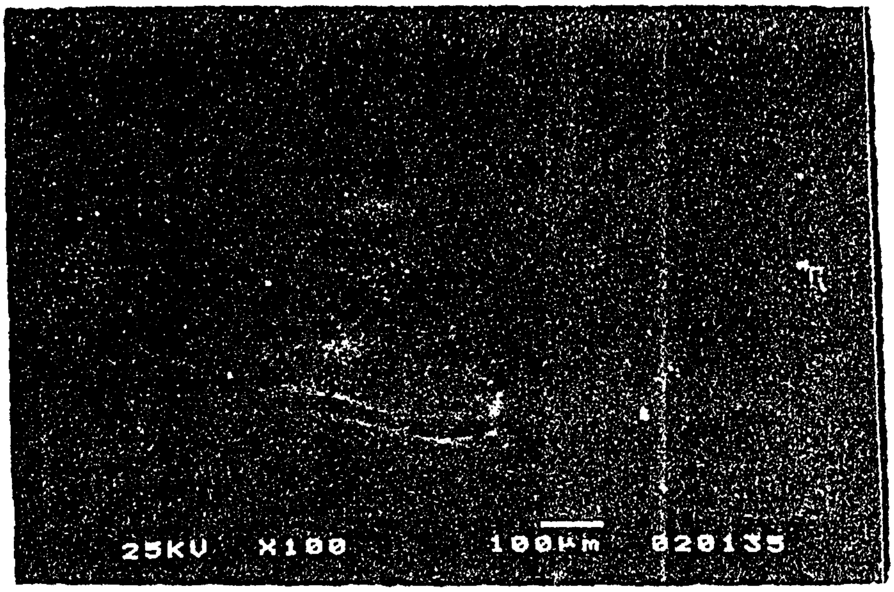


Figure 3.18 : SEM Photograph of Nickel Coated [0.01M Ni^{2+}] Aluminium Plate Magnification 100 X

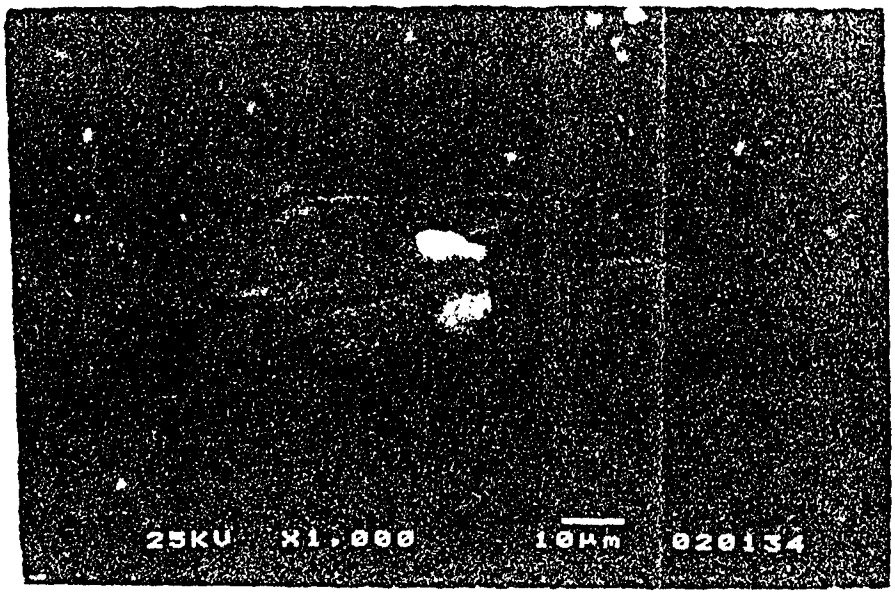


Figure 3.19 SEM Photograph of Nickel Coated [0.01M Ni^{2+}] Aluminium Plate Magnification 1000 X

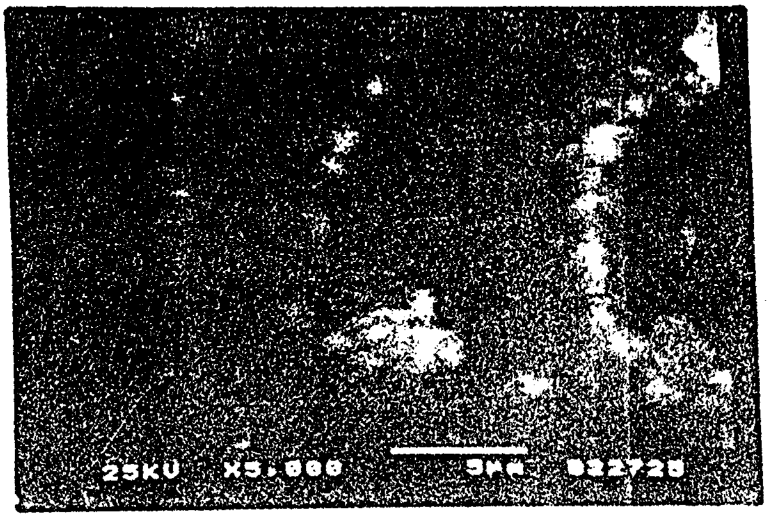


Figure 3.20 : SEM Photograph of Nickel Coated [0.01M Ni^{2+}] Aluminium Plate
Magnification 5000 X

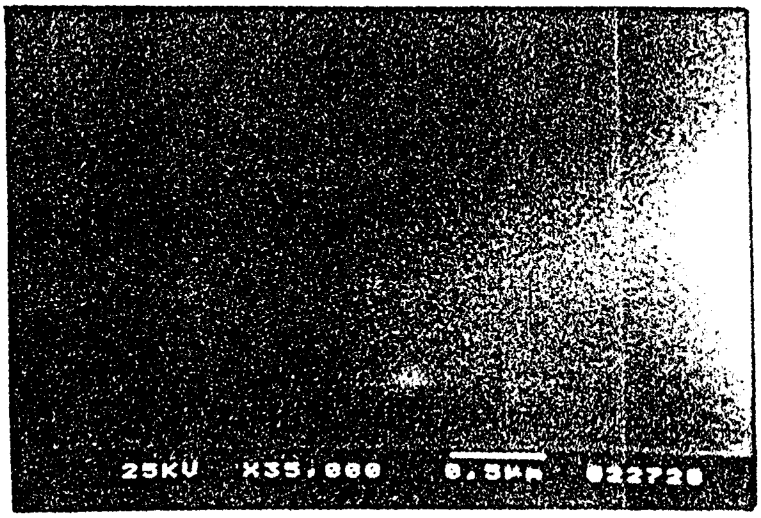


Figure 3.21 SEM Photograph of Nickel Coated [0.01M Ni^{2+}] Aluminium Plate
Magnification 35,000 X

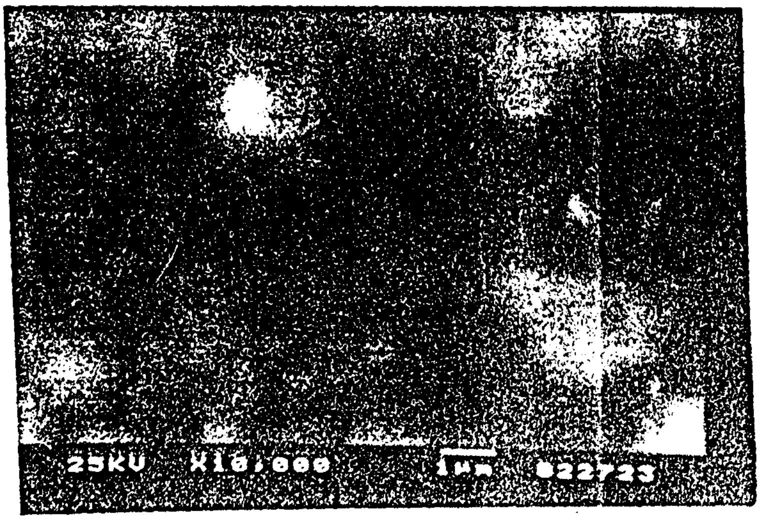


Figure 3.22 : SEM Photograph of Nickel Coated [0.01M Ni^{2+}] Aluminium Plate
Magnification 10,000 X

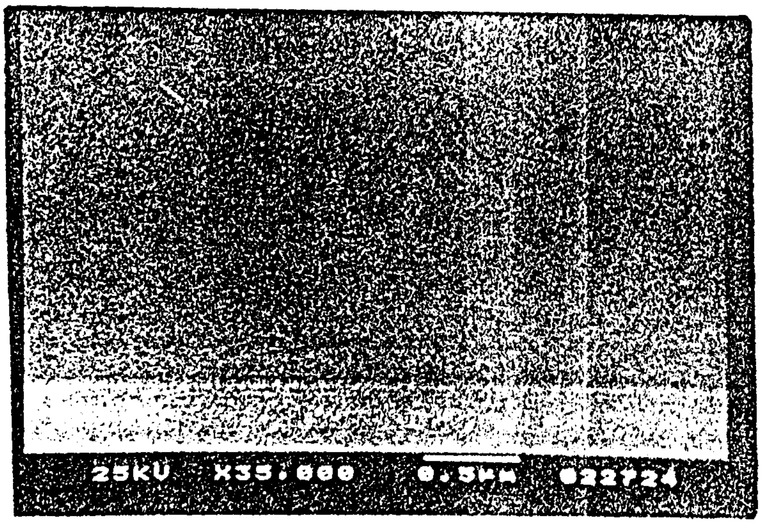


Figure 3.23 SEM Photograph of Nickel Coated [0.01M Ni^{2+}] Aluminium Plate
Magnification 35,000 X

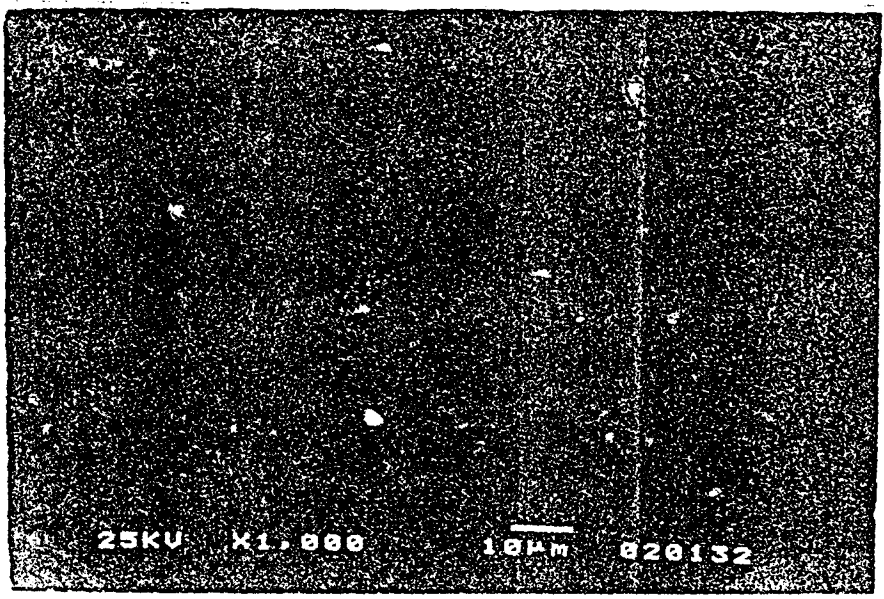


Figure 3.24 : SEM Photograph of Nickel Coated [0.01M Ni^{2+}] Aluminium Plate Magnification 1000 X

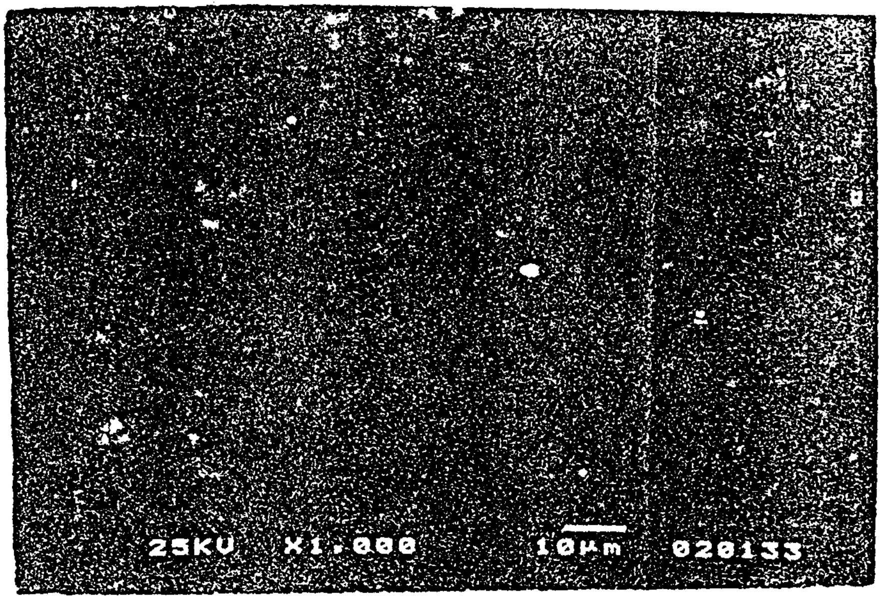


Figure 3.25 SEM Photograph of Nickel Coated [0.01M Ni^{2+}] Aluminium Plate Magnification 1000 X

Table -3.25: d – values of EN coated Aluminium and Copper plates.

Plate code	2θ	d values	I/I$_0$ %	Figure
x-1	64.7	1.4394	100	3.26
	65.1	1.43159	76.92	3.26
	44.5	2.03420	42.6	3.26
	38.3	2.34802	4.68	3.26
x – 2	64.6	1.44146	100	3.27
	64.8	1.43756	77.06	3.27
	44.3	2.03985	28.44	3.27
	44.4	2.03855	26.60	3.27
	38.0	2.36562	4.5871	3.27
x – 3	64.9	1.43552	100	3.28
	44.4	2.03855	39.79	3.28
	44.6	2.0300	42.85	3.28
	38.3	2.3480	9.1836	3.28
x – 4	65.62	1.4216	100	3.29
	65.83	1.4175	49.89	3.29
	44.82	2.0206	21.63	3.29
	44.6	2.0300	28.65	3.29
	38.82	2.3179	3.56	3.29
x- 5	65.80	1.4181	100	3.30
	66.05	1.4135	46.19	3.30
	44.985	2.0135	92.34	3.30
	45.090	2.0091	75.1	3.30
	44.60	2.0301	49.18	3.30
	38.98	2.3085	3.231	3.30
x - 6	51.2	1.7826	100	3.31
	44.0	2.0561	24.82	3.31
x – 7	51.6	1.7697	100	3.32
	44.8	2.0212	69.73	3.32
	44.6	2.0300	68.42	3.32

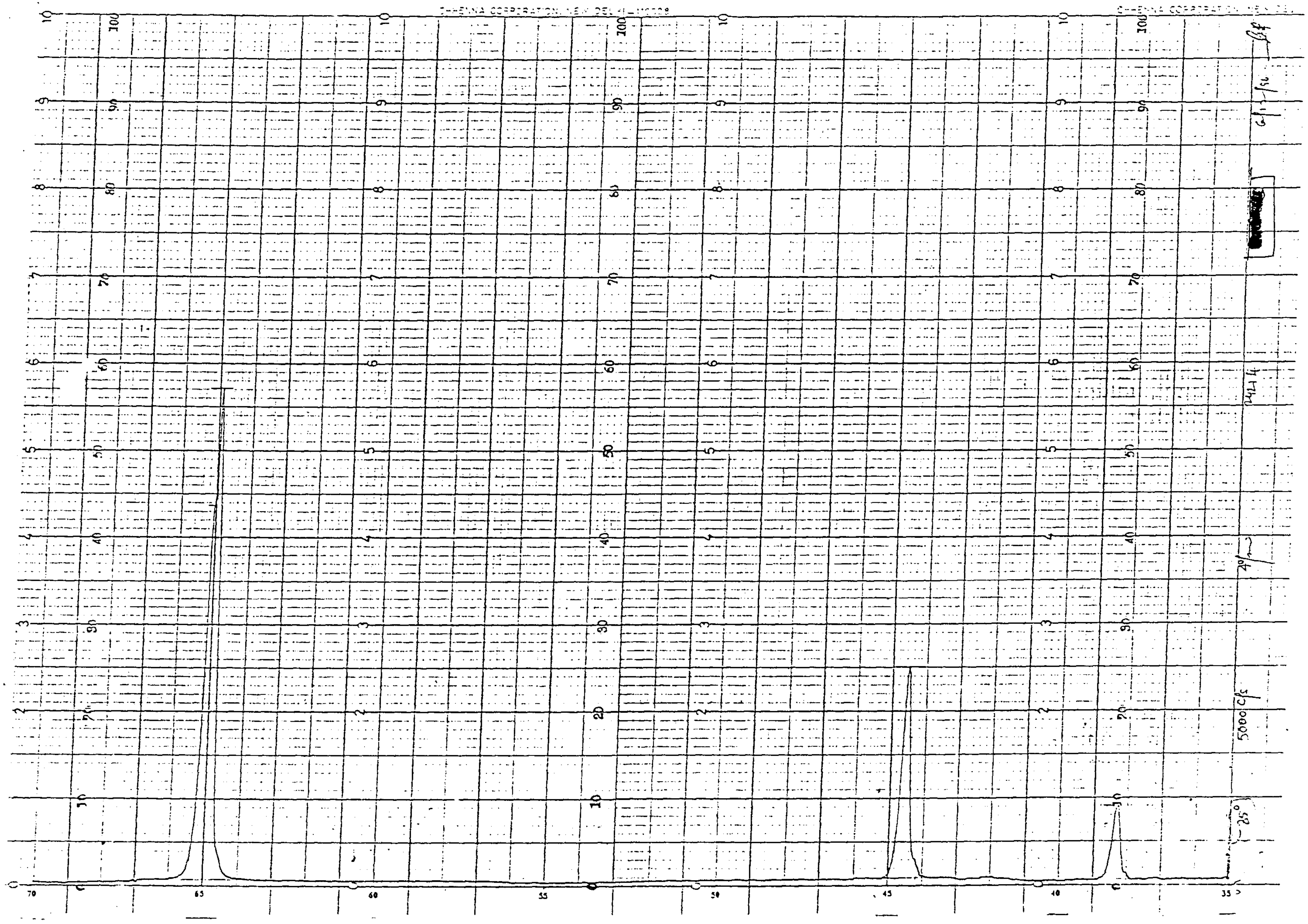


Fig. 3.26 :X- ray diffraction pattern of Aluminium plate, x-1.

Fig. 3.27: X– ray diffraction pattern of EN coated Aluminium plate, x-2.

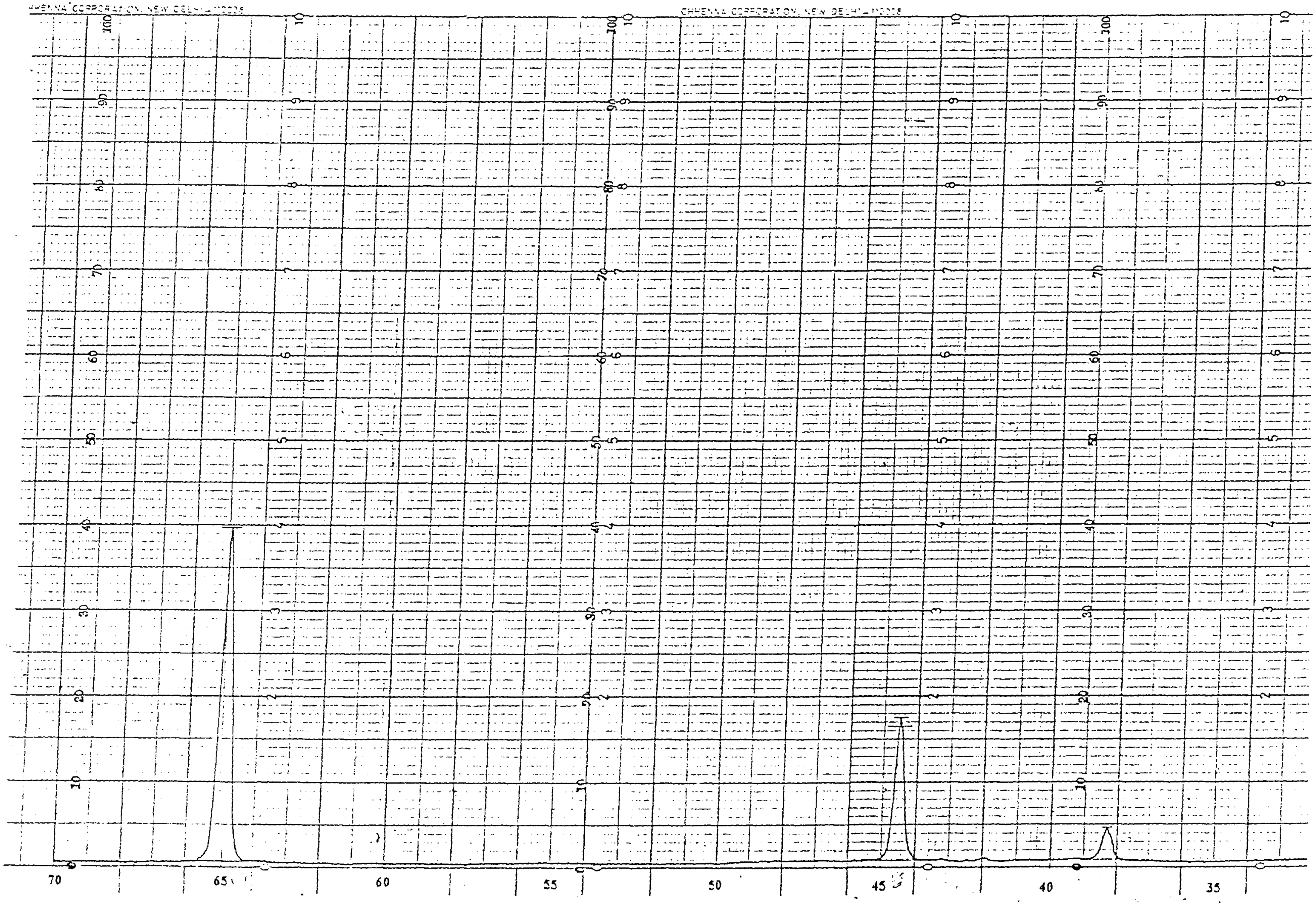


Fig. 3.28: X– ray diffraction pattern of EN coated Aluminium plate, x-3.

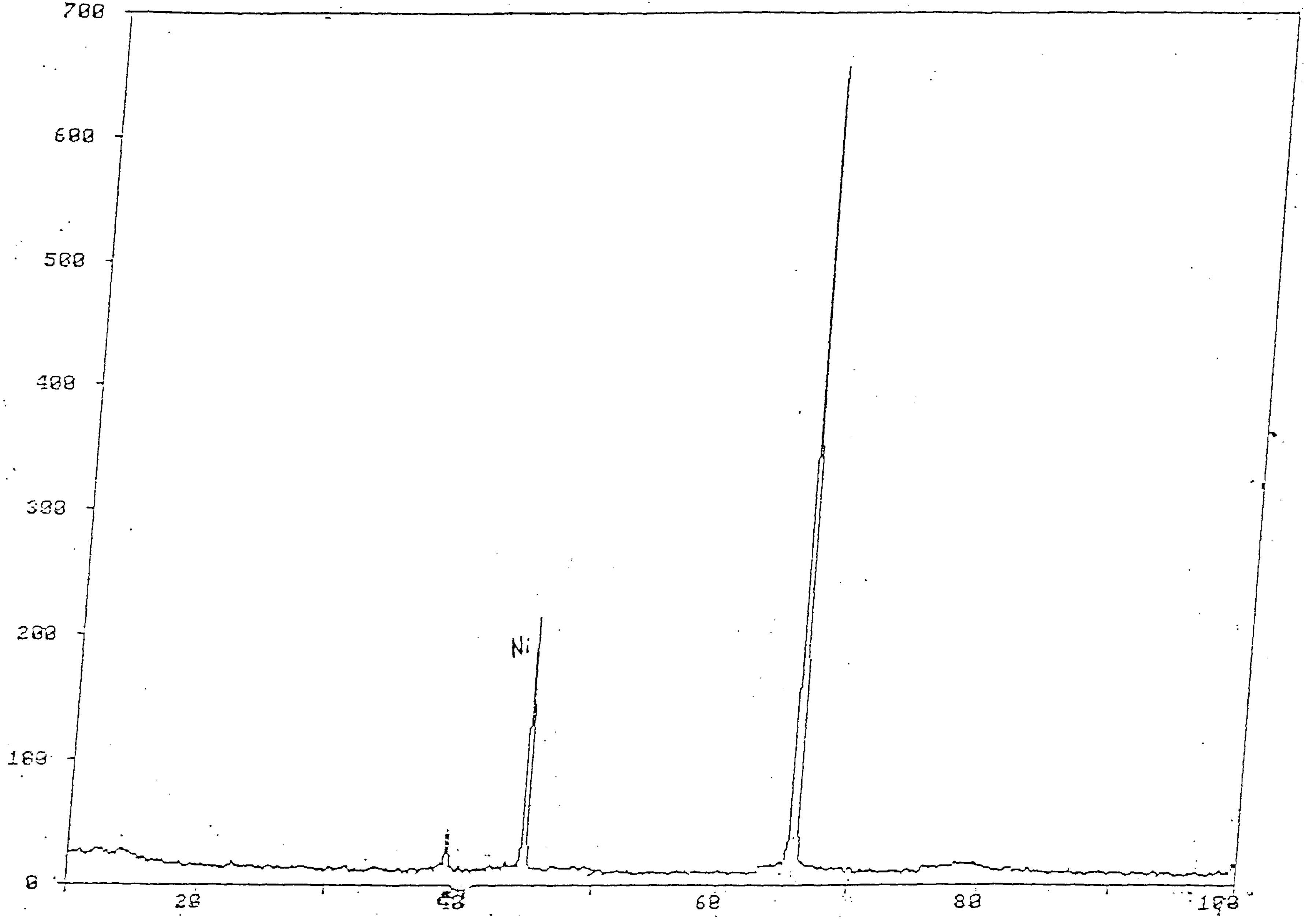


Fig. 3.29: X– ray diffraction pattern of EN coated Aluminium plate, x-4

As mentioned earlier , black coating was obtained from EN bath with a different pre –plate zincating treatment . Figure 3.30 shows the X-ray diffraction patterns of this black coated Al plates . The d- values calculated (Table –3.25) from these patterns also indicate the presence of nickel metal (d = 2.0300) . Black nickel coating obtained from EN bath solution also shows uniform deposition .

Similarly, calculated d-values from the X-ray patterns obtained for EN depositon on Copper substrate (Fig3.31-3.32) are in agreement with those reported[16] for pure Cu. This new bath formulation gives an uniform deposit of nickel also on Copper substrate.

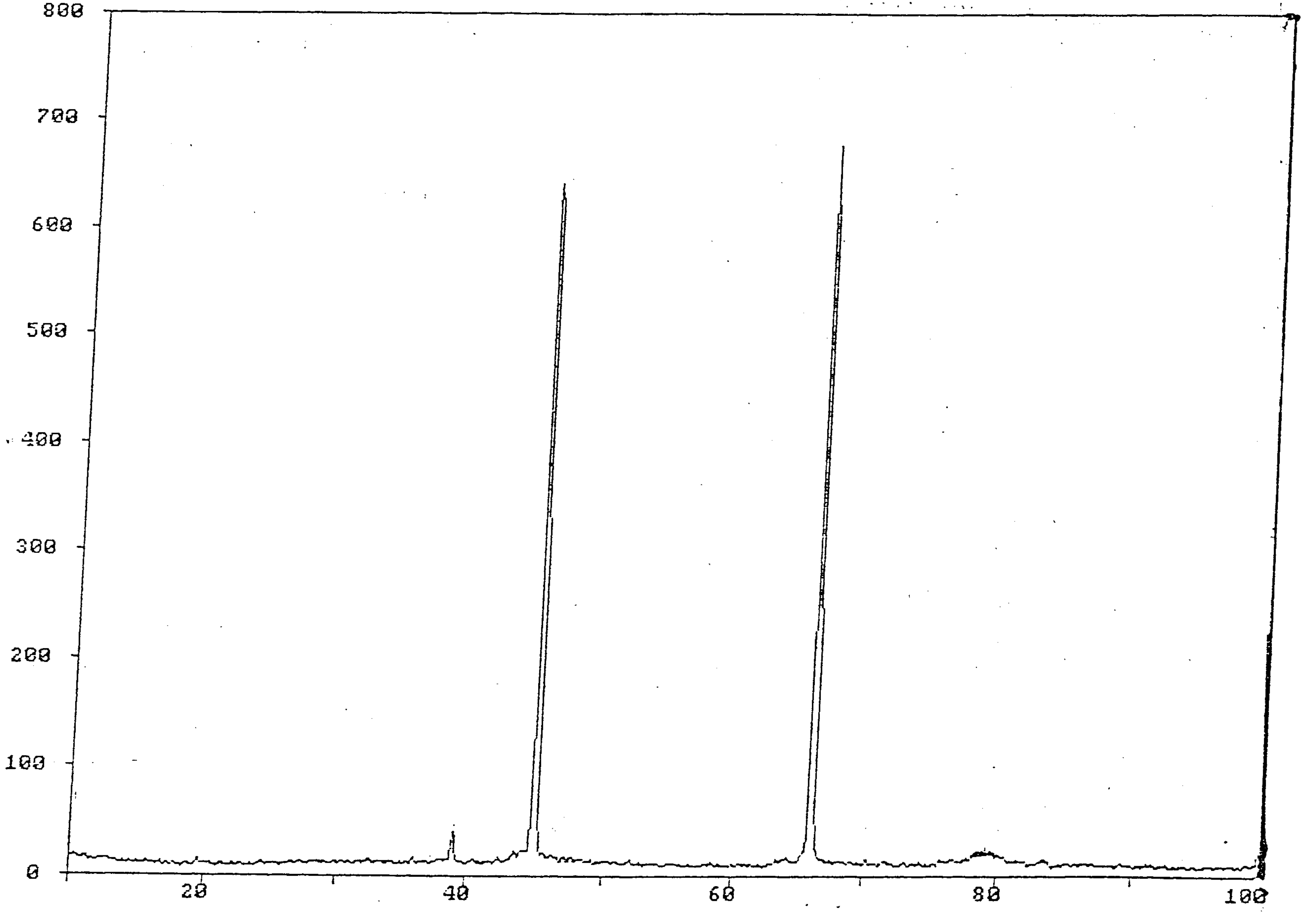


Fig. 3.30: X– ray diffraction pattern of EN coated Aluminium plate, x-5

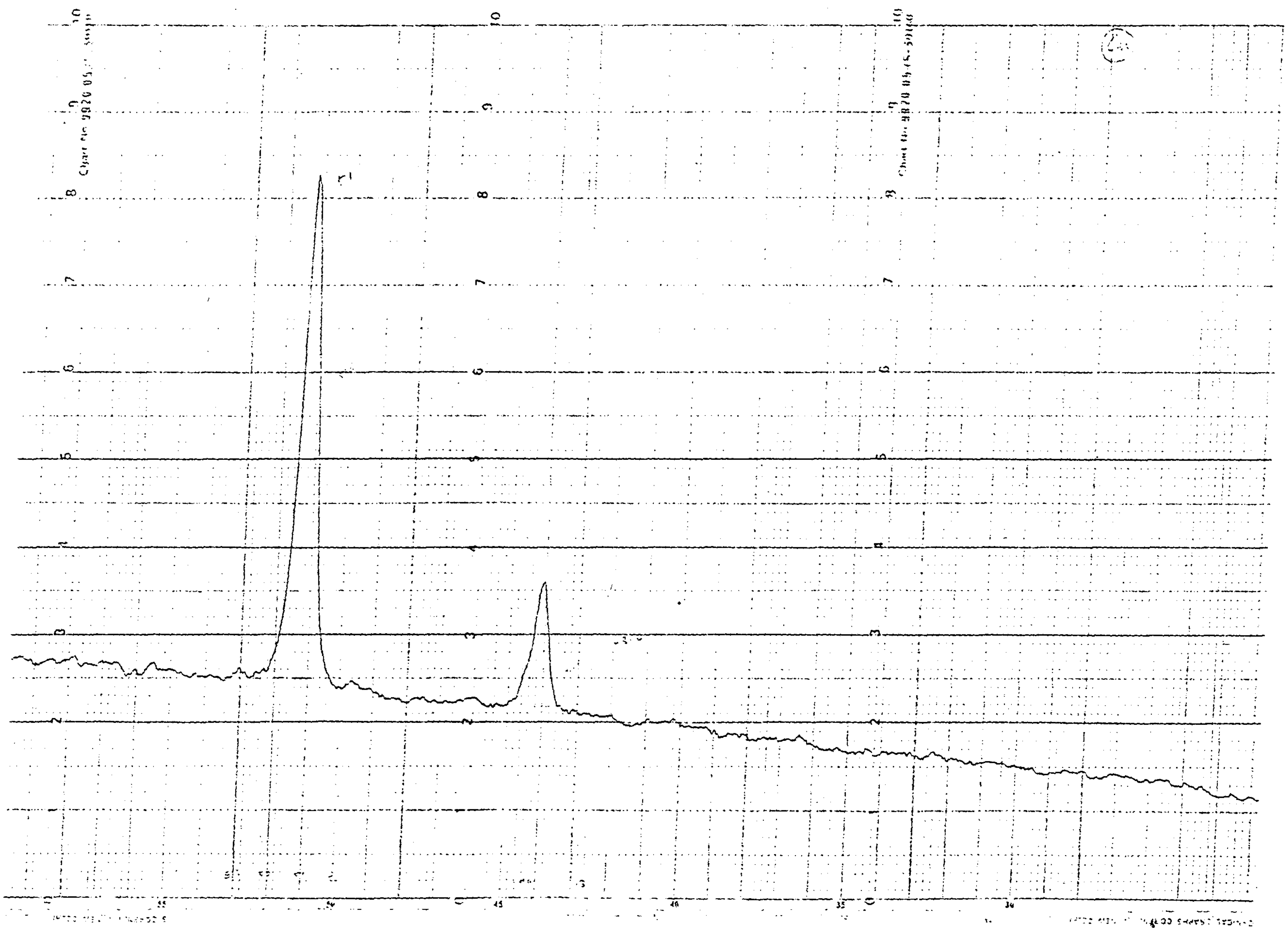


Fig. 3.31: X– ray diffraction pattern of Copper plate, x-6

Fig. 3.32: X-ray diffraction pattern of EN coated Copper plate, x-7.

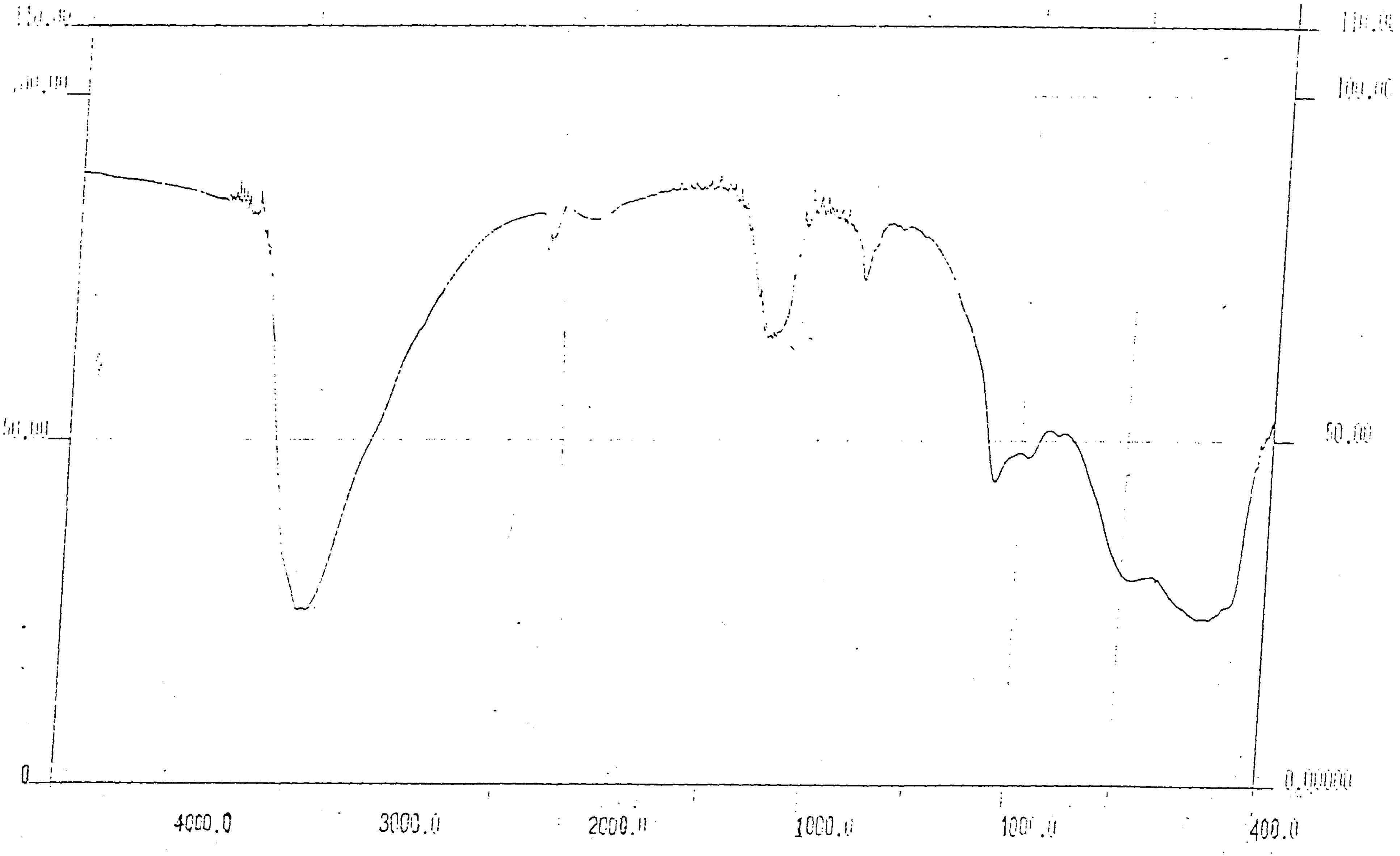


Figure 3.33 Infrared spectra of EN bath residue

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CHAPTER FOUR

CORROSION STUDIES OF THIN FILM

4 INTRODUCTION

After the advent of electroless plating or chemical deposition as a new coating technique[1] in 1946, its major application has been for the protection of metal from corrosion which was commercially available only four years later. Subsequently, other engineering applications were also realized, due to the hardness and wear resistance property of the deposits.

Although corrosion resistance[2] is one of the important characteristics of the electroless plating, in most of the applications this coated layer will be cathodic to the substrate or base material. It is therefore essential that the deposition should be uniformly continuous and also free from pits and cracks. In fact, such defects in the deposited layer contribute towards the initiation of the corrosion of the substrate material which spreads underneath the coating and lifts it.

In recent times, electroless plating technique has been widely put to use in the electronic industry[3] where also the plated film is required to withstand corrosive environment and wear. In this industry, it was initially used only in the printed circuit boards for the deposition of copper, gold etc. However, presently its use has been extended to such diverse items such as disks, semi-conductors.This shows the wide range of applications available to this technique and the extensive use to which it can be put.

It is therefore necessary to evaluate the metal deposition obtained by electroless plating technique by subjecting it vigorously to various corrosive environment. The electrochemical[4] and the non-electrochemical methods, as described in Chapter Two, are particularly useful for such assessment. Surface probing techniques can also be employed for this purpose. The results of the corrosion studies and surface probing are given in this chapter.

4.1 EXPERIMENTAL

Aluminium plates coated with thin layer nickel deposits are stripped in 3.5 % NaCl in an electrochemical analyser. Potential of the substrate electrode is measured by using galvanostatic set up at various current densities. Current is increased at regular intervals and the resultant electrode potential is measured. The plot of potential versus logarithmic current is obtained and an extrapolation of the linear region to corrosion potential ($\eta = 0$) gives the corrosion current[5]. Similar experiments are carried out with 1.0 N HCl and 2.0 N H_2SO_4.

4.2 CORROSION RESISTANCE OF ELECTROLESS NICKEL

Corrosion resistance studies[6] were carried out, as described above and in Chapter Two, by using plates of appropriate dimensions. Aqueous 3.5 % NaCl, 1.0 N HCl, 2.0 N H_2SO_4, solutions were employed as environments.

4.2.1 CORROSION RESISTANCE IN 3.5 % NaCl

It is observed from the experiments which have been carried out with various sample plates that the corrosion current ($I_{corr.}$) values are lower for plates coated from the bath solution at higher pH value. This phenomenon can probably be attributed to the porosity of the deposits obtained at lower pH of the EN bath. Partial decomposition of $N_2H_5^+$, results in the formation of H^+ ions as described in Chapter Three. Simultaneous reduction of H^+, along with Ni^{+2} ions, liberates H_2 while rendering porosity to the deposits.

$$N_2H_5^+ \rightarrow N_2H_4 + H^+$$

$$H^+ + 1e \rightarrow H$$

$$H + H \rightarrow H_2$$

Figures 4.1 to 4.10 are the Tafel plots obtained during the corrosion studies of the nickel coated Al - plates obtained at various pH of bath, from pH = 9.0 to pH =11.00. From the calculated values of the rate of corrosion (Table - 4.2) it can be seen that the deposition obtained at pH = 10.75 is found to be more resistance to corrosion in saline environment. As low as 0.0245 mils per year corrosion rate is observed, although the thickness of the EN coated layer of the sample plate is only 0.20 mμ.

4.2.2 CORROSION RATE IN 1.0 N HCl

Table 4.6 shows the corrosion behaviour in 1N HCl of the EN coated aluminium panel. The aluminium panels were coated by using the standard bath as described earlier in Chapter Three. It is observed from the data, that the Corrosion resistance of EN coated aluminium plate in 1.0 N HCl is almost the same as that in 3.5% NaCl , with corrosion rate of 0.0277m p y The corresponding Tafel plot is shown in figure 4.35.

Such a low corrosion rate of with the 0.2 mμ thin Ni film is perhaps due to the absence of chloride or sulphate ions in the novel EN bath employed in the present investigation.

4.2.3 CORROSION RATE IN 2.0 N H_2SO_4

Table 4.6 shows the corrosion behaviour of the EN coated aluminium panel in 2N H_2SO_4 . The aluminium panels were coated using the standard bath as described earlier. It is observed from the data, that the Corrosion resistance of EN coated aluminium plate in 2N H_2SO_4 is less than that in 3.5% NaCl , with a corrosion rate of 0.0277m p y and the corresponding Tafel plot is shown in figure 4.36

It is observed that the aluminium substrate EN coated with the Novel bath with a thin film coating of about 0.02 μm on an average, shows a low rate of corrosion ,in almost all the environment .This may be due to the good adhesion of the coating with the substrate material ,and also as mentioned earlier due to the total absentee of the chloride /sulfate ions in the novel bath solution.

4.3 EFFECT OF EN BATH TEMPERATURE ON CORROSION

Figures 4.11 to 4.18 are the Tafel plots obtained during the corrosion studies of the nickel coated plates obtained at various bath temperatures from 338 K to 353 K. Here again, the corrosion current and the calculated corrosion rate (Table – 4.1) are found to be lowest for the plate for which plating was carried out at the optimum temperature of 348K. Since the deposition of metal from an aqueous solution is a diffusion controlled process, as such the movement of the metal ions is accelerated at higher temperature thus resulting in higher rate and better deposition. Nevertheless, beyond the optimum temperature the bath decomposes.

TABLE – 4. 2

Corrosion data of EN plated panels at various pH in 3.5 % NaCl

Sweep rate : 1 mV / sec.

Current range : 1000mA

Reference electrode : Saturated Calomel electrode

Counter electrode : Platinum electrode

Area of electrode : 1.0 cm^2

Plate code	pH	β_a mv	β_c mv	Rp	I cor. µ A /cm^2	Corrosion rate mpy	Figure
P-30	9.0	390	240	305	0.21151	0.090620	4.1
P-30.H	9.0 (H)	280	160	85	0.521059	0.223244	4.2
P-31	9.5	280	250	315	0.182061	0.078003	4.3
P-31.H	9.5 (H)	250	220	103	0.493320	0.211350	4.4
P-32	10.0	440	200	321	0.185996	0.079688	4.5
P-32.H	10.0(H)	400	140	105	0.367590	0.157491	4.6
P-33	10.5	300	180	355	0.137603	0.058955	4.7
P- 33.H	10.5 (H)	240	120	110	0.315793	0.135299	4.8
P-34	10.75	90	110	375	0.057316	0.0245566	4.9
P-34.H	10.75 (H)	100	120	111.1	0.293182	0.125612	4.10

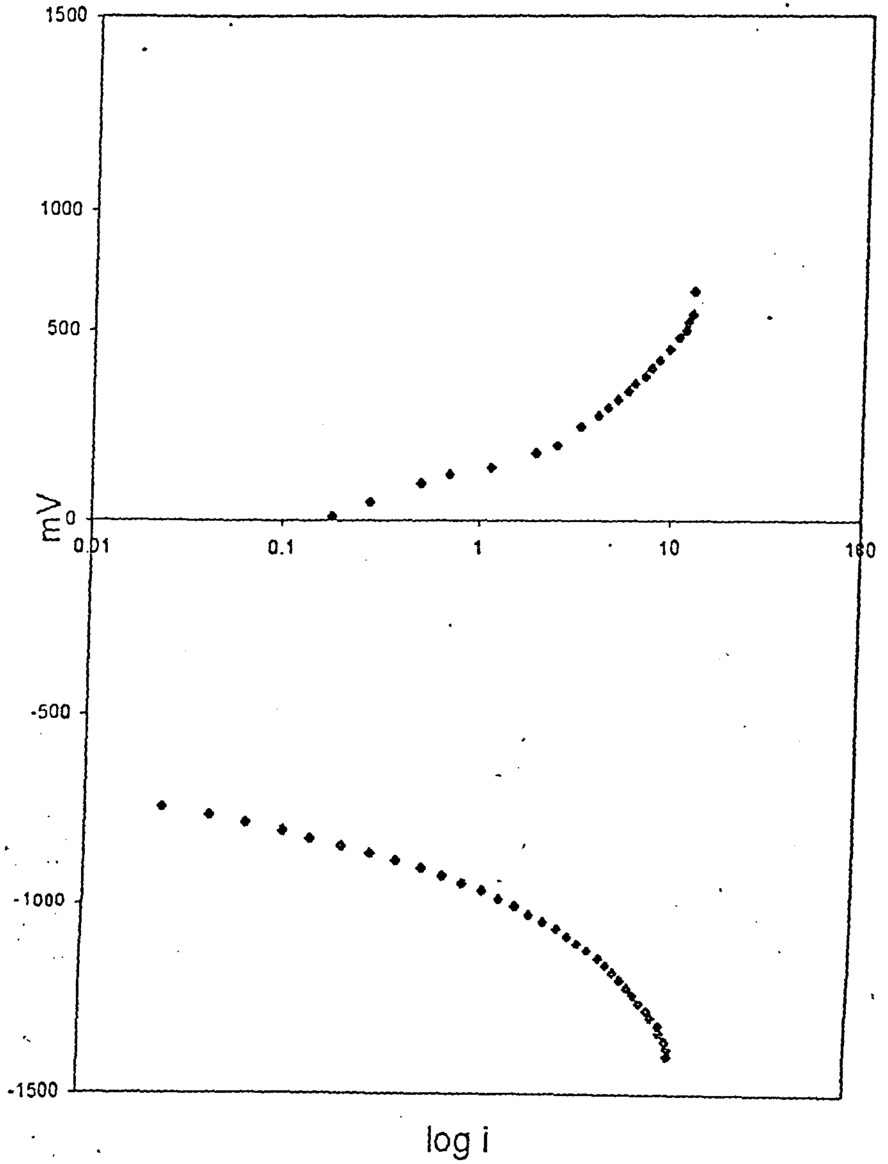


Fig.4.1-Corrosion studies: Tafel plot of plate P-30 [EN-bathpH = 9.0] in 3.5%NaCl.

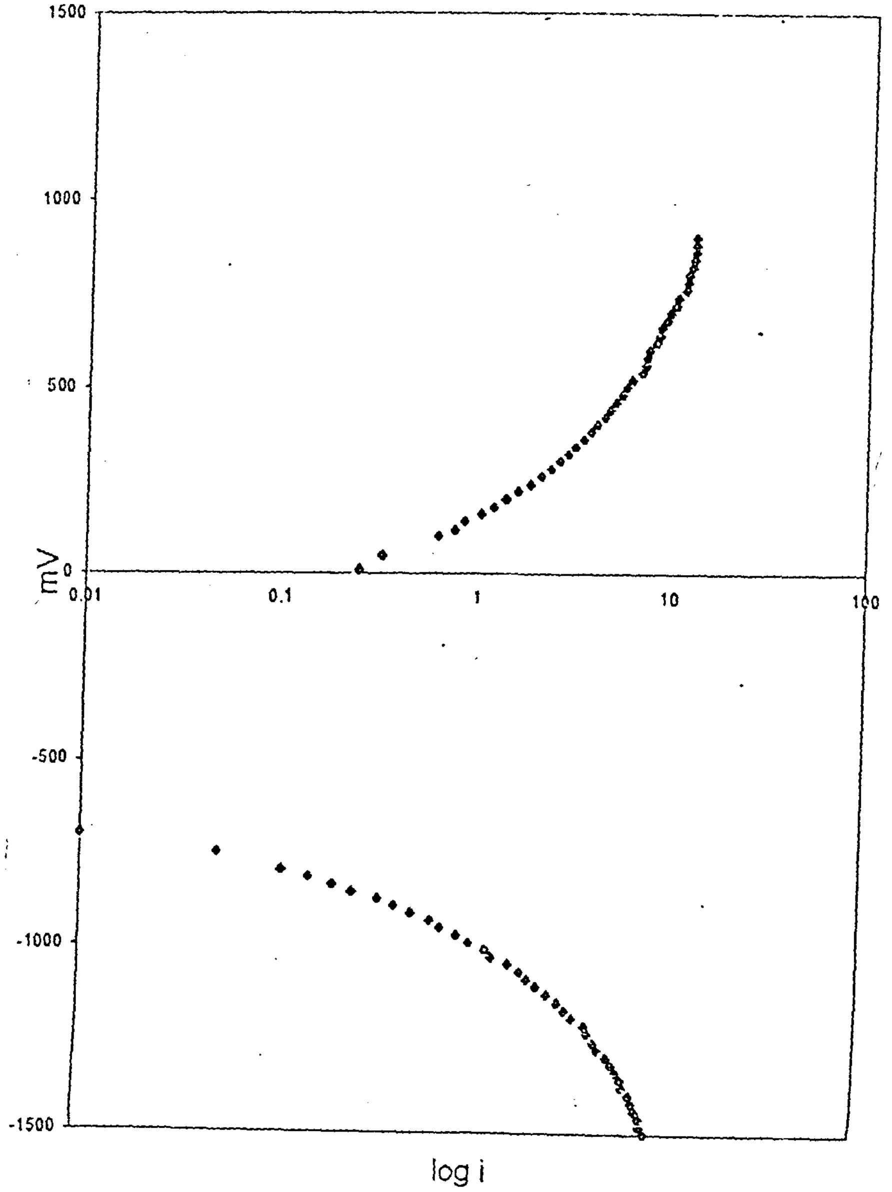


Fig.4.2-Corrosion studies: Tafel plot of plate P-30.II [EN- bath pH = 9.0] in 3.5%NaCl.

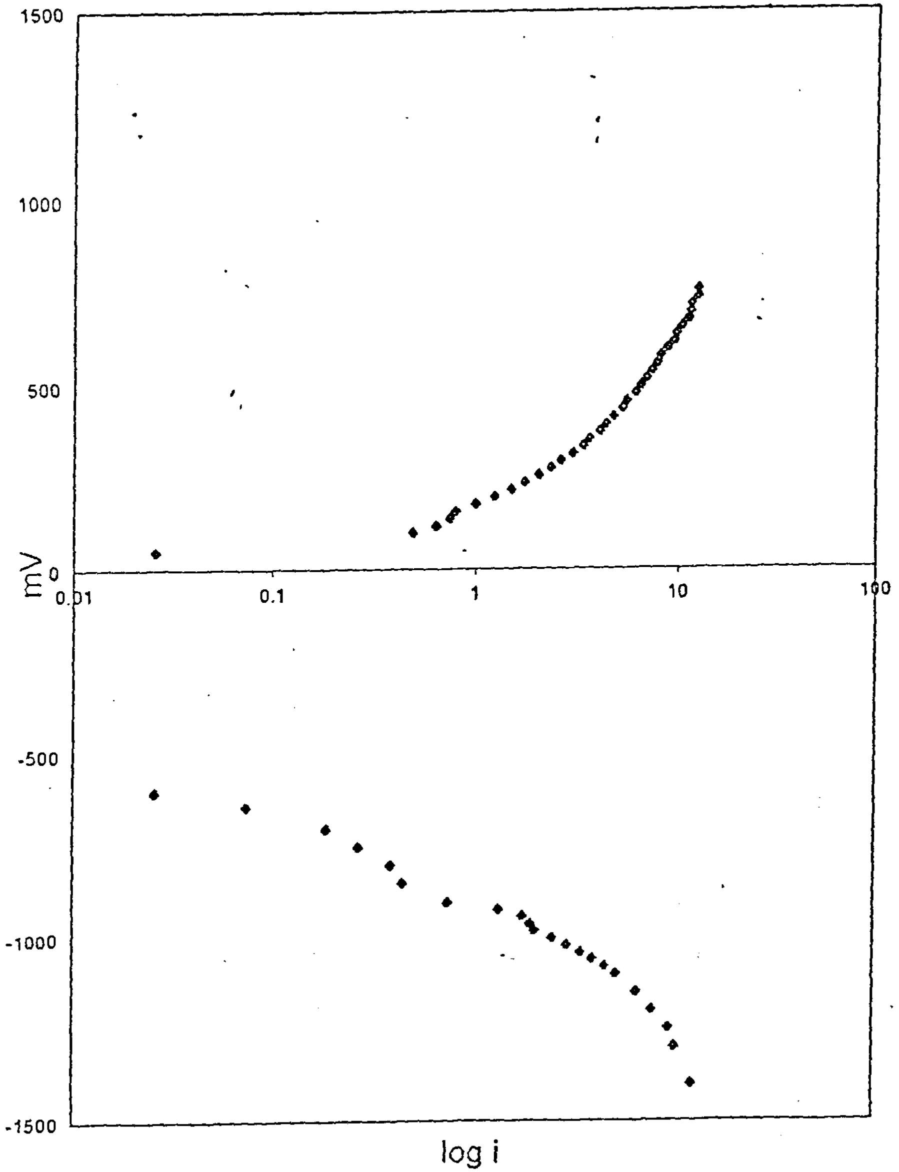


Fig.4.3-Corrosion studies.Tafel Plot of plate P-31[EN -bath pH = 9.5] in 3.5%NaCl .

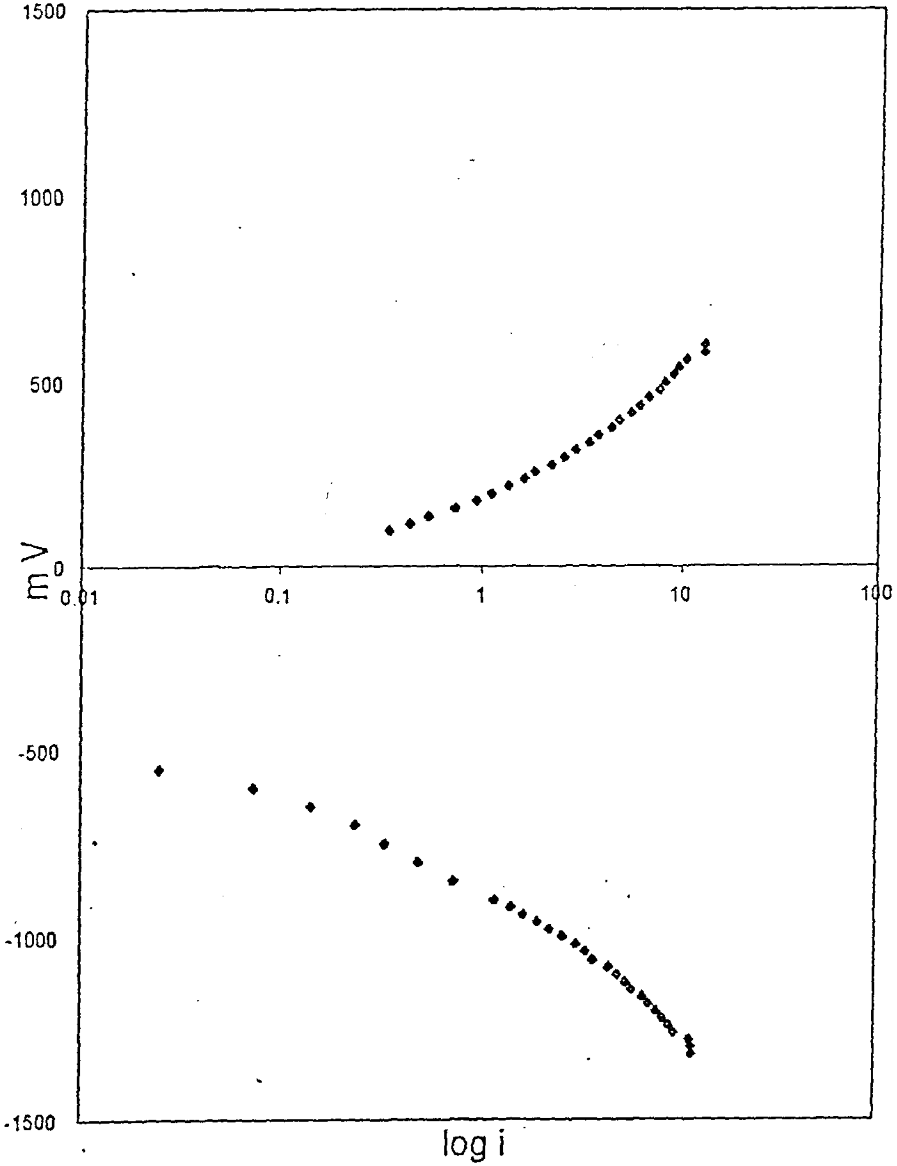


Fig.4.4-Corrosion studies.Tafel plot of plate P-31.H [EN - bath pH = 9.5] in 3.5%NaCl.

Fig.4.3-Corrosion studies:Tafel Plot of plate P-31[EN-bath pH = 9.5] in 3.5%NaCl.

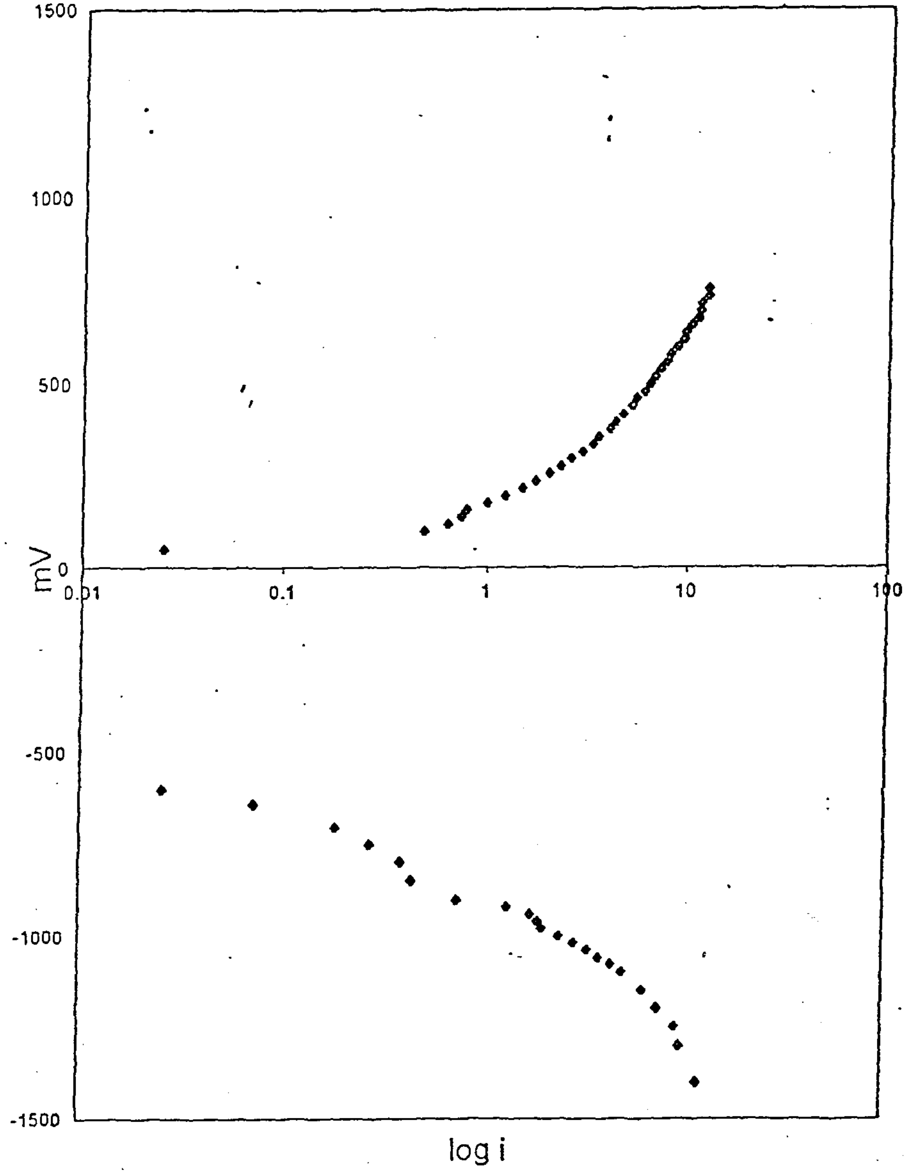


Fig.4.4-Corrosion studies:Tafel plot of plate P-31.H [EN - bath pH = 9.5] in 3.5%NaCl.

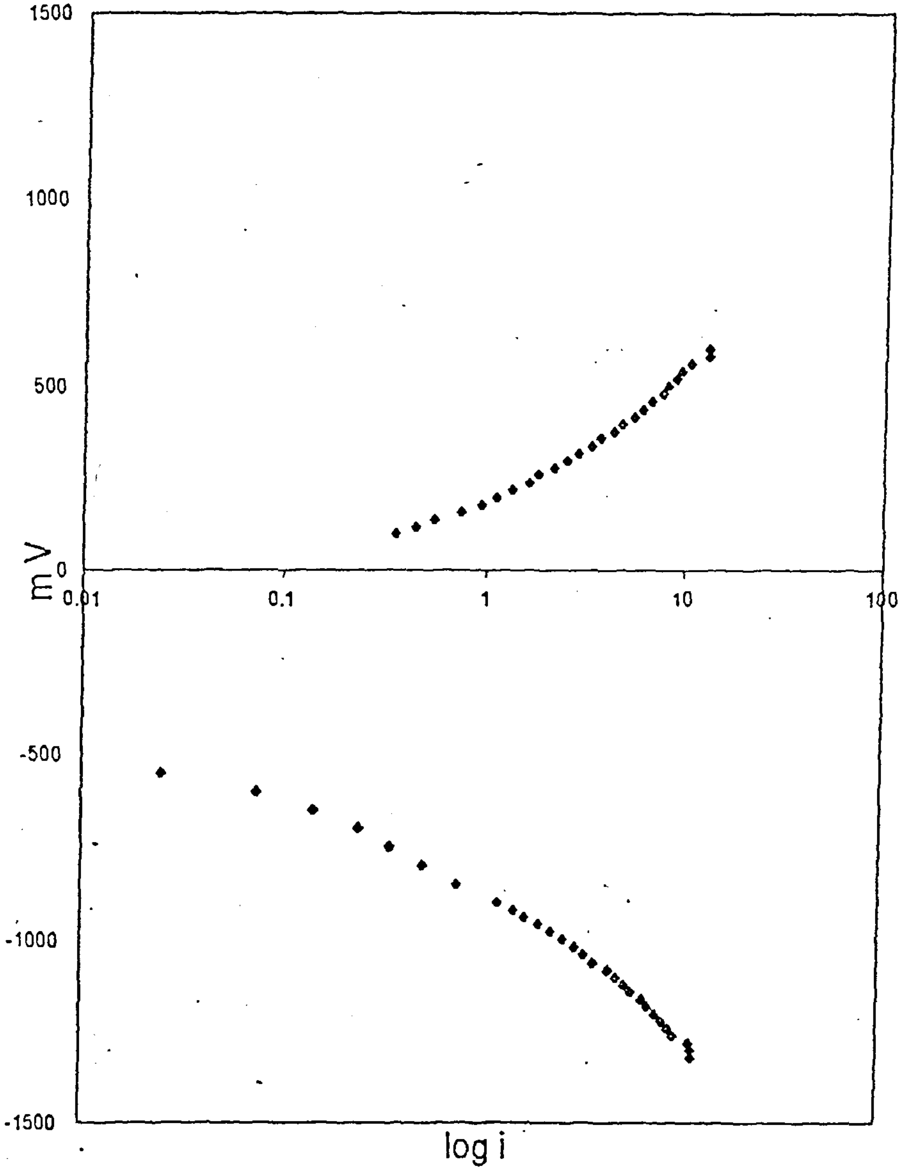


Fig.4.5-Corrosion studies: Tafel Plot of plate P-32 [EN - bath pH = 10] in 3.5%NaCl.

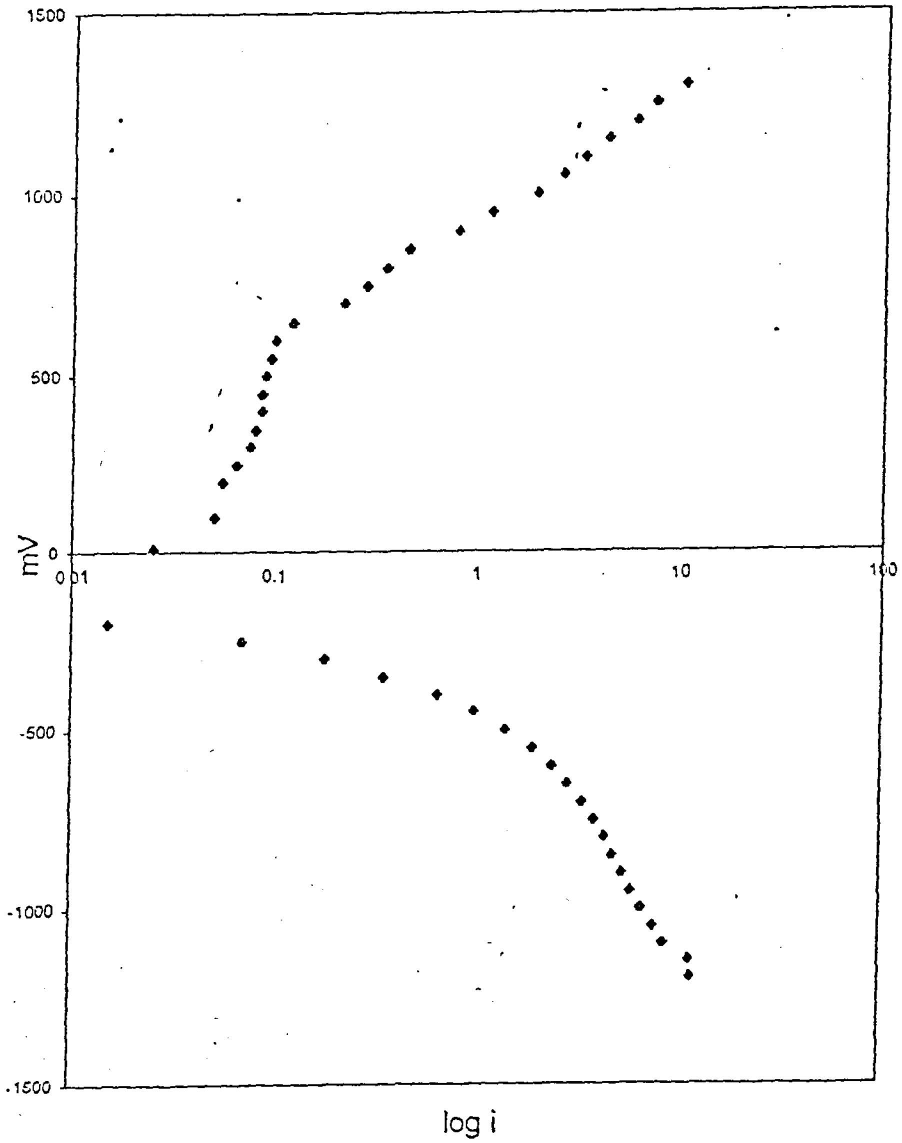


Fig.4.6-Corrosion studies.Tafel plot of plate P-32.H [EN - bath pH = 10] in 3.5%NaCl.

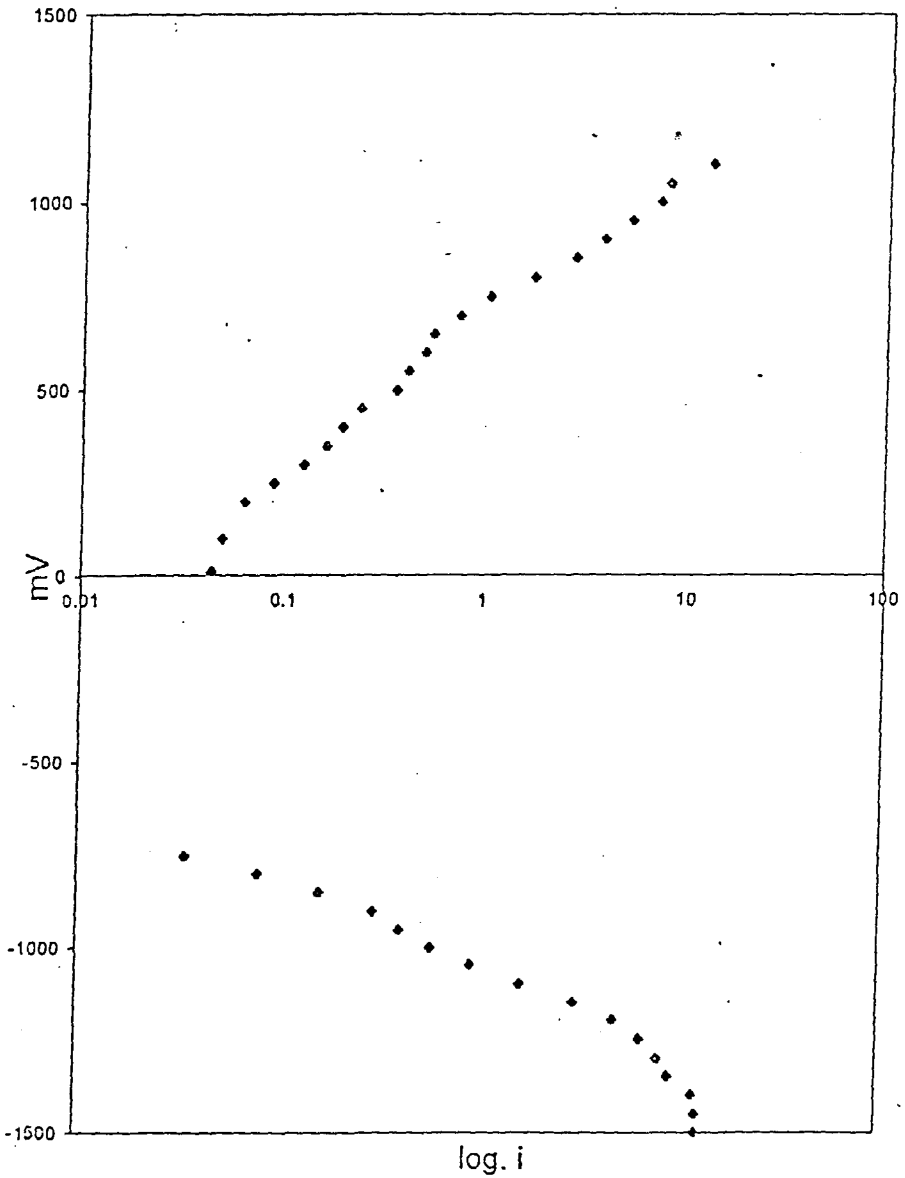


Fig.4.7-Corrosion studies:Tafel plot of plateP-33 [EN - bath pH =10.5]
in 3.5%NaCl.

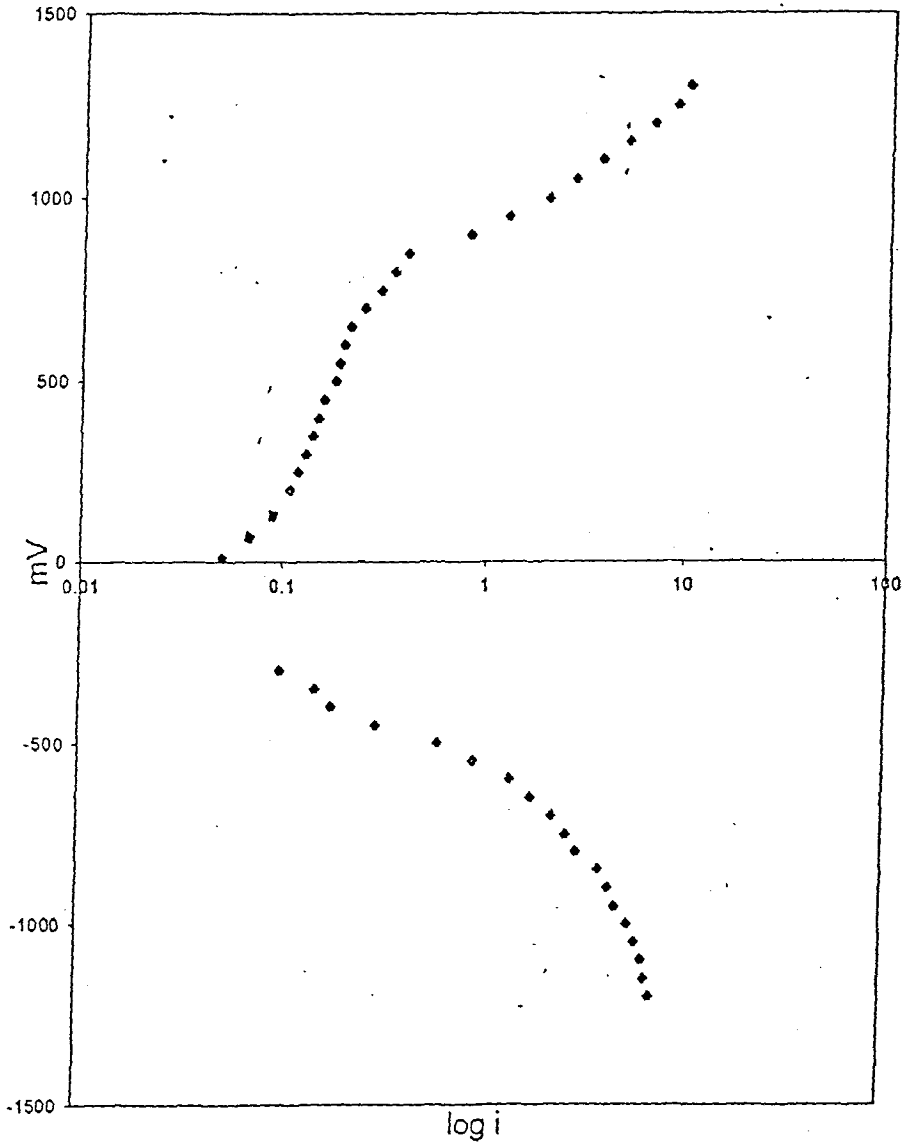


Fig.4.8-Corrosion studies:Tafel plot of plate P-33.H [EN - bath pH = 10.5] in 3.5% NaCl.

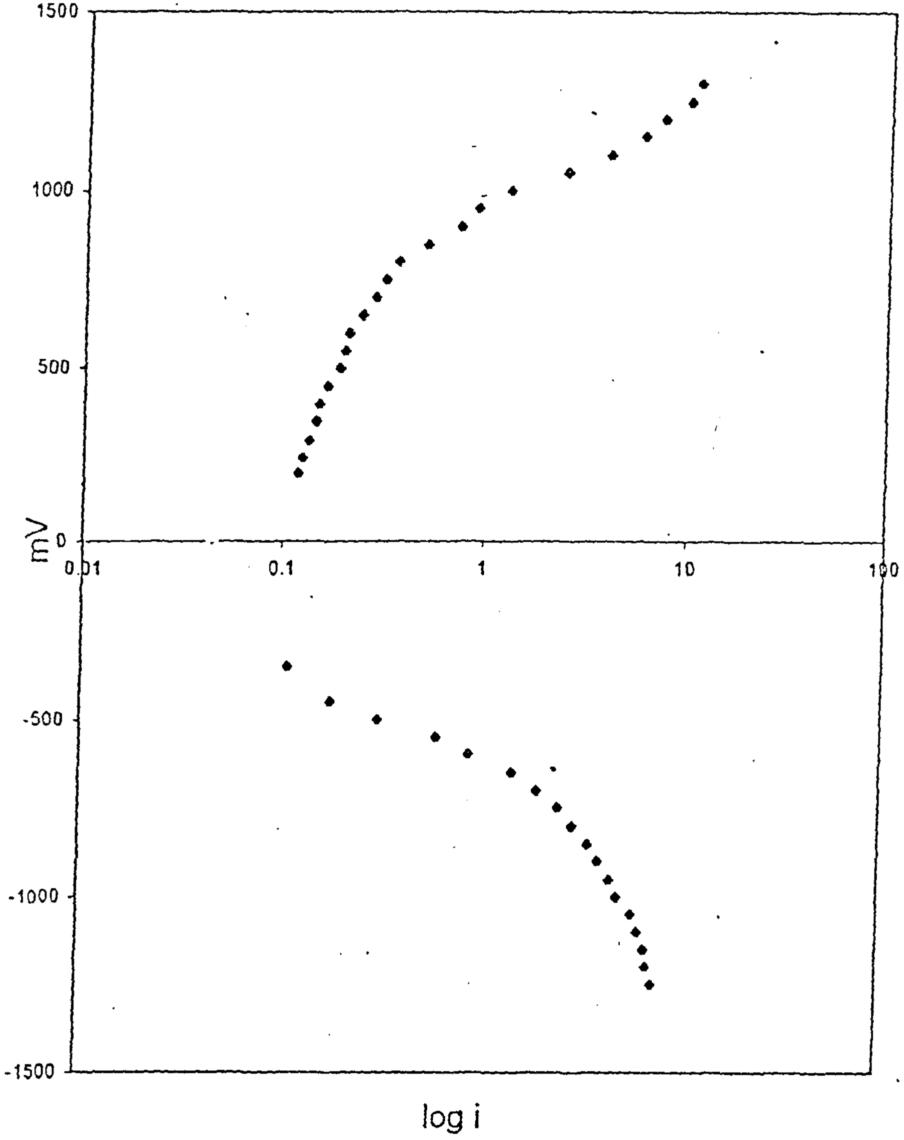


Fig.4.9-Corrosion studies:Tafel plot of plate P-34 {EN - bath pH = 10.75 } in 3.5% NaCl .

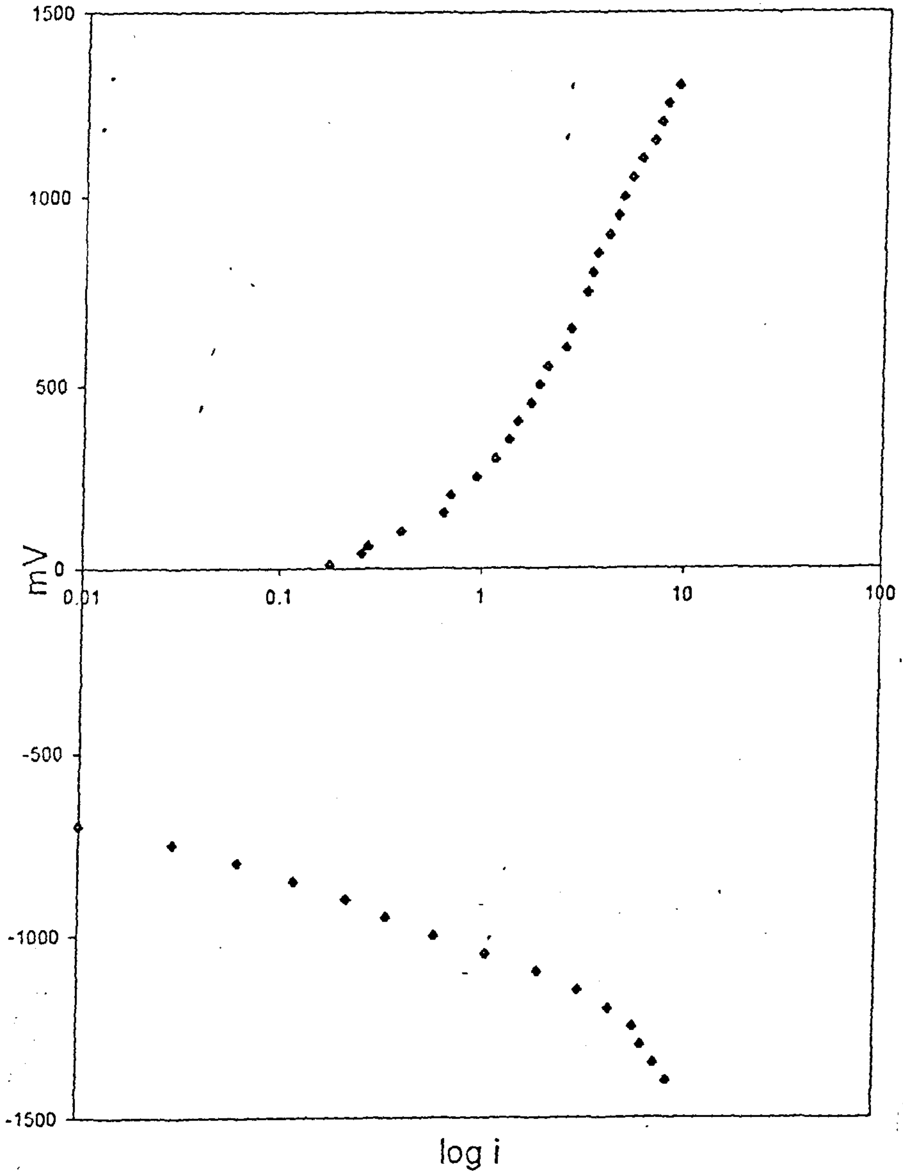


Fig4.10-Corrosion studies:Tafel plot of plate P-34.H {EN -bath pH = 10.75 } in 3.5%NaCl .

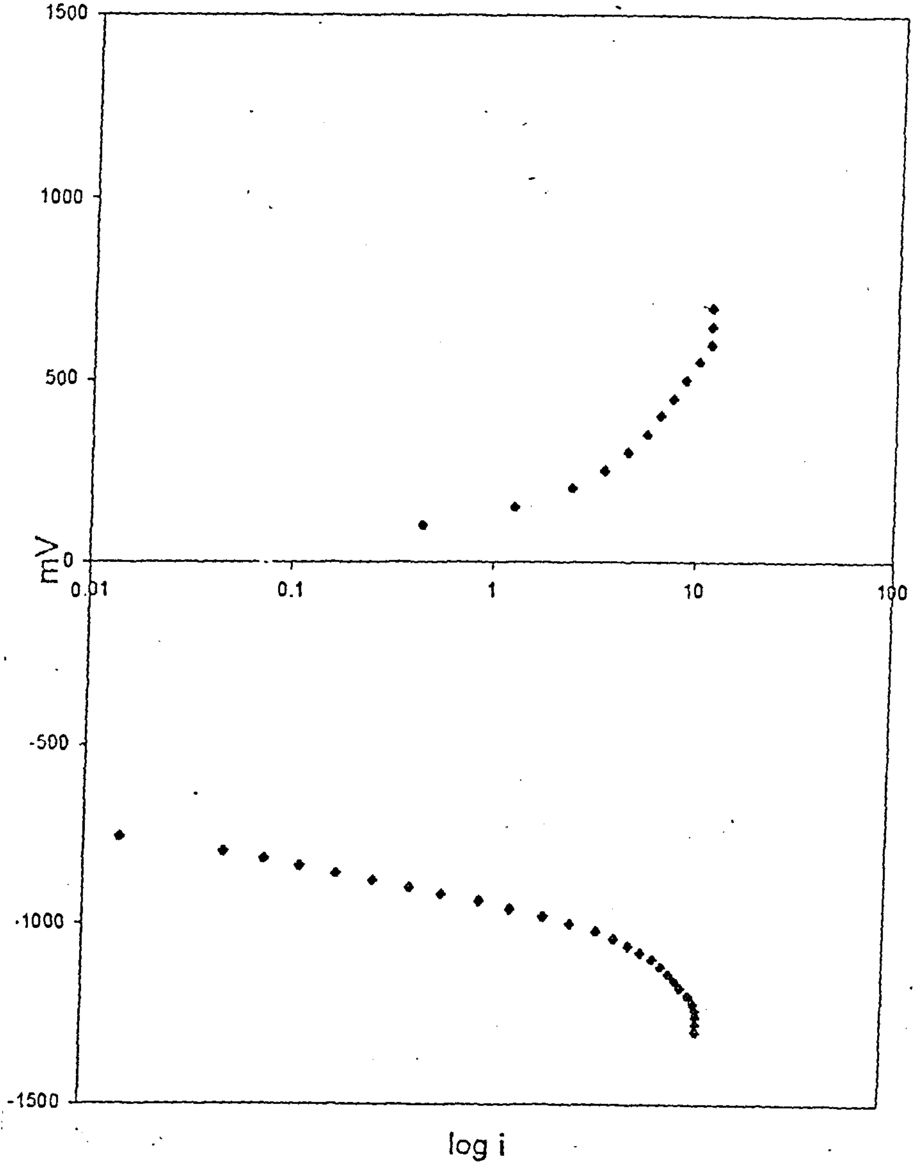


TABLE – 4.6

Corrosion data of EN plated Aluminum panels in various Environment by potentiodynamic method

Sweep rate : 1.5 mV / sec.

Current range : 1000mA

Reference electrode : Saturated Calomel electrode

Counter electrode : Platinum electrode

Area of electrode : 1.0 cm^2

Plate code	Environment	β_a mv	β_c mv	E cor mv	I cor $\mu A/cm^2$	Corrosion rate mpy	Figure
P –34	1N HCl	98.65	240.07	-435.39	0.060	0.0277	4.35
–	–	–	–	–	–	–	–
P –34	2N H_2SO_4	1942.5	224.9	-113.78	0.066	0.0239	4.36

Fig.4.35-Corrosion studies : Tafel plot of EN coated Aluminium plate P-34, in 1N HCl

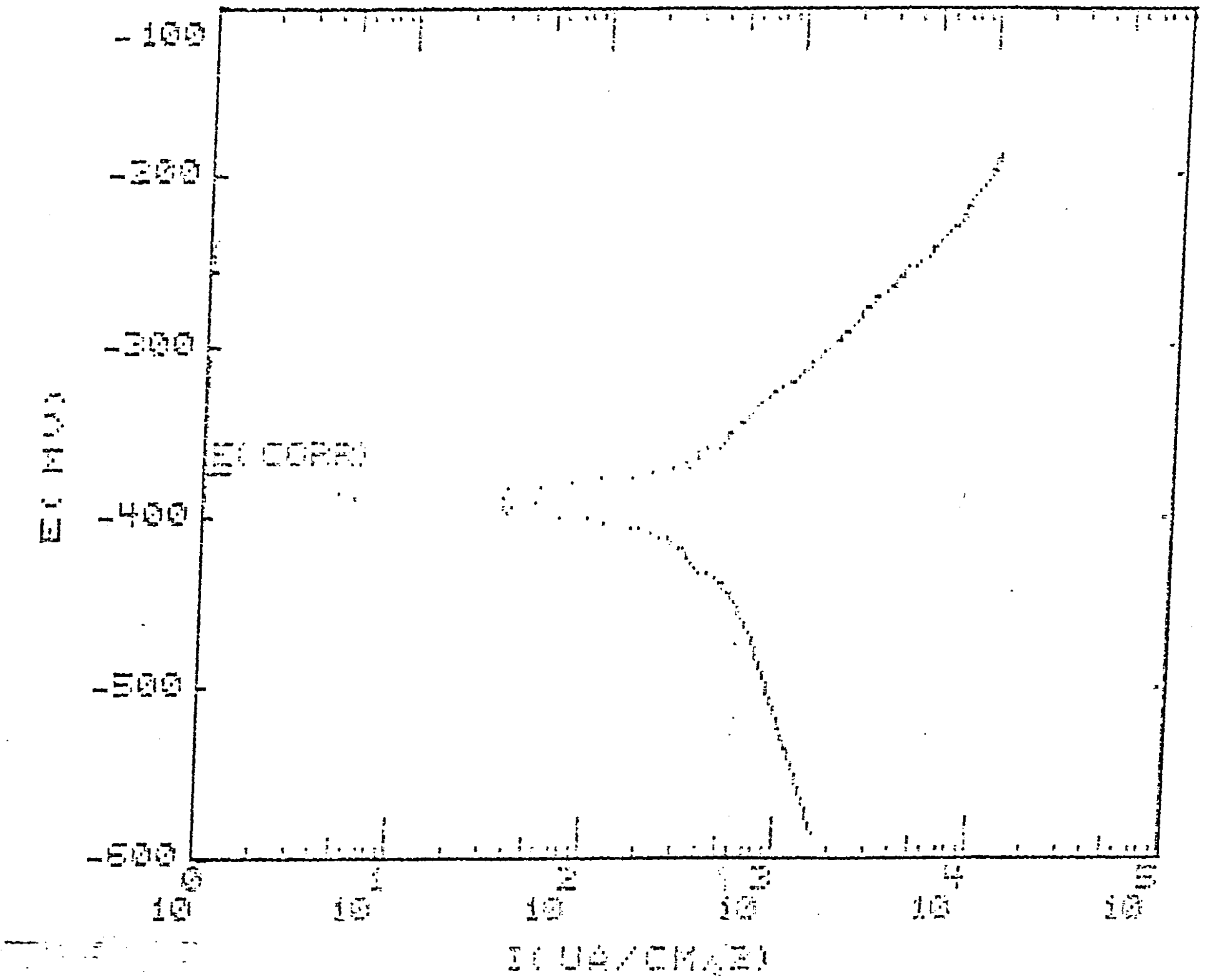


Fig.4.36-Corrosion studies: Tafel plot of EN coated Aluminium plate P-34, in $2N H_2SO_4$

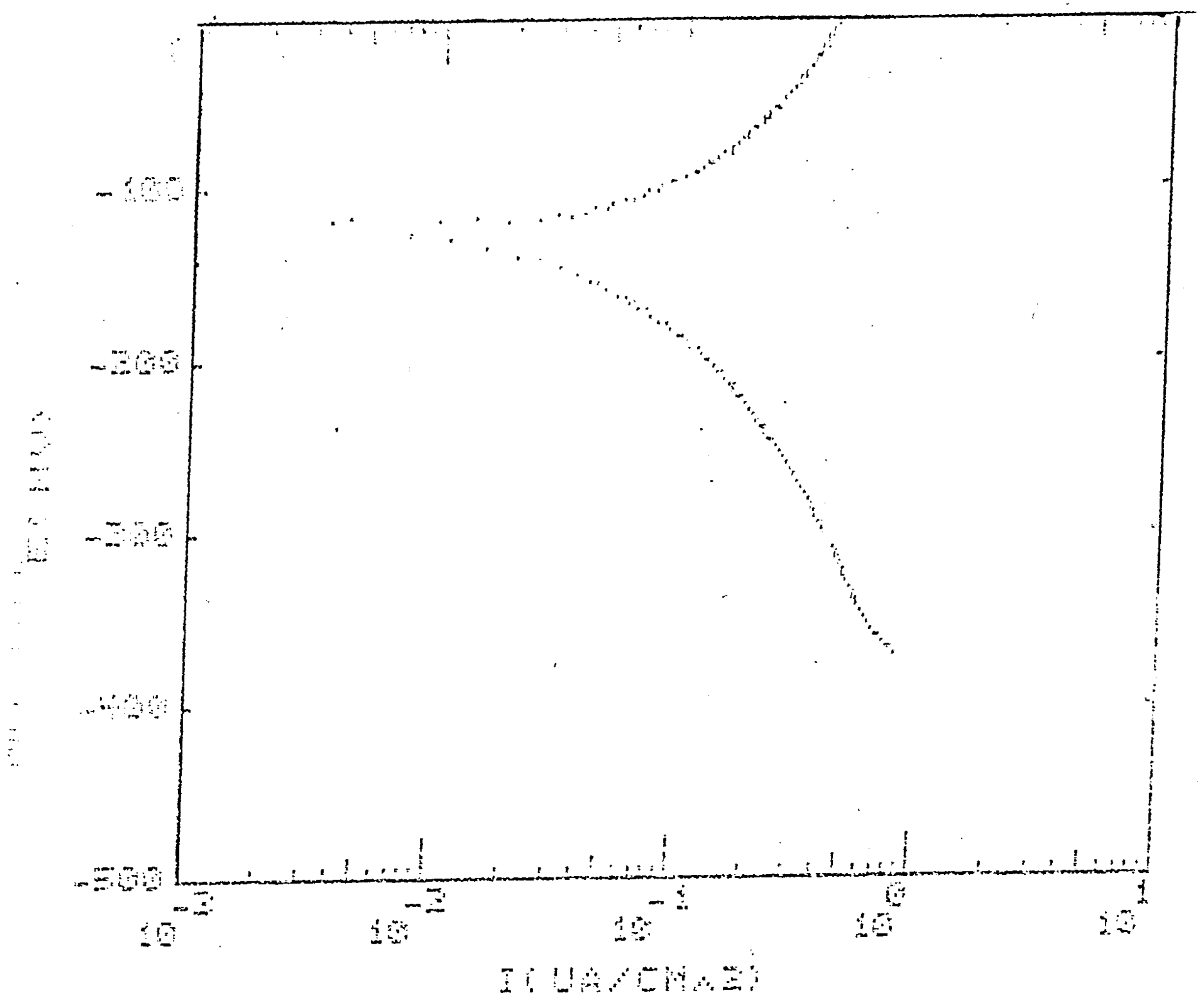


Fig. 4.11-Corrosion studies :Tafel plot of plate T- 1 [coated at 338K] in 3.5 % NaCl.

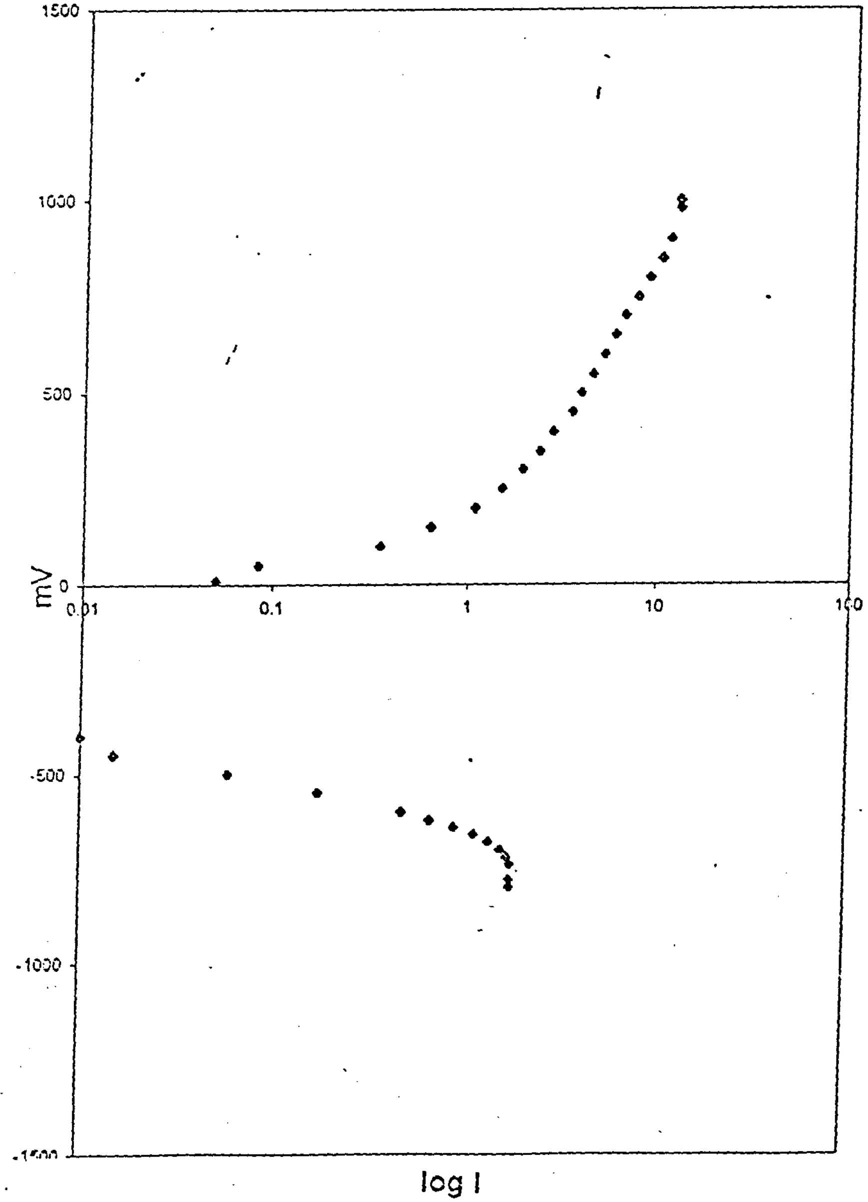
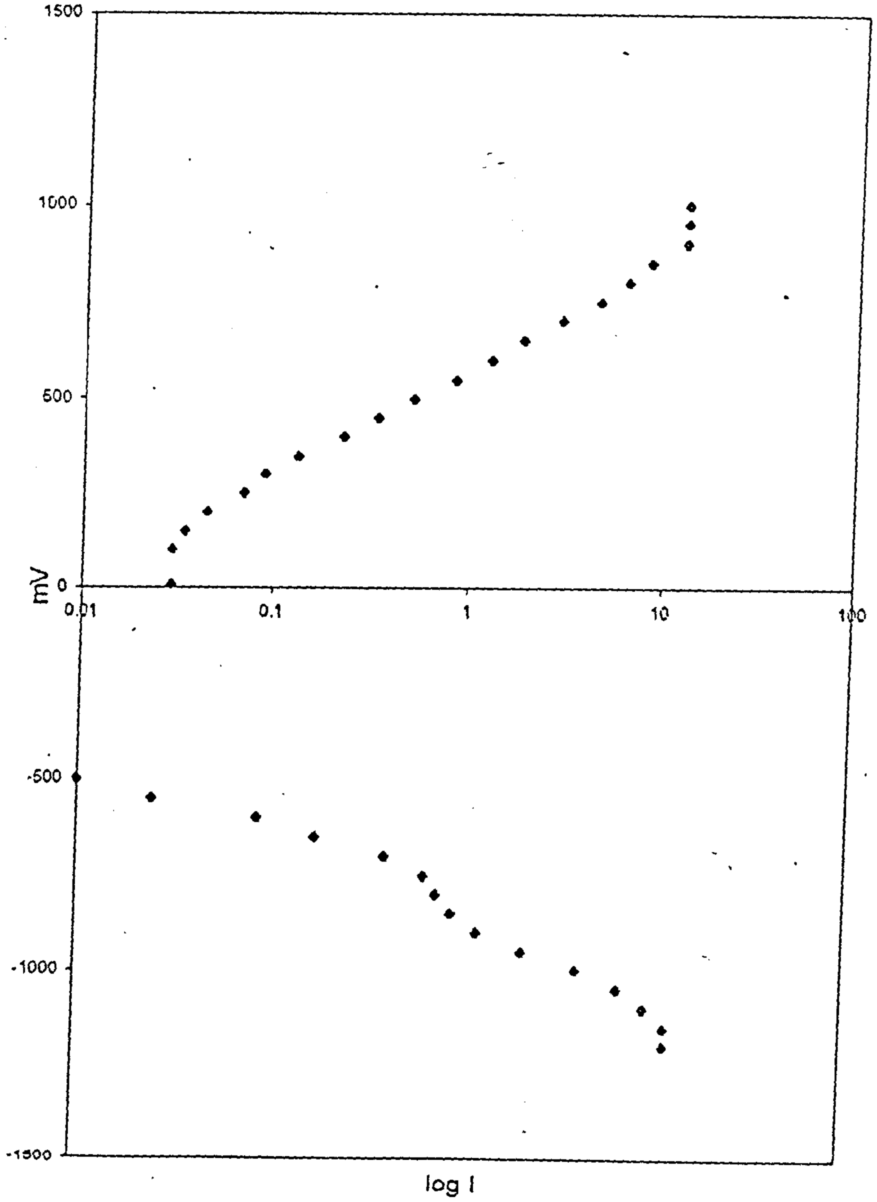


Fig.4.12-Corrosion studies: Tafel plot of plate T-1.H [Coated at 338 K ,Heated] in 3.5%NaCl .



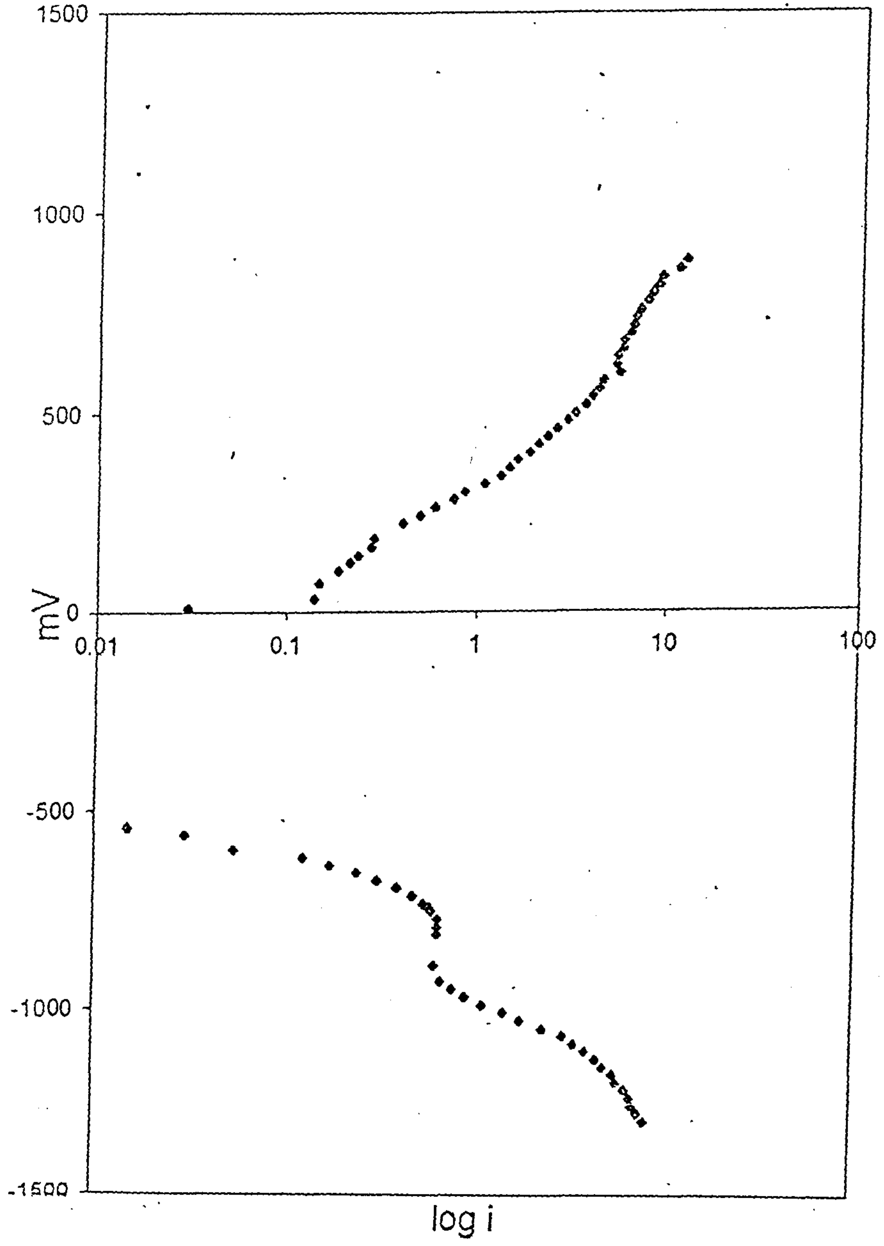


Fig.4.13 - Corrosion studies :Tafel plot of plateT-2 [Coated at 343K] in 3.5%NaCl .

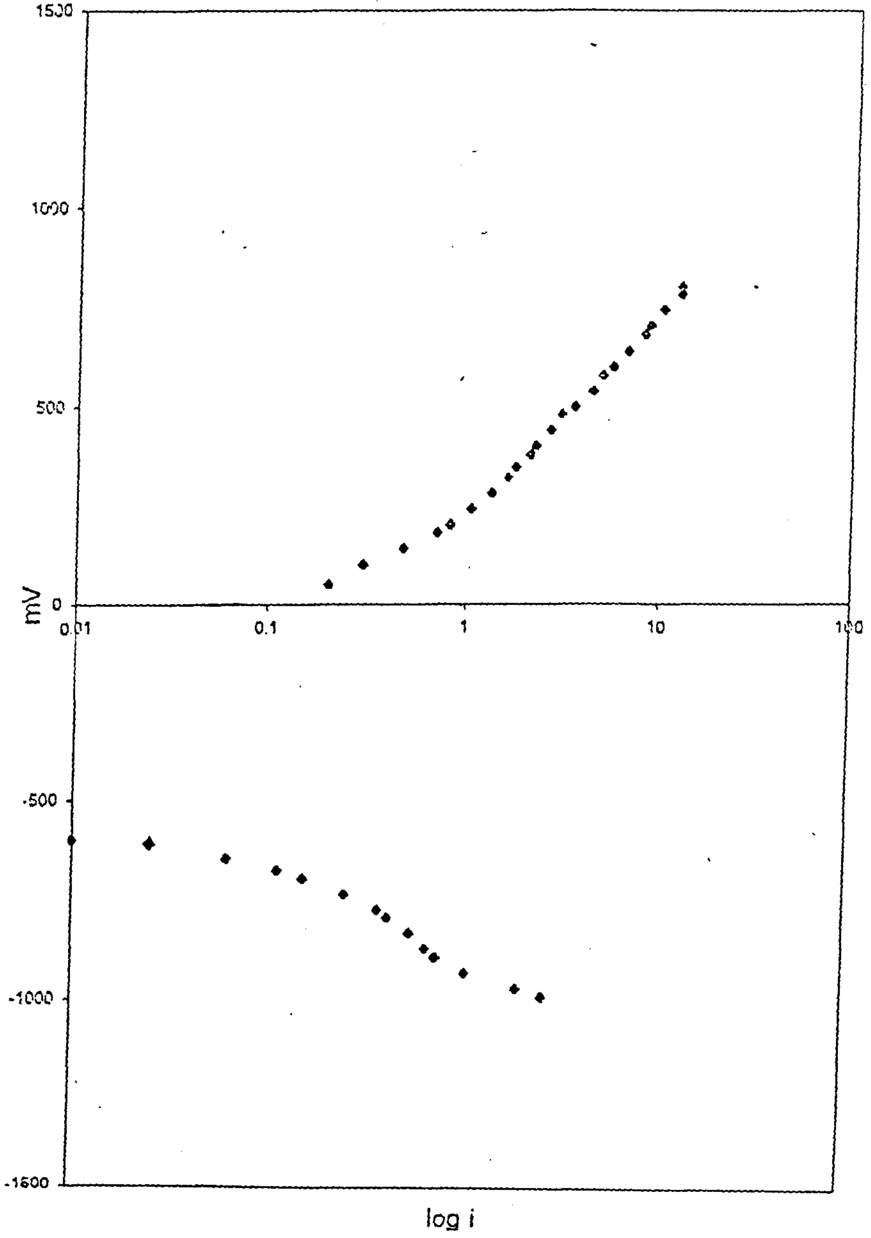


Fig.4.14-Corrosion studies:Tafel plot of plate T-2.H [Coated at 343 K,Heated] in 3.5%NaCl

Fig.4.15 - Corrosion studies :Tafel plot of plate T-3 [Coated at 348K] in 3.5%NaCl.

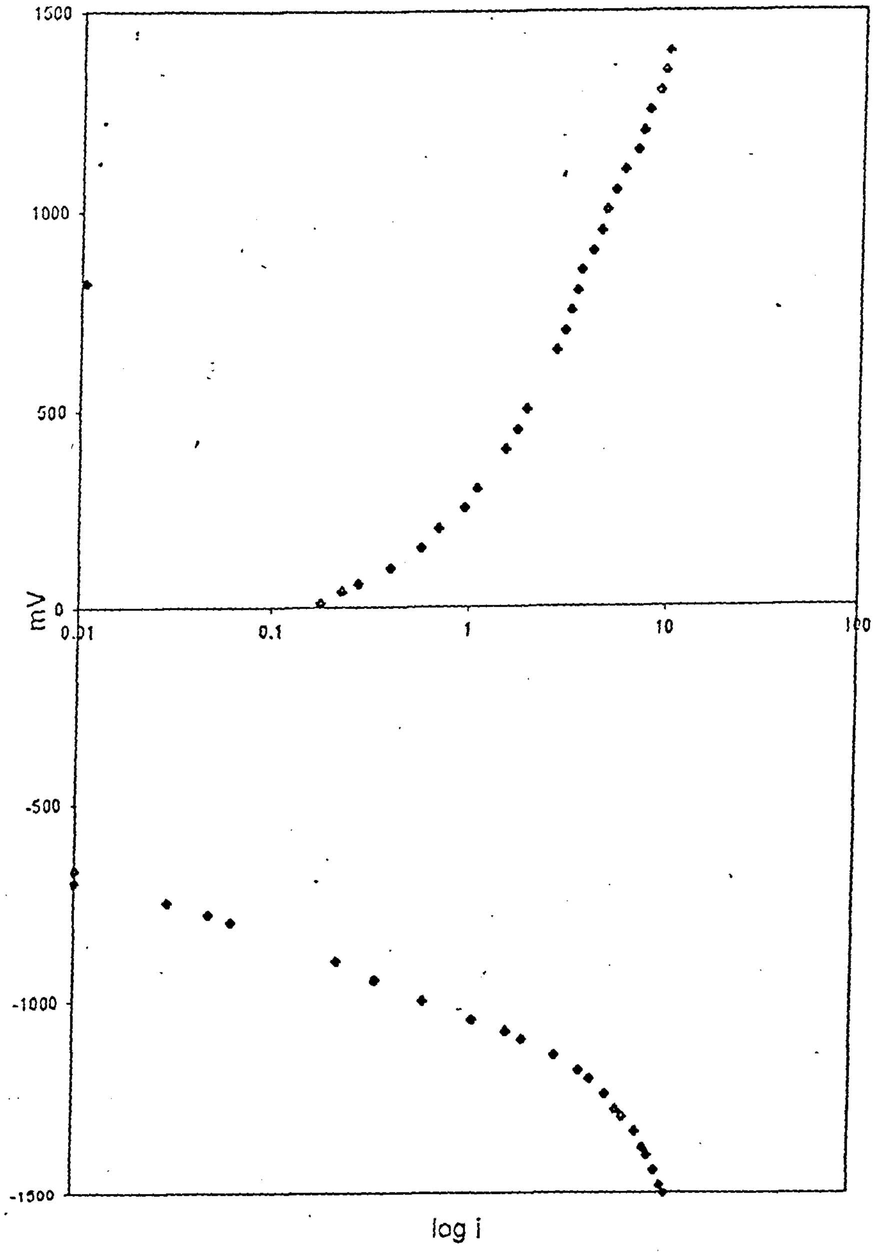


Fig.4.16-Corrosion studies:Tafel plot of plate T-3.H [Coated at 348K ,Heated]in 3.5%NaCl.

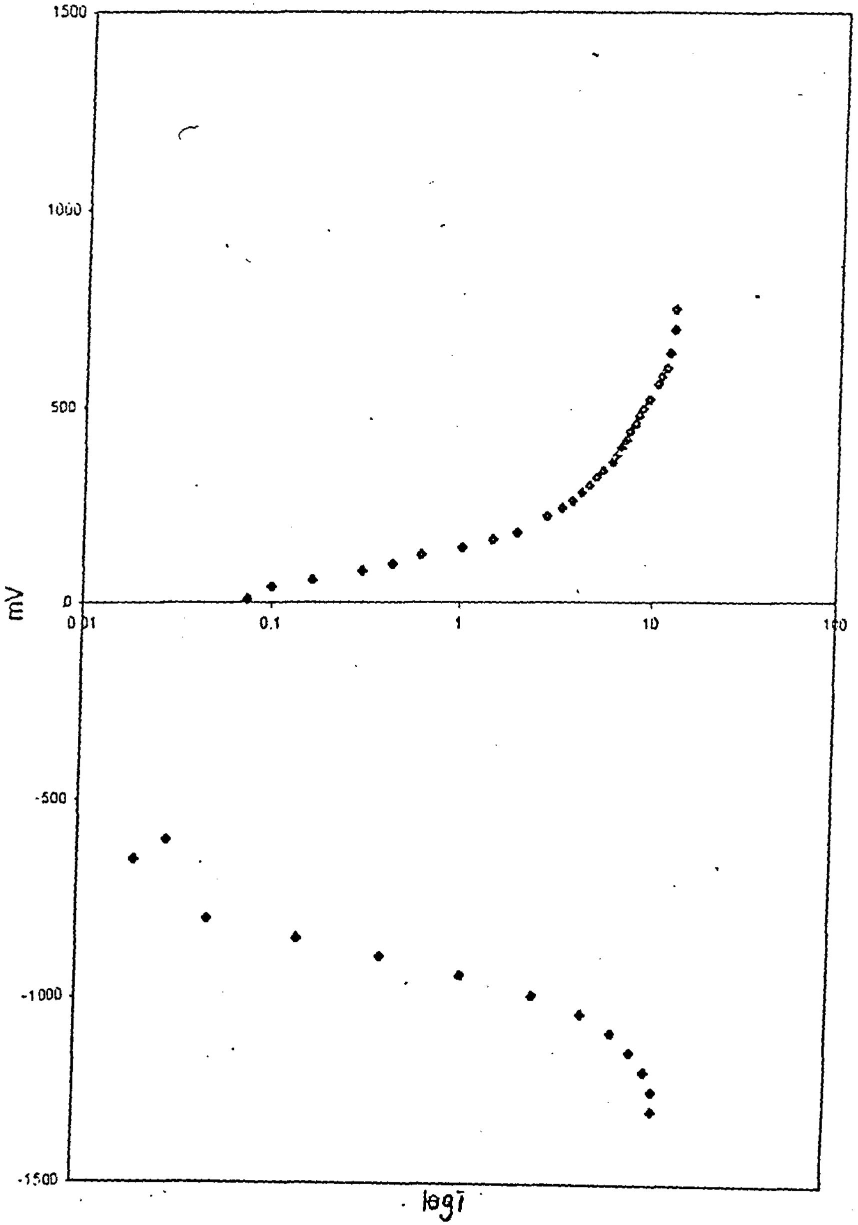


Fig.4.17- Corrosion studies:Tafel plot of plateT-4 [Coated at353K] in 3.5%NaCl.

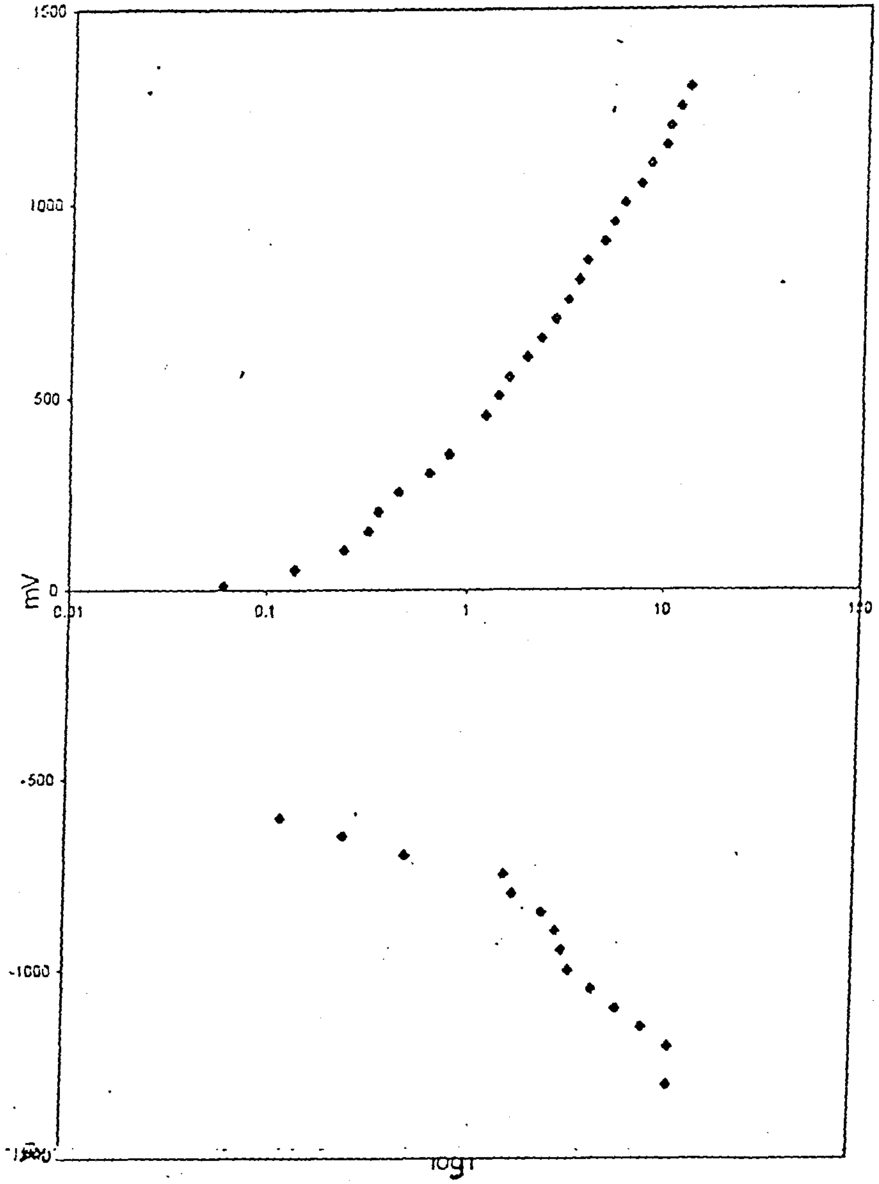
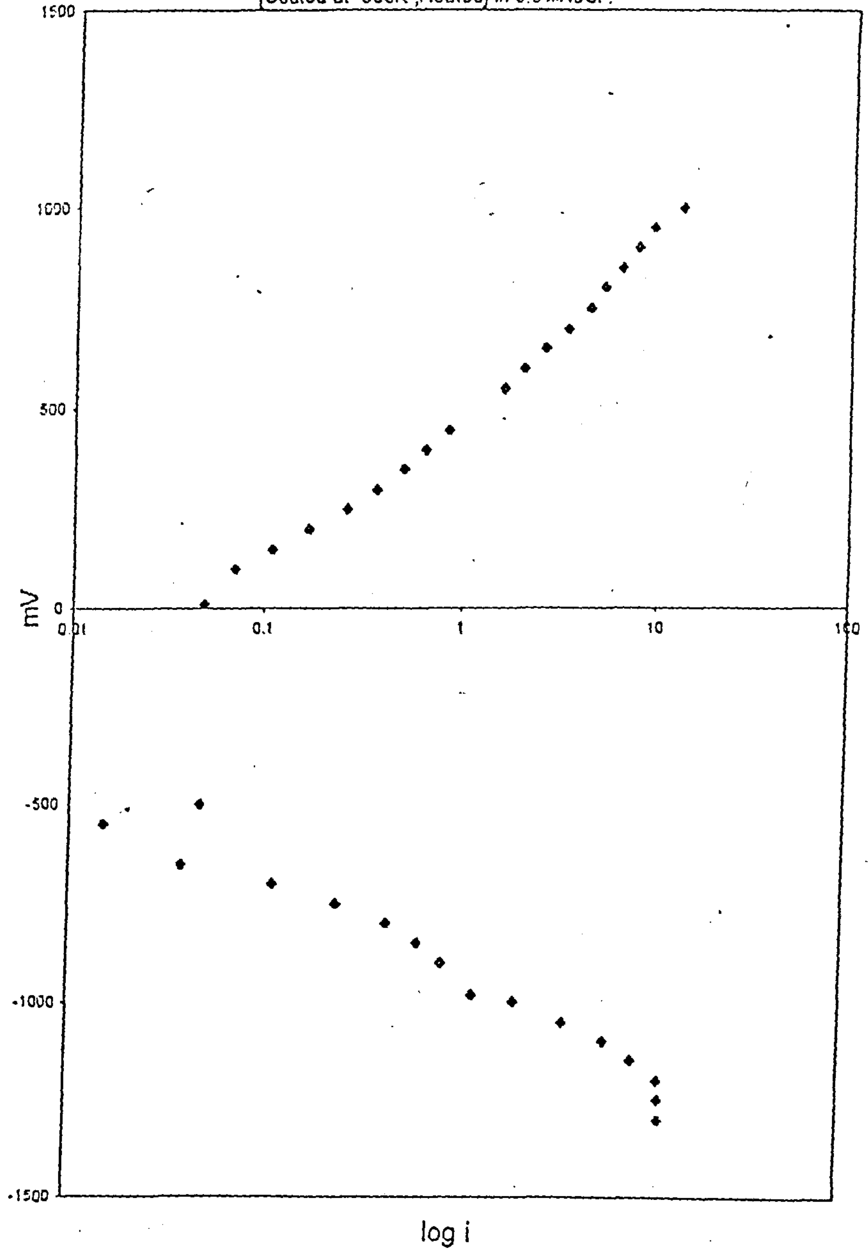


Fig.4.18- Corrosion studies :Tafel plot of plate T-4.H [Coated at 353K ,Heated] in 3.5%NaCl .



4.4 EFFECT OF EN BATH CONCENTRATION ON CORROSION

Tafel plots obtained during the corrosion studies of the nickel coated plates obtained from EN baths with various nickel ion concentrations from 0.01M to 0.05M are shown in figures 4.19 to 4.24 . Interestingly, although desired nature of coating is not obtained from bath with higher Ni^{+2} concentrations (Chapter Three), the calculated corrosion rate (Table – 4.3) is lowest for plating obtained with 0.05M concentration of metal ion. Since the increase in the concentration of the nickel ion increases the thickness of the coating, though not of the desired texture, it enhances the resistance to corrosion.

4.5 EFFECT OF ZINCATING MODE ON CORROSION

Zincating as a pre-plate[7-18] step in electroless plating process plays an important role in this technique. It is a well known fact that ,the pre-plate treatment governs the quality of EN plating ,especially on aluminium substrate and also the modified pre-plate treatment cycle[19] enhances corrosion resistance. As mentioned in Chapter 2, EN plating on aluminium, with single zincating , double zincating and excessive zincating have been tried out and the corrosion resistance data of the coated plates is tabulated in Table – 4.4.

It is seen that corrosion rate in 3.5 % NaCl is lower with single zincating. Figure 4.25 - 4.30. are the Tafel plots obtained during the corrosion studies of nickel coated aluminium plates with different zincating mode. Figure 4. shows the surface morphology (magnified) of the zincated aluminium surface. A thin uniform layer of zinc on the aluminium substrate is considered to be responsible for plating a strongly bonded nickel layer on to it .

4.6 EFFECT OF VARIOUS pH ADJUSTERS ON CORROSION

In the present investigation, different pH adjusting compounds like ammonia, hydrazine hydrate, sodium hydroxide and potassium carbonate are tried, in which the first two mentioned, have yielded the desired results, without disturbing the stability of the bath. Corrosion data in 3.5 % NaCl of EN plated panels, with two different pH adjusters, namely ammonia and hydrazine hydrate, is presented in Table- 4.5 and the figures 4.31 to 4.34 shows the corresponding Tafel plots obtained during the corrosion studies. It is observed that ammonia as a pH adjuster in EN bath solution yields better resistance to corrosion of the plated aluminium.

Fig.4.19-Corrosion studies: Tafel plot of plate C-2 [0.01m Ni 2+ EN bath] in 3.5%NaCl.

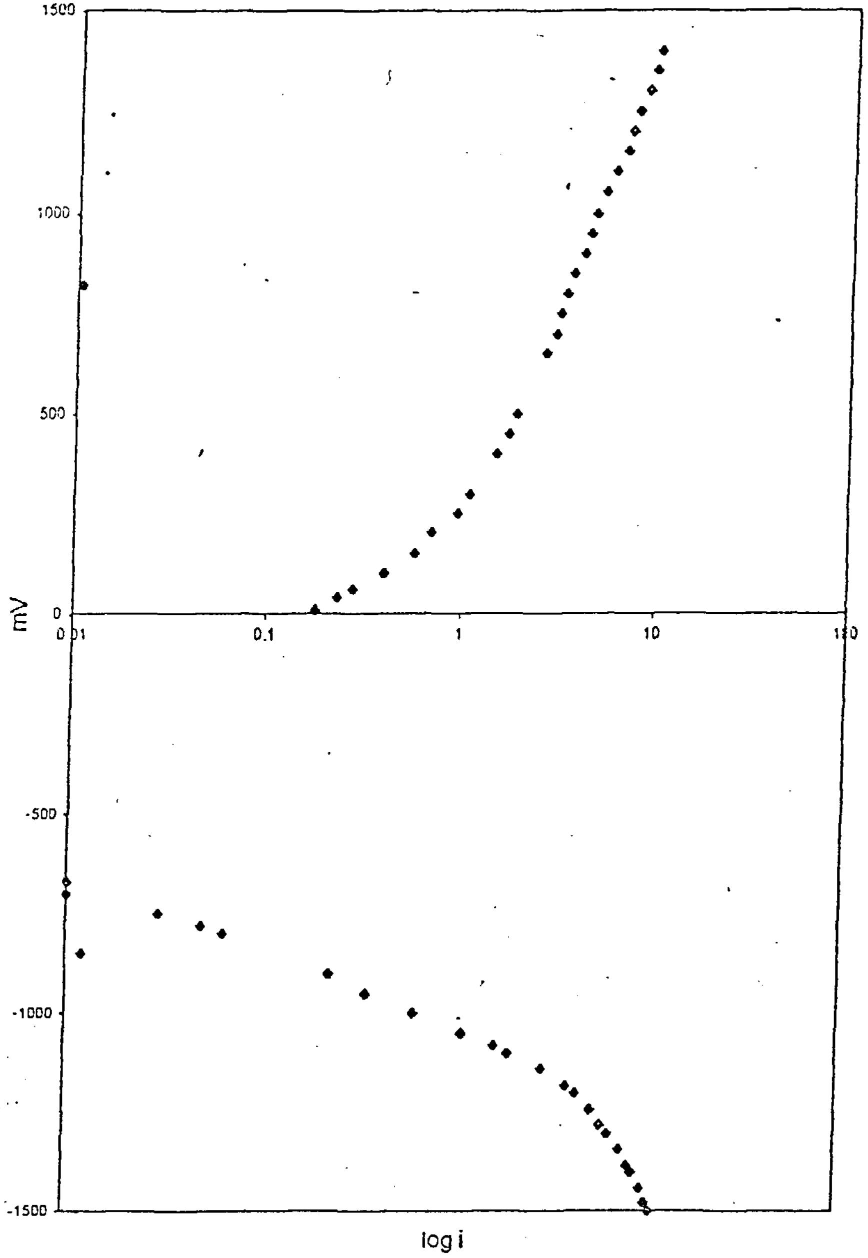


Fig.4.20-Corrosion studies:Tafel plot of plate C-2.H [0.01M Ni -ion, EN bath] in 3.5%NaCl.

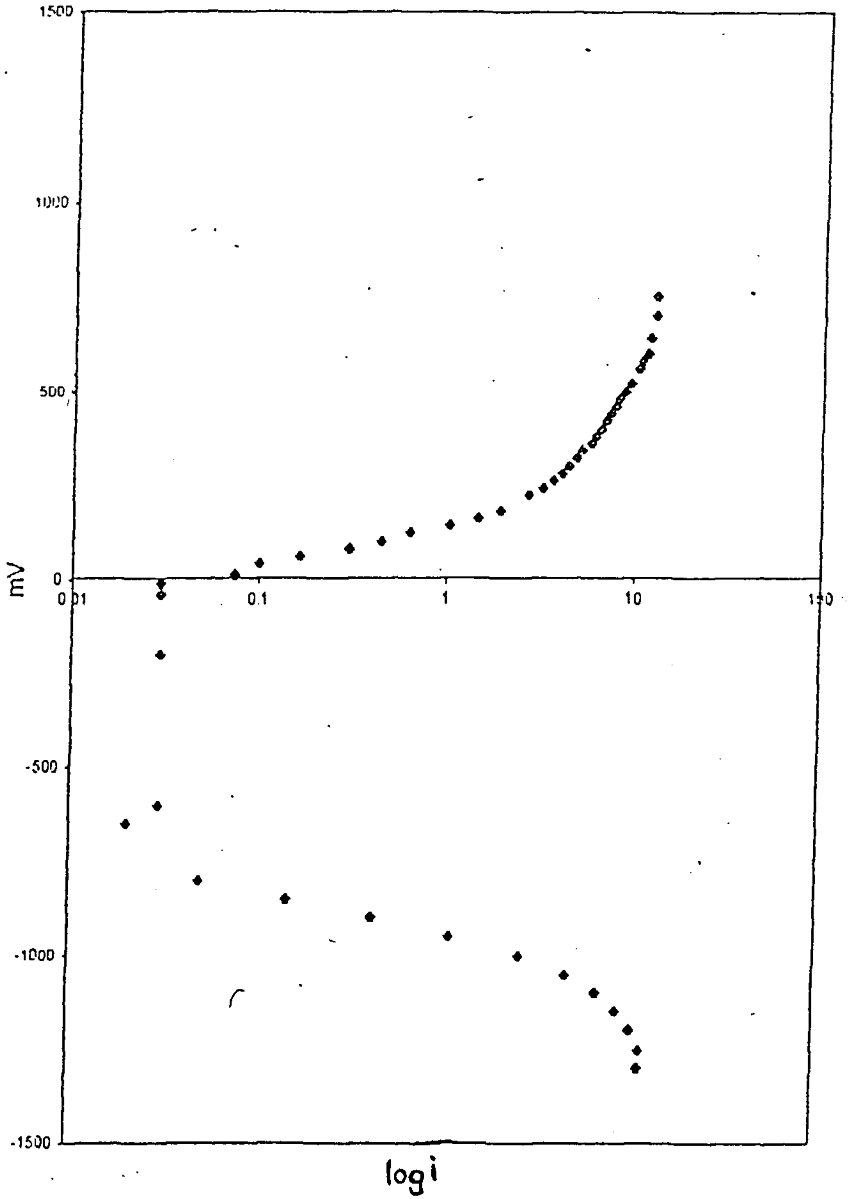


Fig.4.21-Corrosion studies:Tafel plot of plate C-3
[0.02M Ni ion,EN bath] in3.5%NaCl

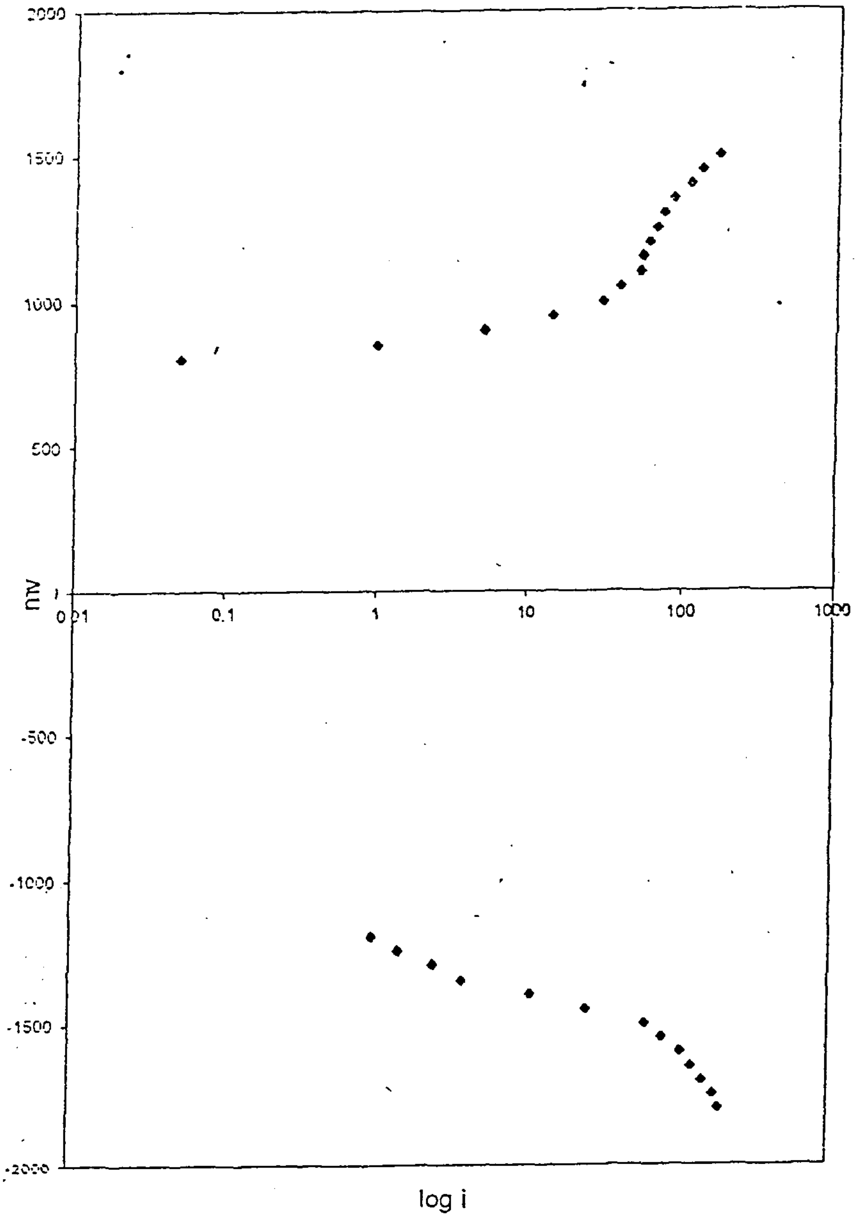


Fig.4.22-Corrosion studies :Tafel plot of plate C-3.H
[0.02M Ni ion,EN bath] in 3.5%NaCl .

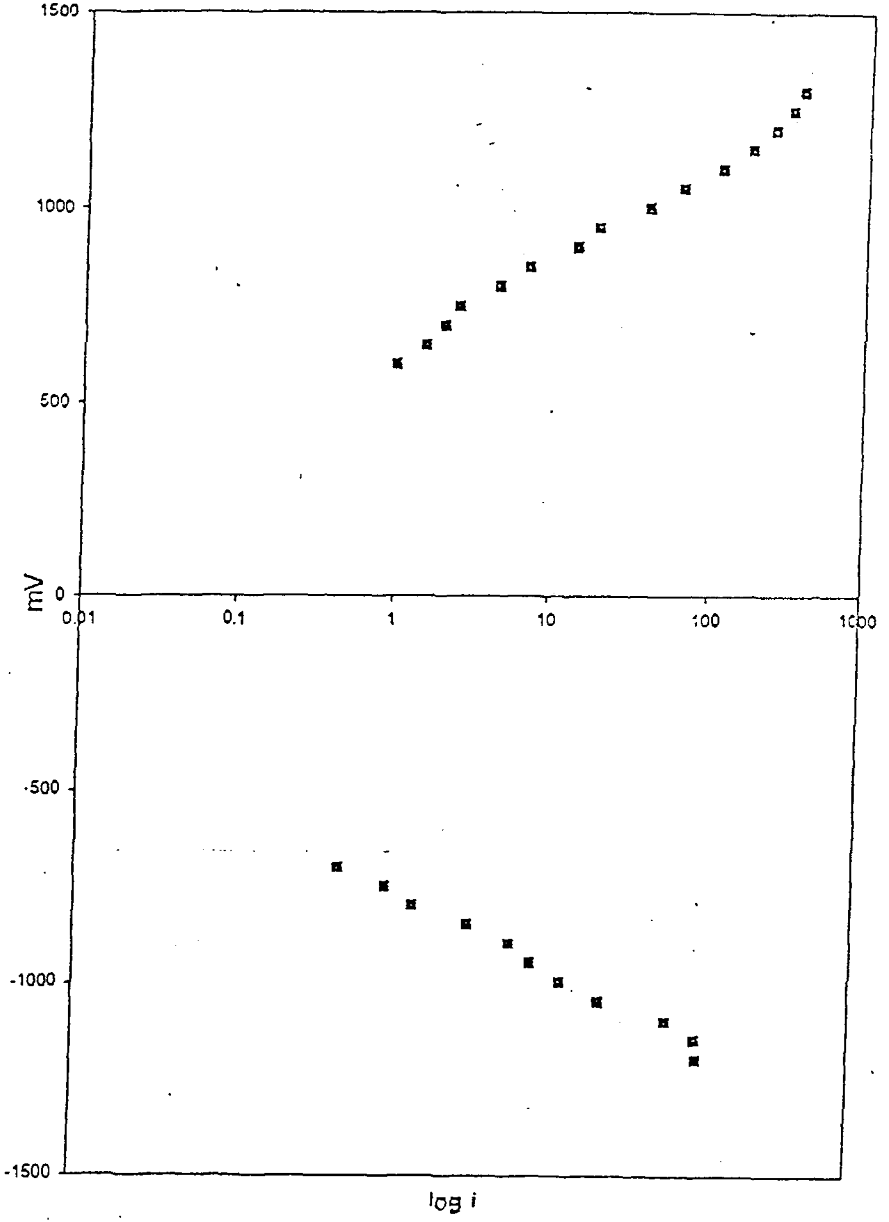


Fig.4.23-Corrosion studies:Tafel plot of plate C-7
[0.05M Ni ion, EN bath] in 3.5%NaCl.

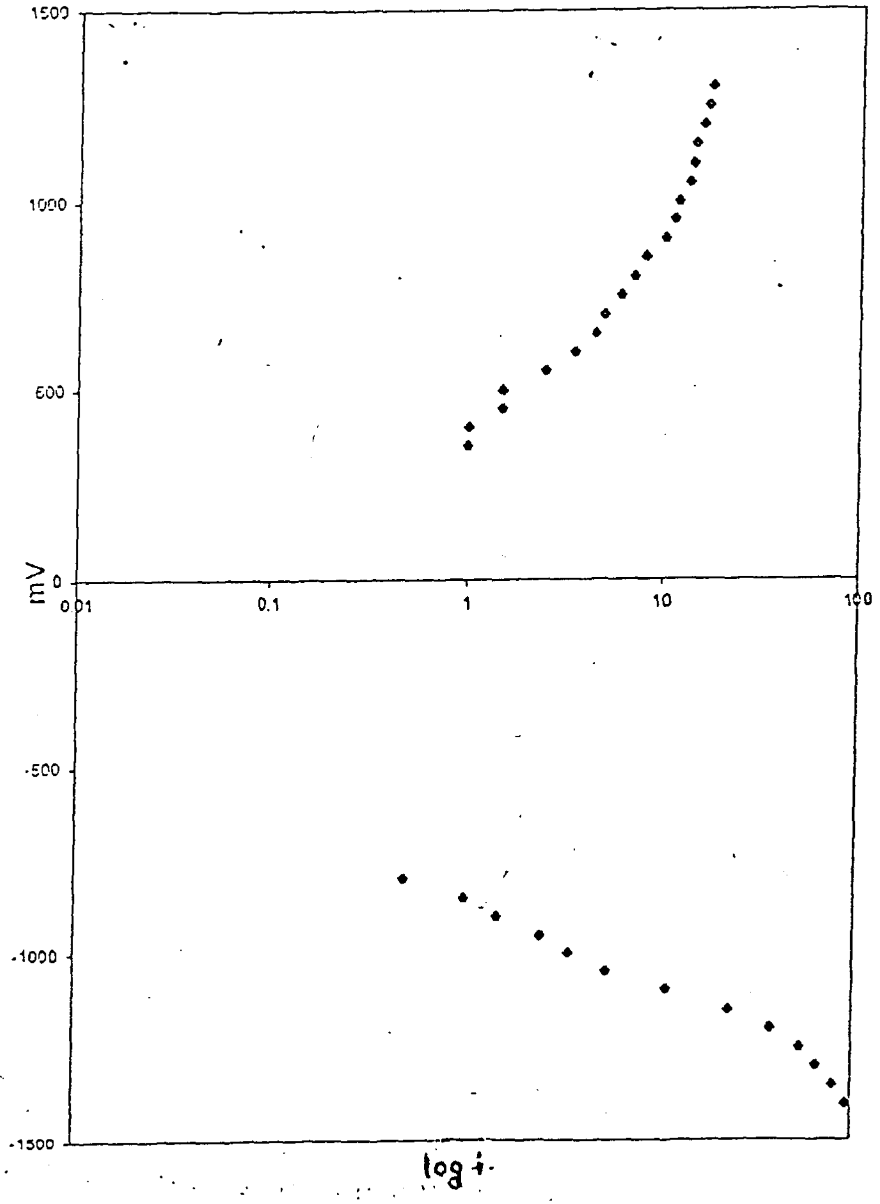


Fig.4.24-Corrosion studies :Tafel plot of plate C-7.H
[0.05M Ni ion, EN bath] in 3.5%NaCl .

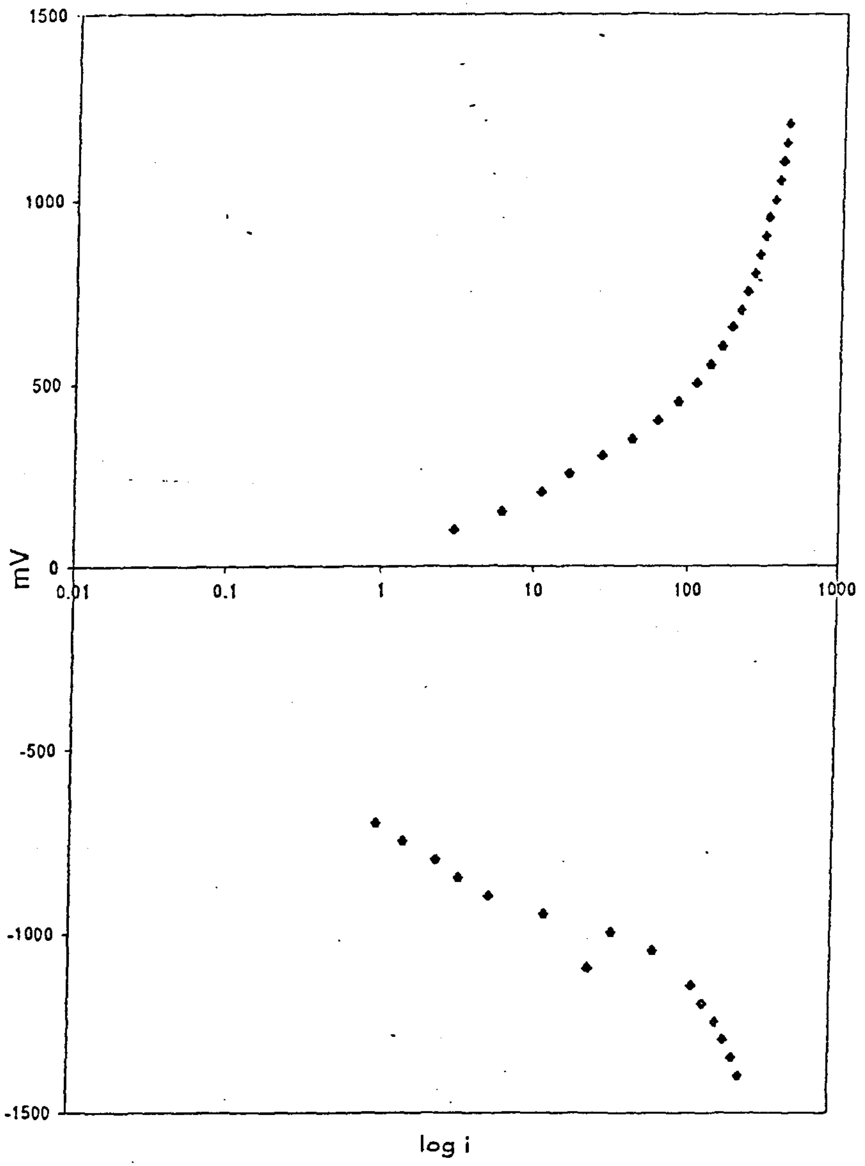


Fig.4.25-Corrosion studies: Tafel plot of plate Z-9 in 3.5%NaCl with Single zincating mode.

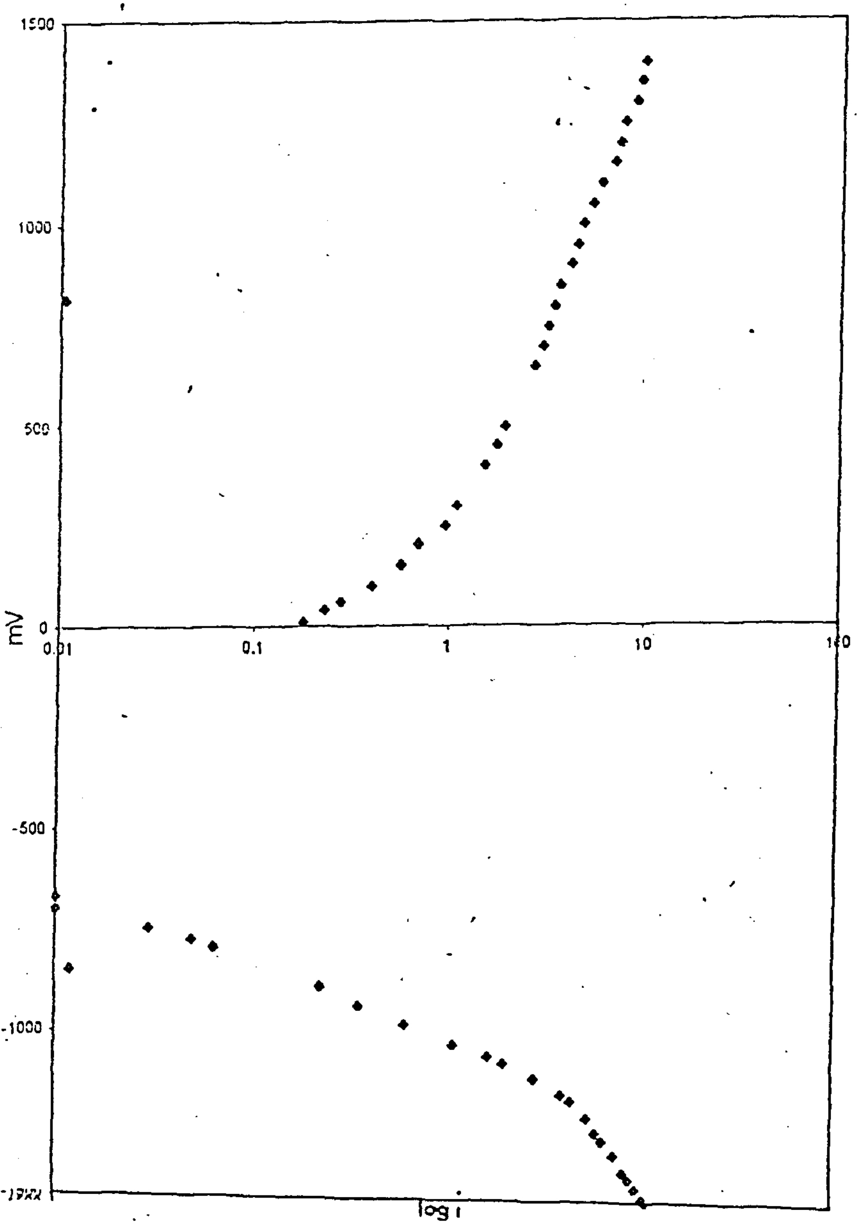


Fig.4.26-Corrosion studies: Tafel plot of plate z-9.H in 3.5%NaCl with Single zincating mode.

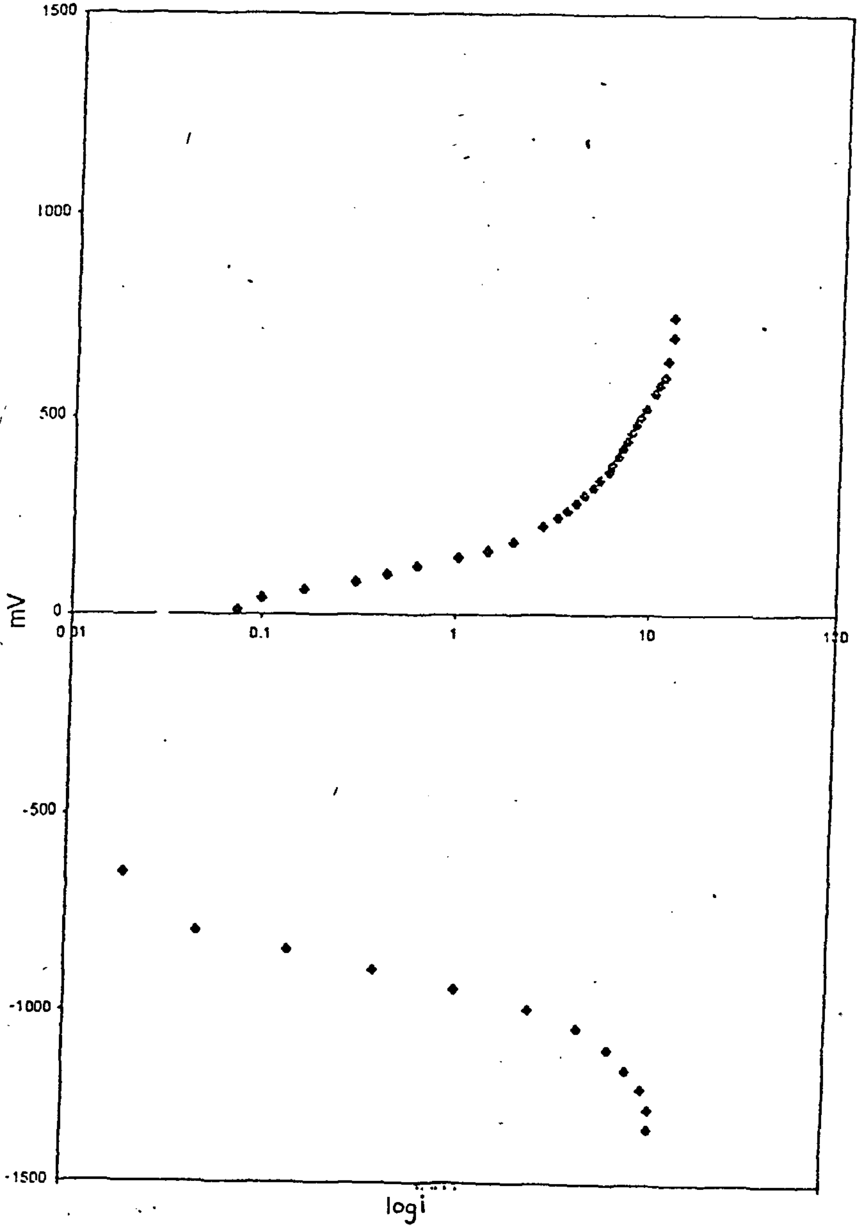


Fig.4.27-Corrosion studies:Tafel plot of plate Z-10 in 3.5% NaCl with Double zincating mode.

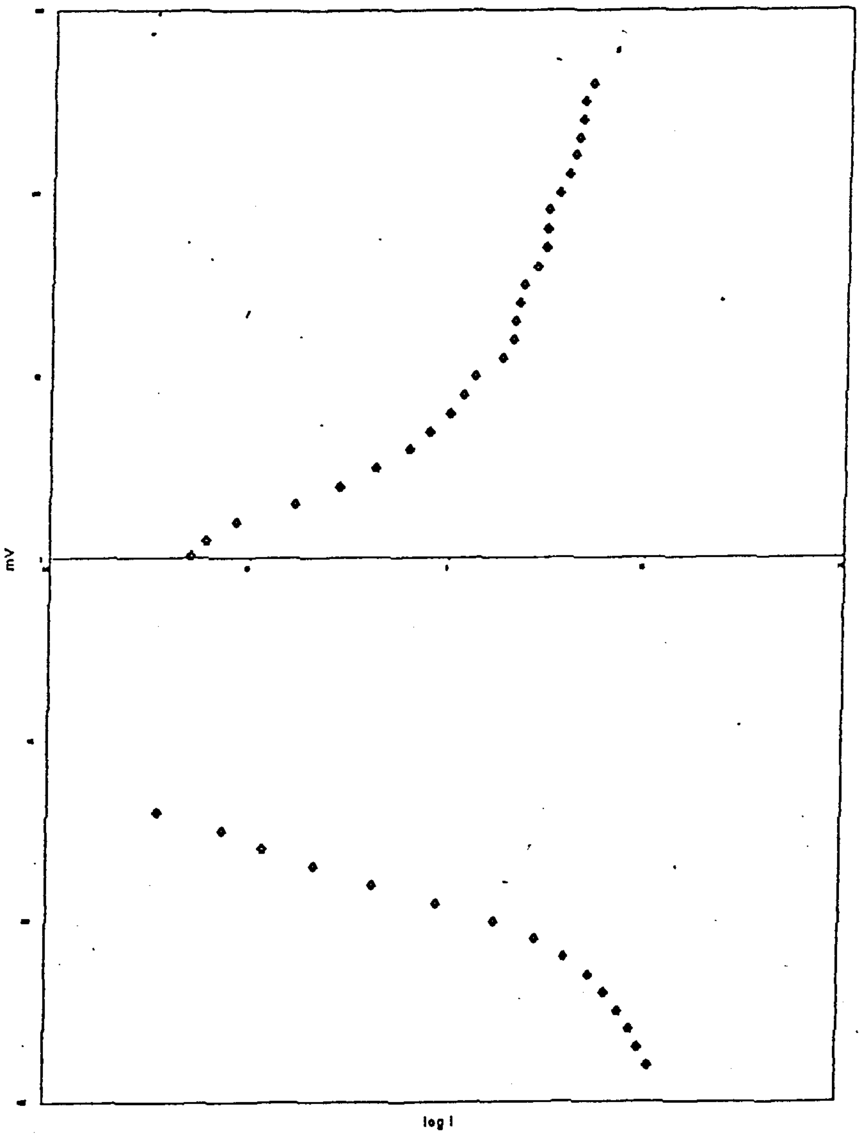


Fig.4.28-Corrosion studies:Tafel plot of plate Z-10.H in 3.5%NaCl with Double zincating mode.

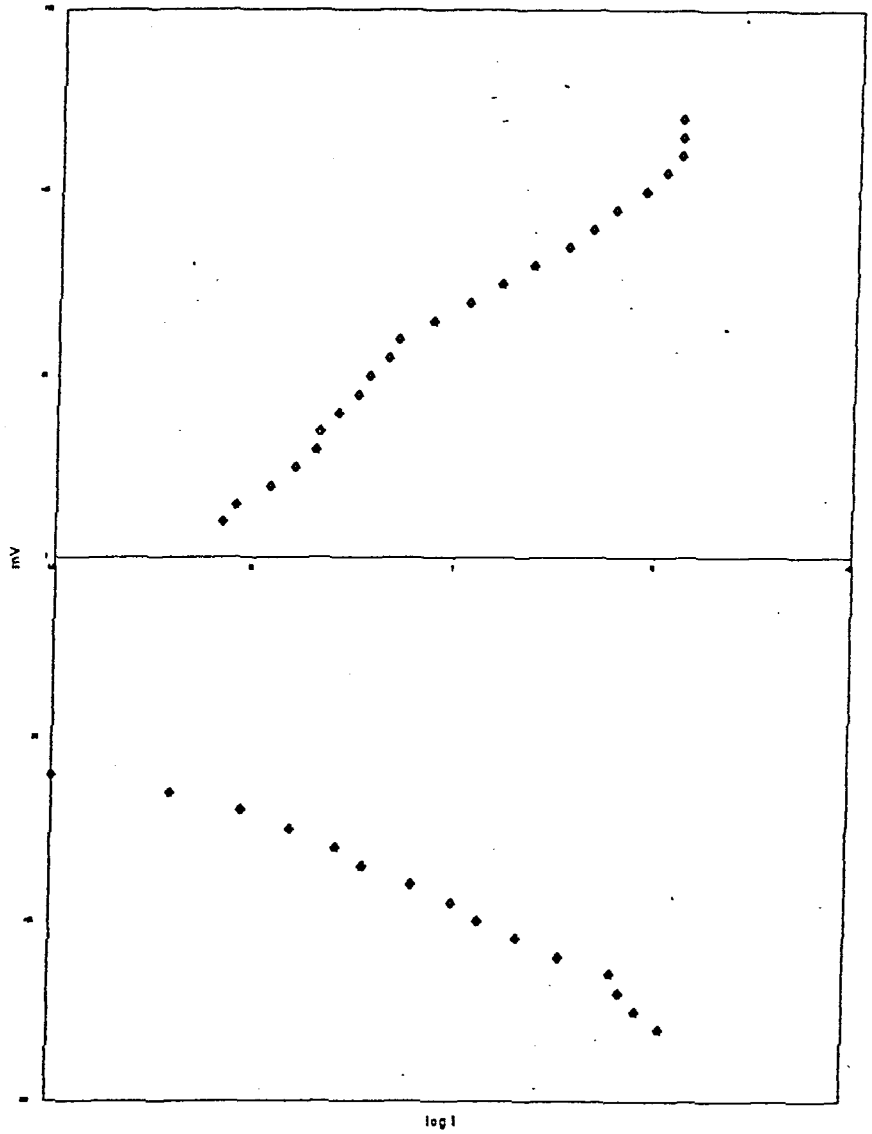


Fig.4.29 - Corrosion studies:Tafel plot of plate z-11,in 3.5%Nacl with Excess zincating.

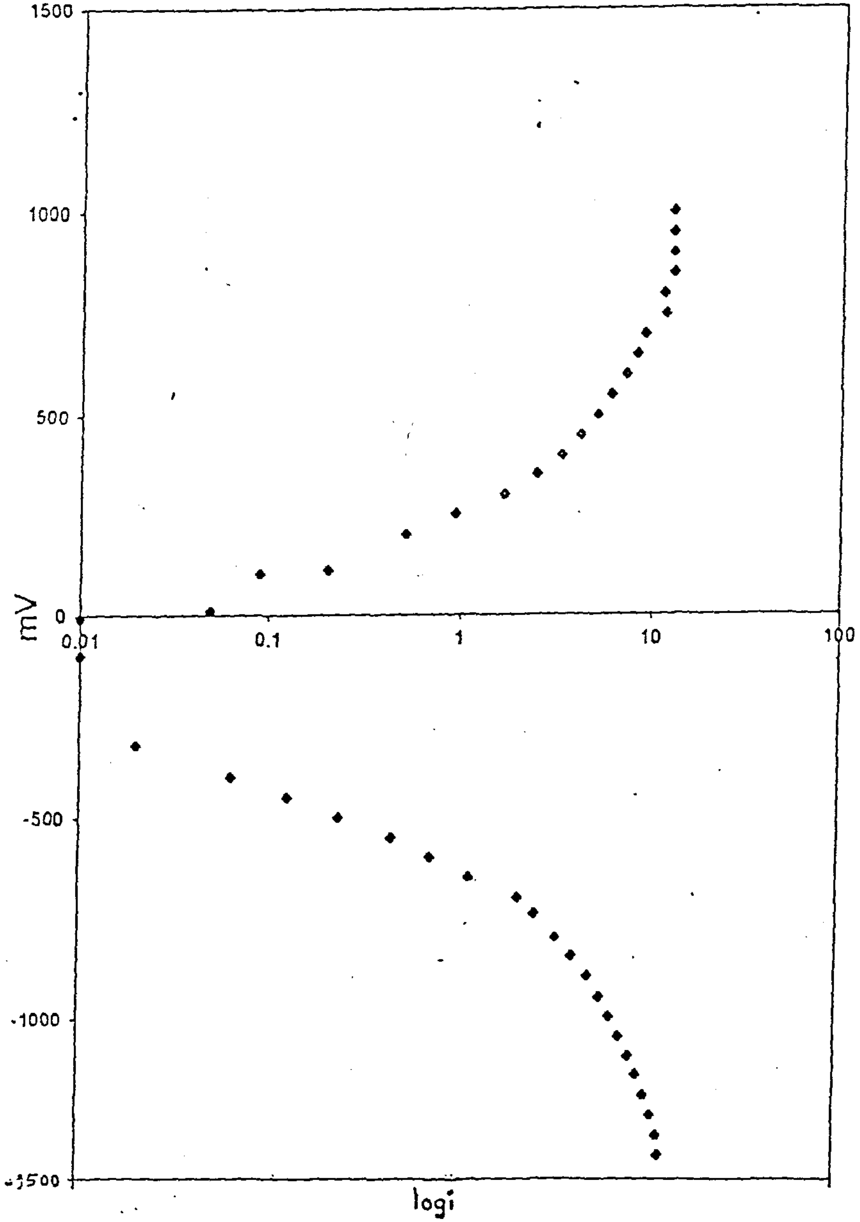


Fig.4.30- Corrosion studies:Tafel plot of plate z-11.H ,in 3.6%NaCl with Excess zincating.

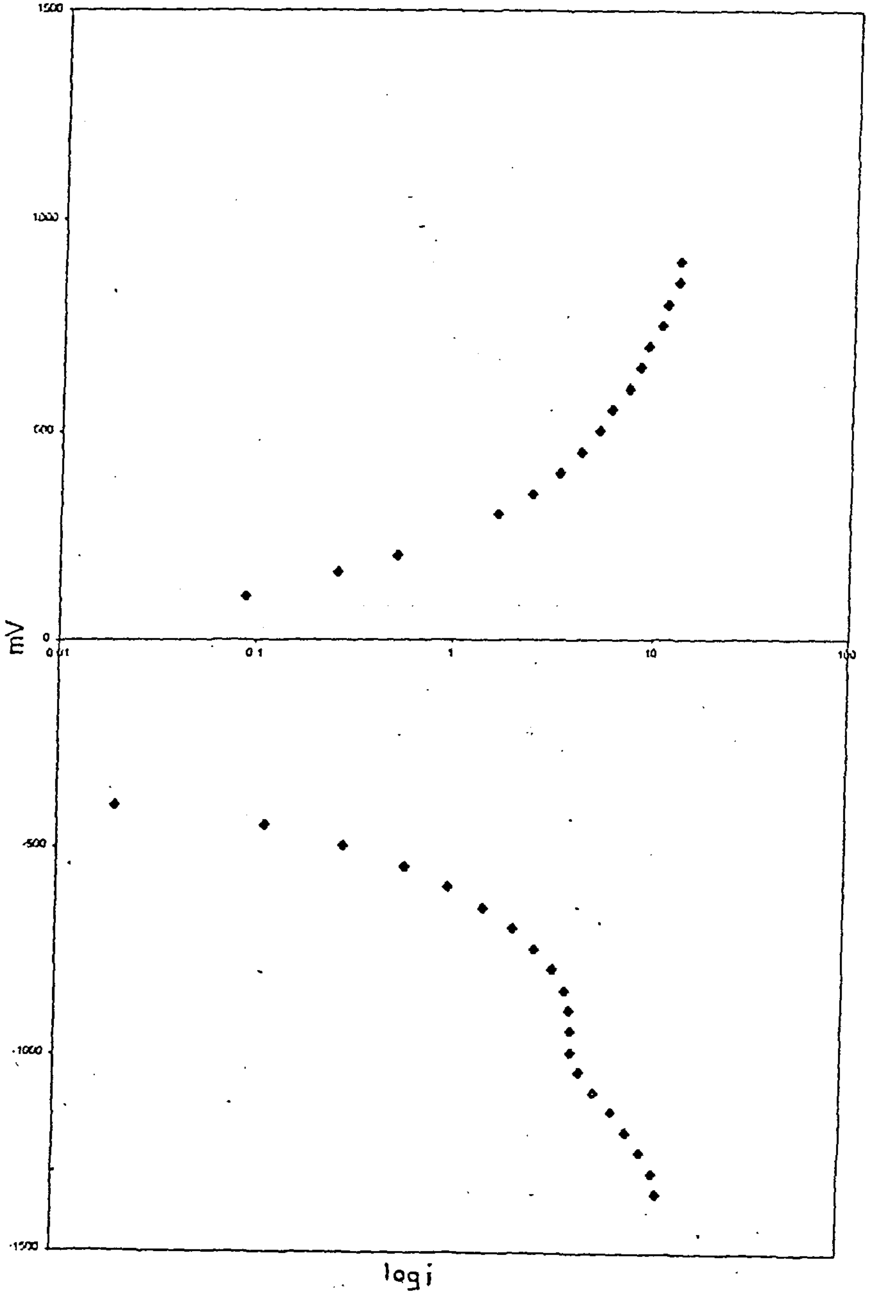


Fig.4.31-Corrosion studies: Tafel plot of plate P-34 in 3.5%NaCl with Ammonia as pH adjuster

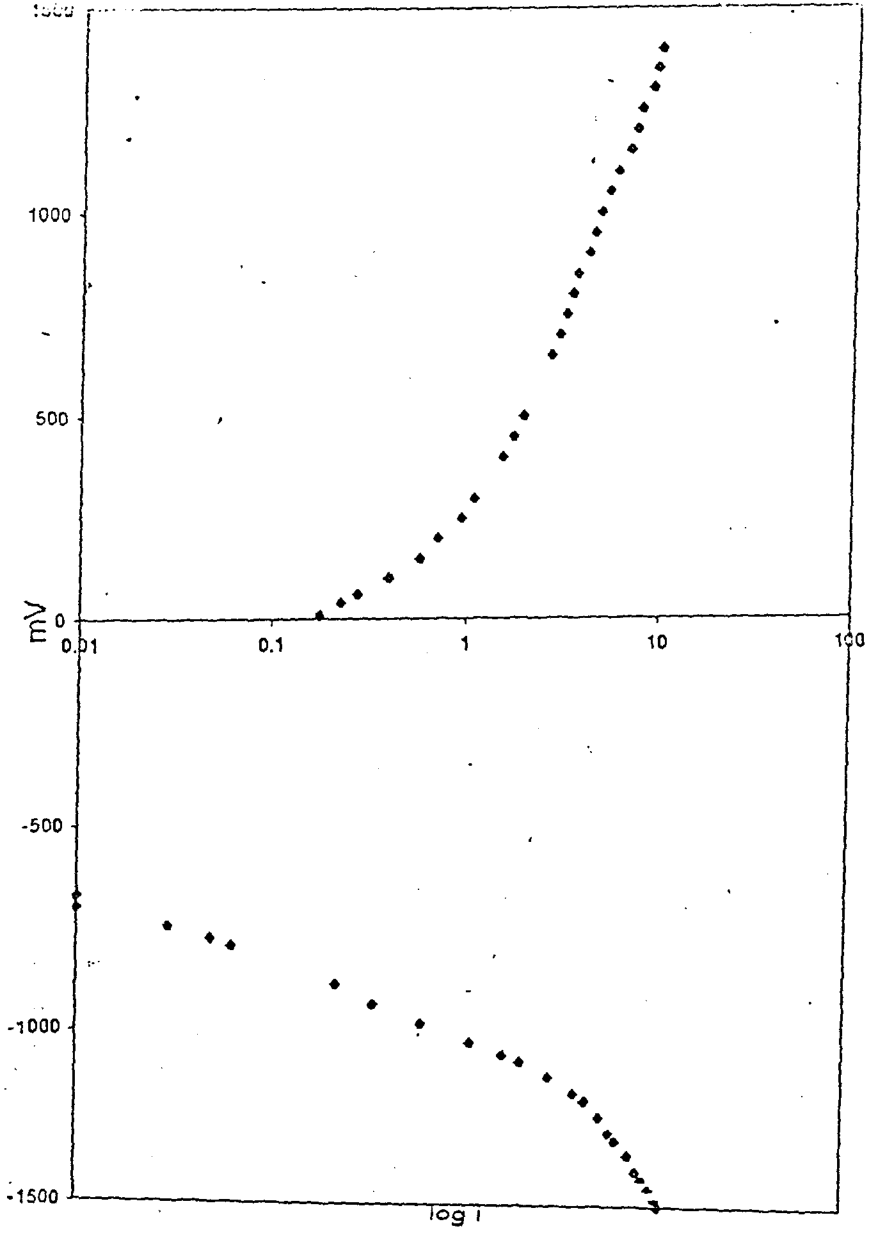


Fig.4.32-Corrosion studies: Tafel plot of plate P-34.H in 3.5%NaCl with Ammonia as pH adjuster

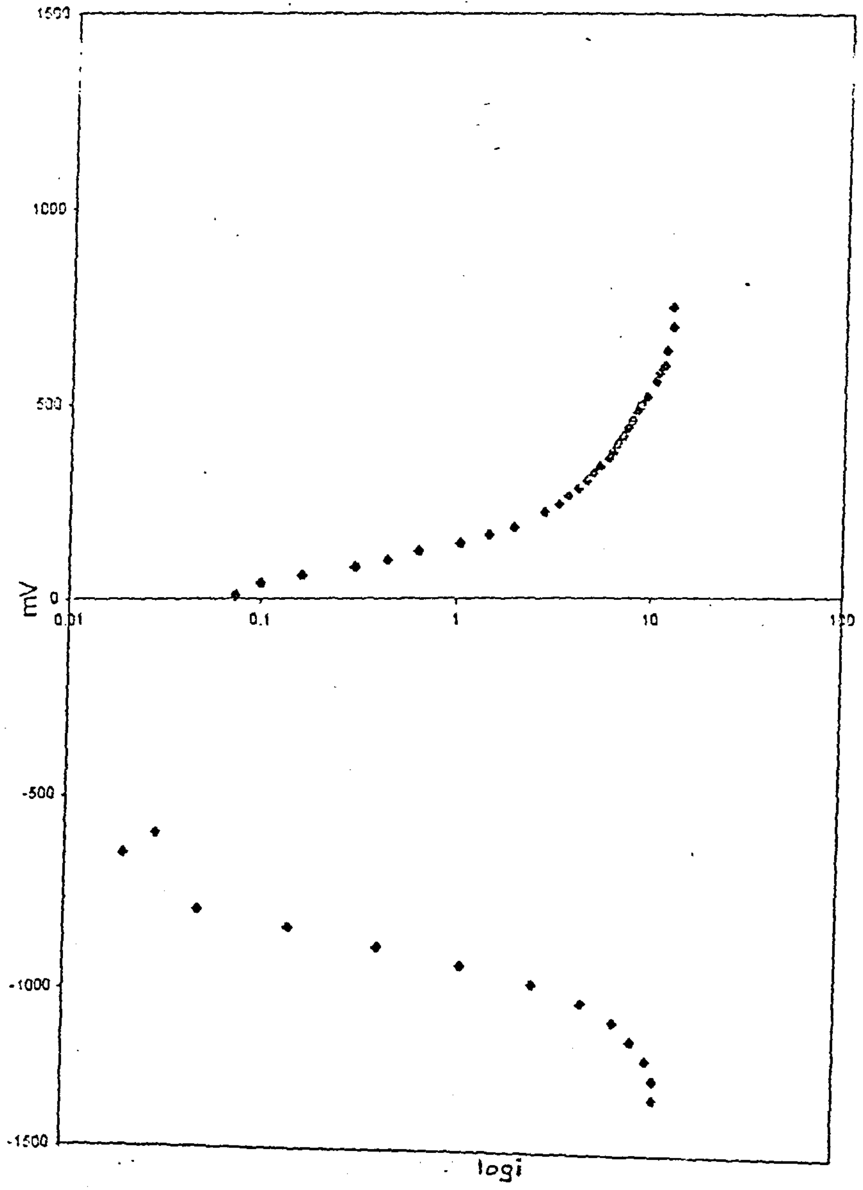


Fig.4.33-Corrosion studies:Tafel plot of plate H-1,in 3.5%NaCl with Hydrazine hydrate as pH Adjuster

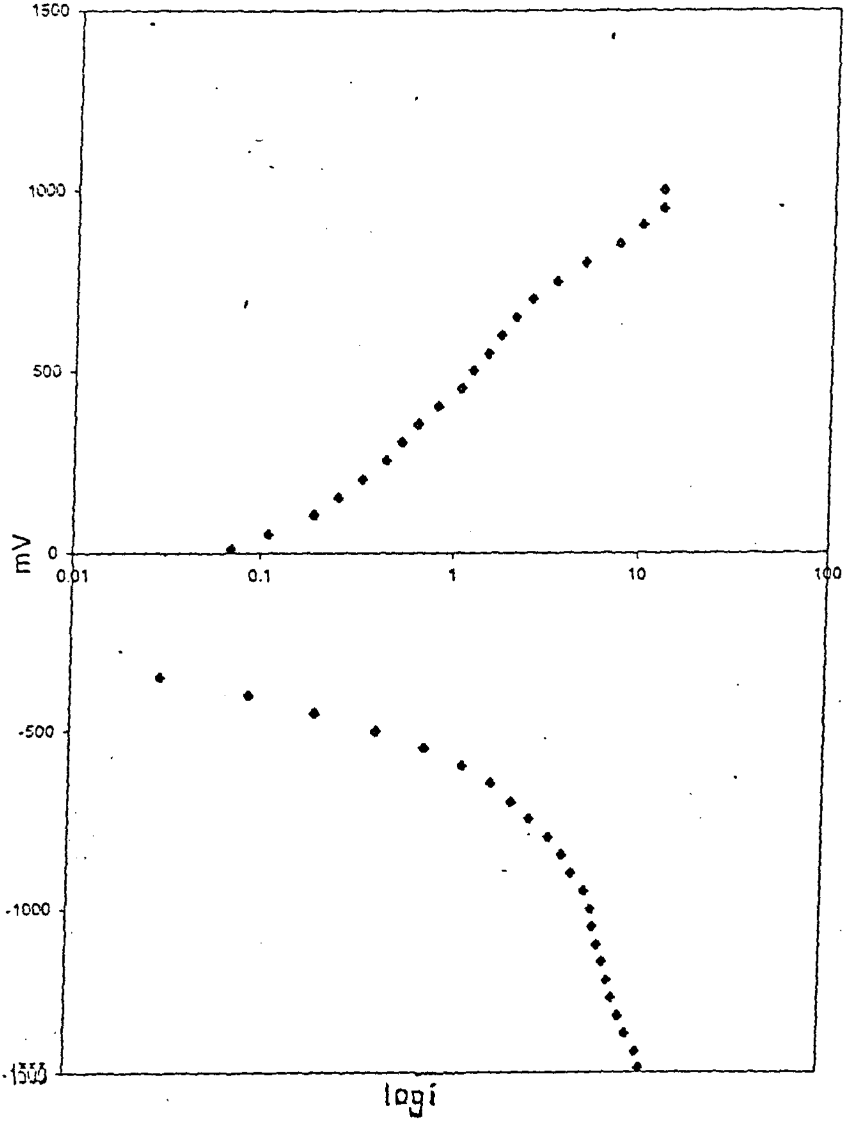
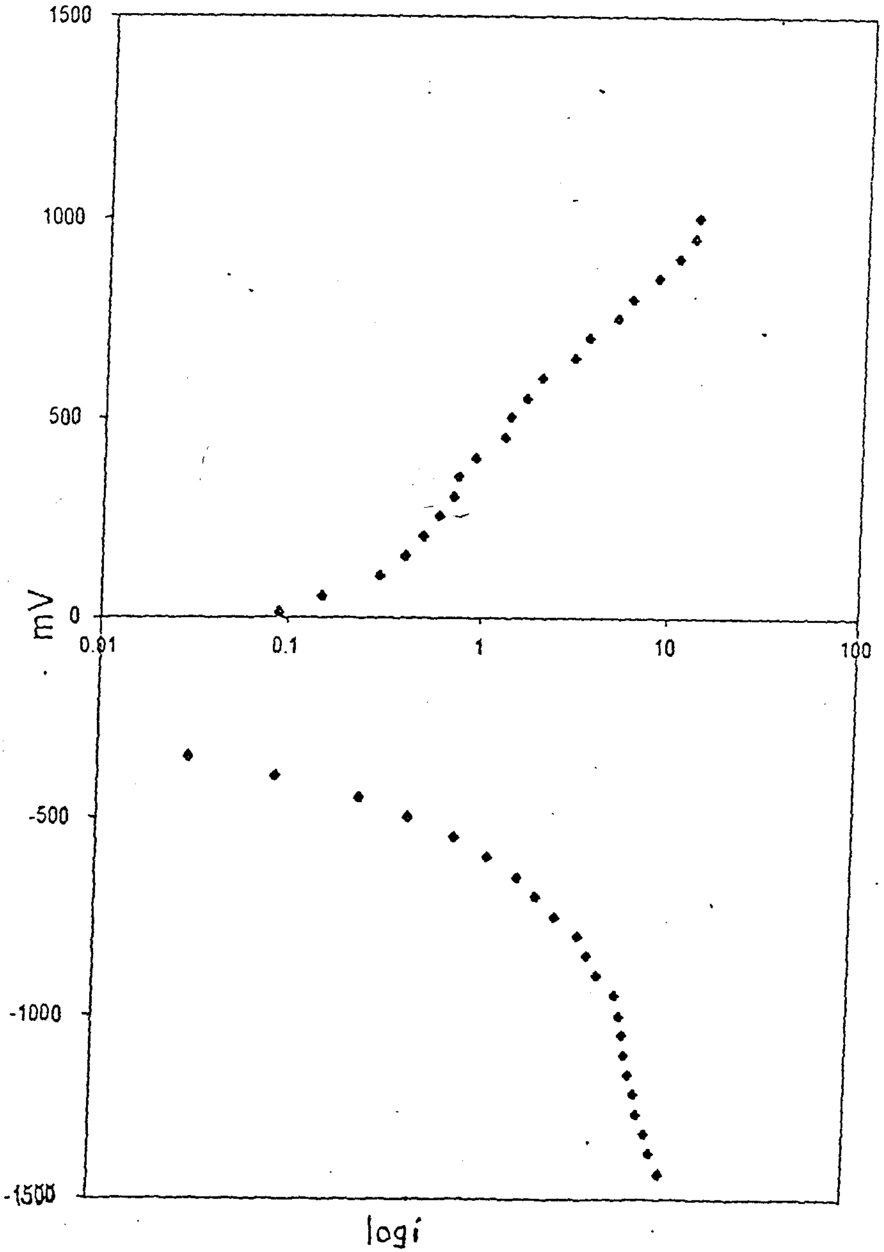


Fig.4.34-Corrosion studies:Tafel plot of plate H-1.H in 3.5%NaCl with Hydrazine hydrate as pH adjuster.



4.7 STABILITY OF COATED FILM AT HIGH TEMPERATURE

The behaviour of the chemically deposited nickel coatings at higher temperature is of upmost important, looking into its applications. It is therefore important to monitor the surface properties of the coated film after it is subjected to the heat treatment. The coated thin film of EN, in this investigation, shows (Fig. 4.41 and 4.43) cracks after heating to about 723K. This cracks are the potent cites for destructive attack on the base metal by corrosive environment thus enhancing the corrosion. The corrosion data presented in Table 4.1 to 4.5, gives the comparison between the corrosion rate of EN plated aluminium plates in various environments before and after heat (labelled as 'H') treatment. The corrosion rate are higher for heated plates. This is in agreement with the earlier report[20] stating that the heat treatment increases the corrosion rate.

4.8 CORROSION RESISTANCE OF EN COATED COPPER

Corrosion resistance studies of EN coated copper plates were also carried out in 3.5%NaCl ,1N HCl, and 2N H_2SO_4 environment . The data is presented in Table 4.7 with the corresponding Tafel plots shown in Figure 4.37- 4.40. It is observed that the rate of corrosion of the EN coated copper plate is lowest in 3.5% NaCl, and the order is:

3.5 % NaCl < 2N H_2SO_4 < 1 N HCl.

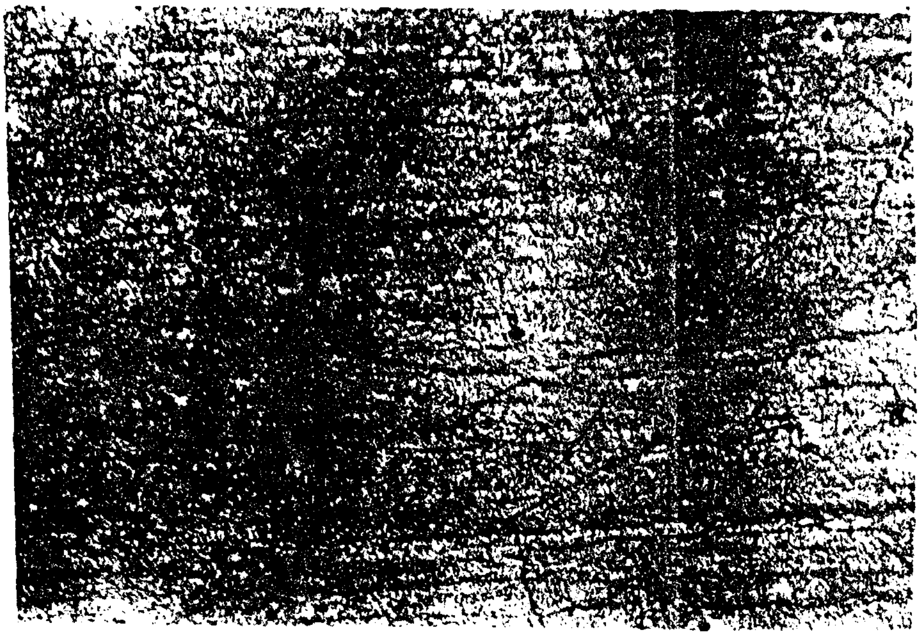


Fig. 4.41 : Photograph (before corrosion) of EN Coated Aluminium Plate, [Heated]
Magnification 600 X

Fig 4.42 : Photograph (after corrosion) of above EN coated Aluminium Plate, kept in 3.5% NaCl, salt spray chamber for 96 hrs, Magnification 600 X

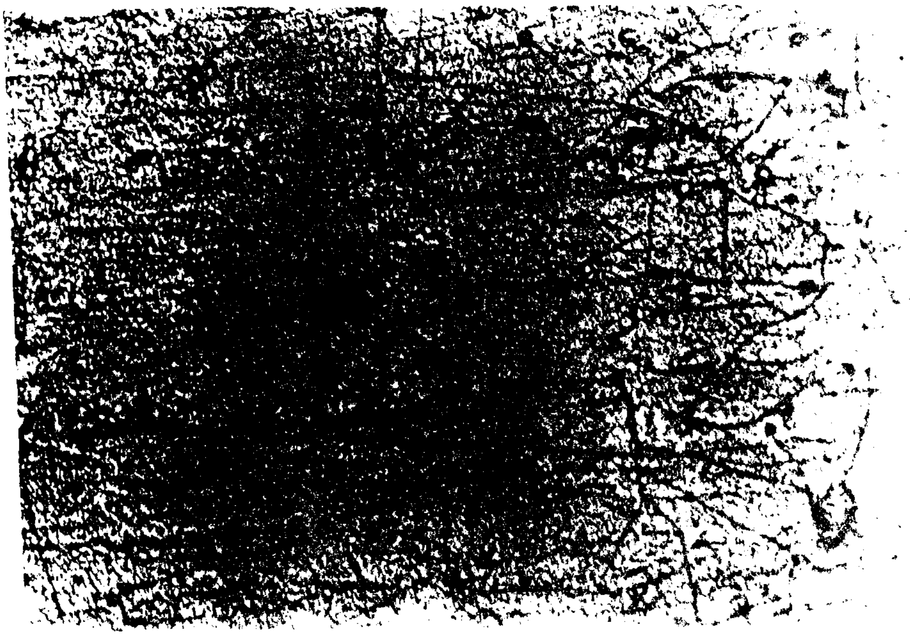


Fig. 4.43: Photograph (before corrosion) of EN Coated Aluminium Plate, [Heated] Magnification 600 X

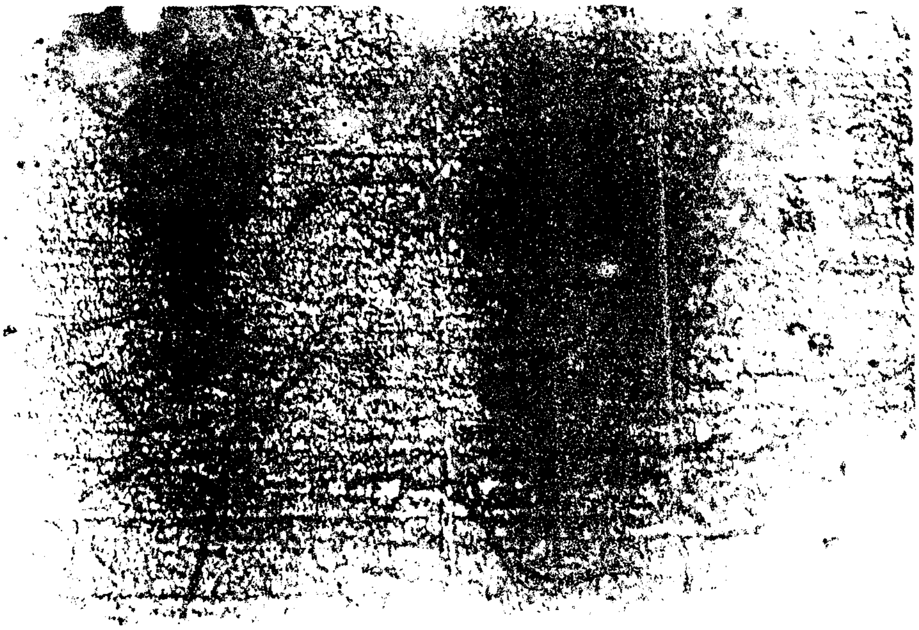


Fig. 4.44: Photograph (after corrosion) of above EN Coated Aluminium Plate, kept in 3.5% NaCl, salt spray chamber for 108 hrs, Magnification 600 X

TABLE – 4. 1

Corrosion data of EN plated panels at various temperatures in 3.5 % NaCl

Sweep rate : 1 mV / sec

Current range : 1000mA

Reference electrode : Saturated Calomel electrode

Counter electrode : Platinum electrode

Area of electrode : 1.0 cm^2

Plate code	Temperature Kelvin	β_a mv	β_c mv	Rp	I cor. μ A/cm^2	Corrosion rate mpy	Figure
T-1	338	200	220	100	0.454893	0.194736	4.11
T-1.H	338	300	160	80	0.566369	0.242466	4.12
T-2	343	300	260	133	0.454737	0.194829	4.13
T-2.H	343	300	400	85	0.87573	0.375201	4.14
T-3	348	90	110	375	0.057316	0.024556	4.15
T-3.H	348	100	120	111.1	0.293182	0.133961	4.16
T-4	353	500	160	250	0.21052	0.090196	4.17
T-4.H	353	300	200	100	0.521059	0.223244	4.18

TABLE – 4.3

Corrosion data of EN plated panels at various Concentration of Ni^{2+} in 3.5 % NaCl

Sweep rate : 1 mV / sec

Current range : 1000mA

Reference electrode : Saturated Calomel electrode

Counter electrode : Platinum electrode

Area of electrode : 1.0 cm^2

Plate code	Concentration of Nickel	β_a mv	β_c mv	Rp	I cor. $\mu A/cm^2$	Corrosion rate mpy	Figure
C - 2	0.01M	90	110	375	0.57316	0.024455	4.19
C - 2.H	0.01M [H]	100	120	211	0.112249	0.048092	4.20
C - 3	0.02 M	70	100	300	0.047678	0.020427	4.21
C – 3.H	0.02 M [H]	70	100	85	0.210346	0.090121	4.22
C - 7	0.05M	90	100	480	0.044770	0.019185	4.23
C – 7.H	0.05 M [H]	260	250	375	0.147576	0.063228	4.24

TABLE – 4.4

Corrosion data of EN plated panels at various Zincating type in 3.5 % NaCl.

Sweep rate : 1 mV / sec

Current range : 1000mA

Reference electrode : Saturated Calomel electrode

Counter electrode : Platinum electrode

Area of electrode : 1.0 cm^2

Plate code	Zincating type	β_a mv	β_c mv	Rp	I cor $\mu A/cm^2$	Corrosion rate mpy	Figure
Z - 9	Single	90	110	375	0.057316	0.024556	4.25
Z - 9.H	Single [H]	100	120	111	0.213182	0.091336	4.26
Z - 10	Double	220	120	480	0.070240	0.030093	4.27
Z - 10.H	Double [H]	300	180	400	0.122123	0.052322	4.28
Z - 11	Black Ni	160	120	375	0.079200	0.034018	4.29
Z - 11.H	Black Ni [H]	120	360	375	0.104211	0.044648	4.30

TABLE – 4.5

Corrosion data of EN plated panels with different pH adjusters, in 3.5 % NaCl.

Sweep rate : 1 mV / sec

Current range : 1000mA

Reference electrode : Saturated Calomel electrode

Counter electrode : Platinum electrode

Area of electrode : 1.0 cm^2

Plate code	pH adjuster	β_a mv	β_c mv	Rp	I cor $\mu A/cm^2$	Corrosion rate mpy	Figure
P - 34	NH_3	90	110	375	0.057316	0.026460	4.31
P – 34.H	NH_3	100	120	111.1	0.2131820	0.098419	4.32
H - 1	N_2H_4	320	160	375	0.123510	0.057020	4.33
H – 1.H	N_2H_4	300	170	300	0.157064	0.067290	4.34

TABLE – 4.7

Corrosion data of EN plated Copper panels in various Environment by potentiodynamic method

Sweep rate : 1.5 mV / sec

Current range : 1000mA

Reference electrode : Saturated Calomel electrode

Counter electrode : Platinum electrode

Area of electrode : 1.0 cm^2

Plate code	Environment	β_a mv	β_c mv	E cor mv	I cor $\mu A/cm^2$	Corrosion rate mpy	Figure
Cu –1	3.5% NaCl	1808	357.91	-291.38	0.08	0.03390	4.37
Cu –2.	3.5% NaCl	274.81	1400.43	-308.68	0.04	0.01890	4.38
Cu –3	1N HCl	71.64	397.57	-212.55	20.22	08.670	4.39
Cu -4	2N H_2SO_4	52.35	183.68	-60.27	3.75	01.608	4.40

Fig.4.37-Corrosion studies : Tafel plot of EN coated Copper plate Cu –1, in 3.5% NaCl

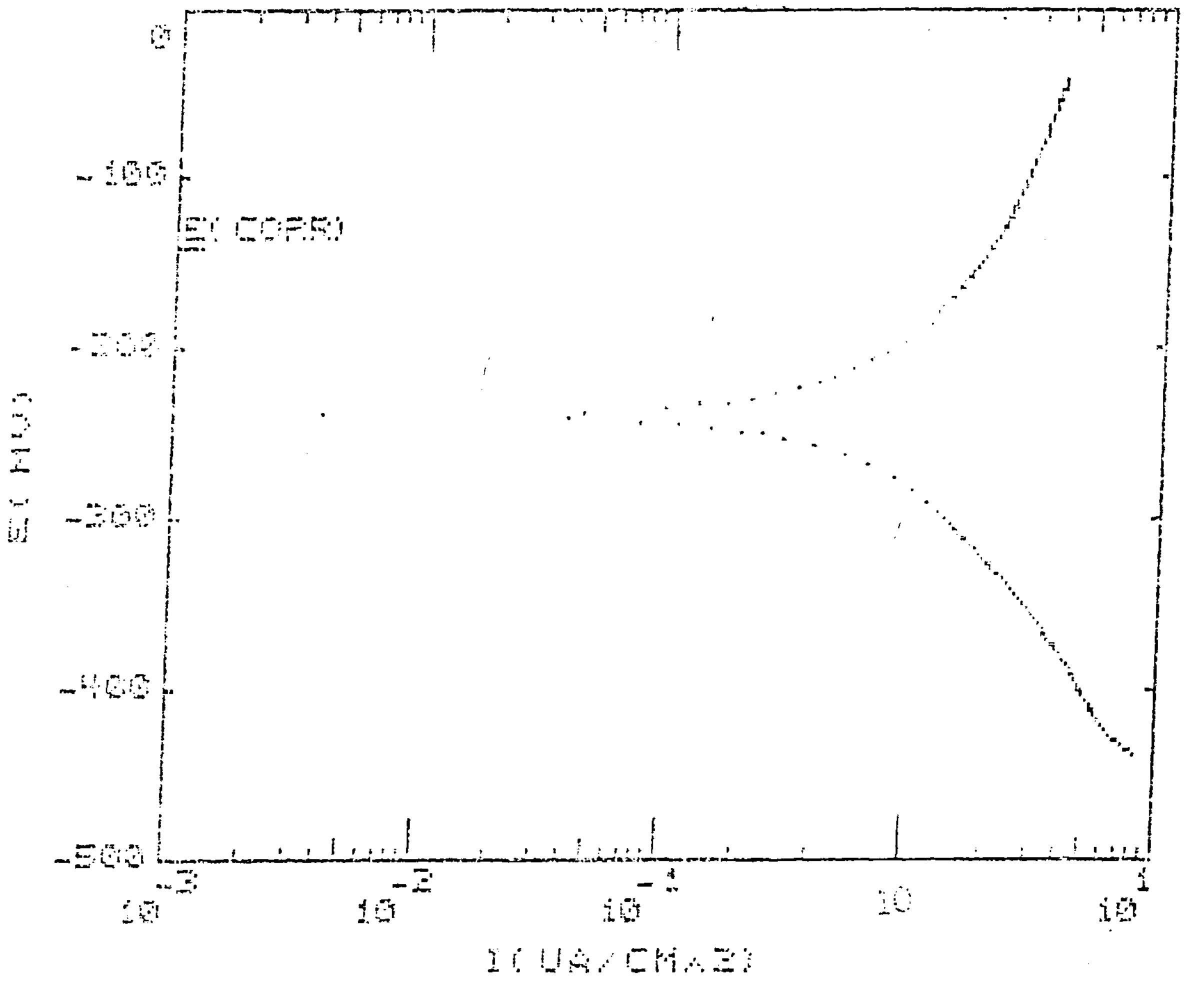


Fig.4.38-Corrosion studies:Tafel plot of EN coated Copper plate Cu –2, in 3.5% NaCl

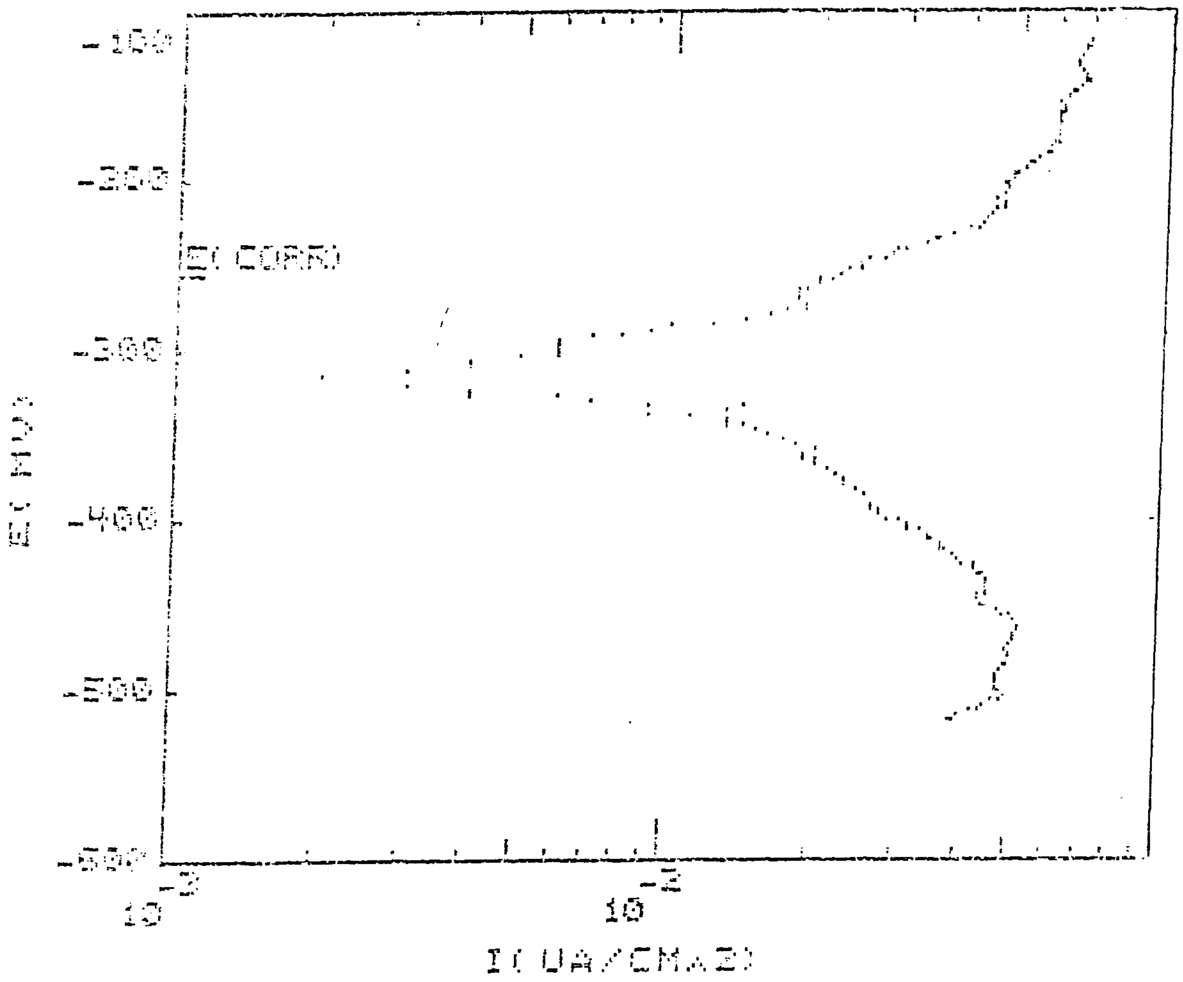


Fig.4.39-Corrosion studies :Tafel plot of EN coated Copper plate Cu –3, in 1N HCl

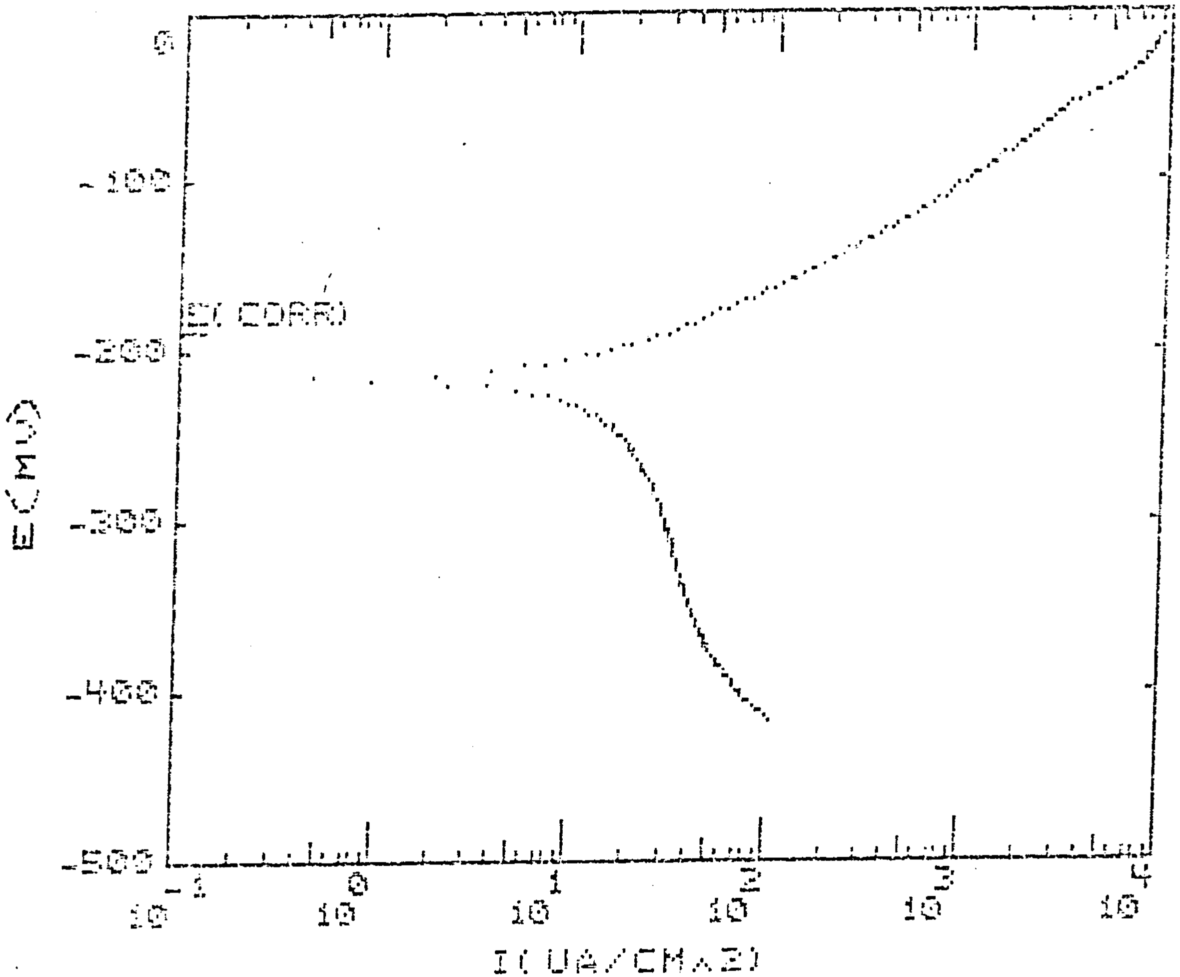
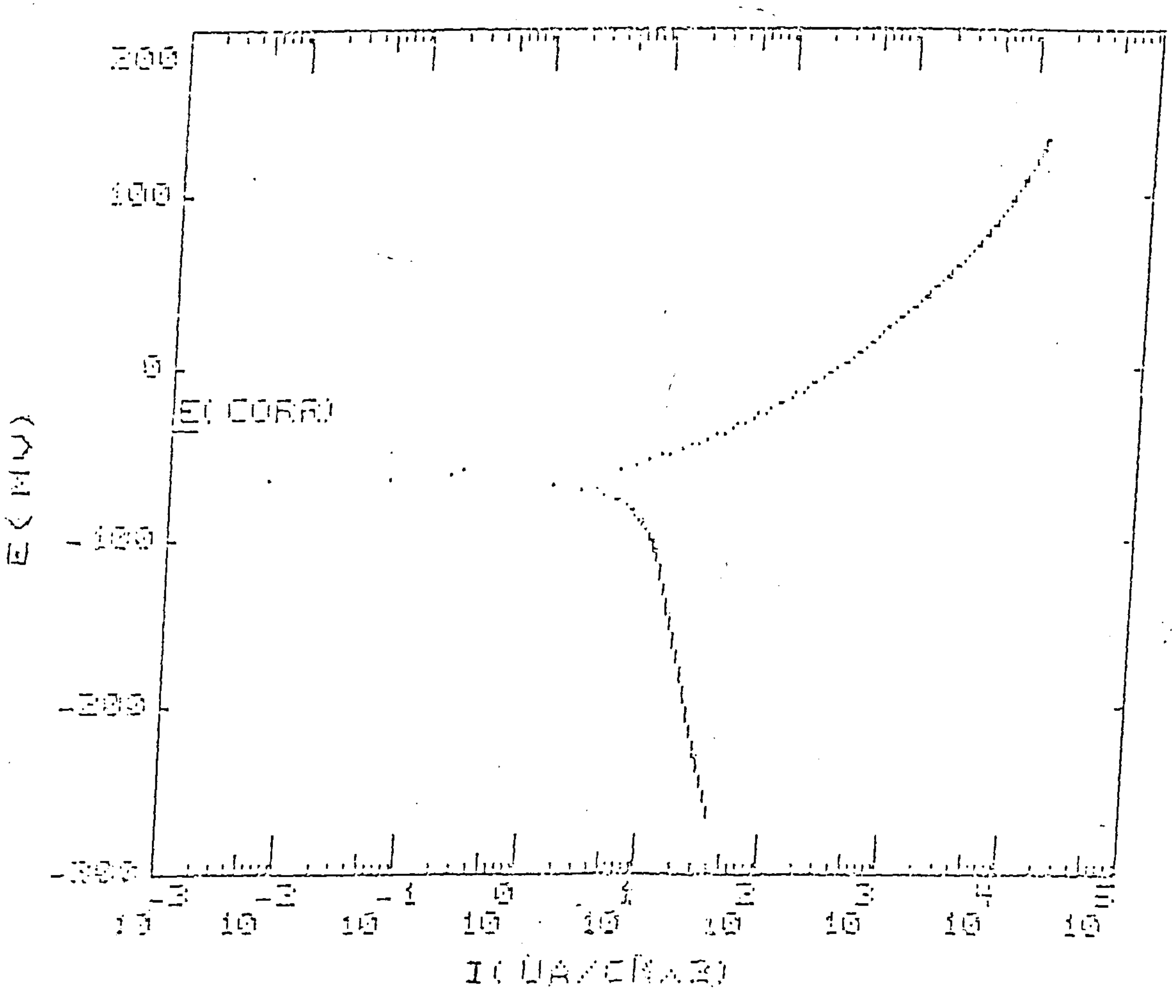


Fig.4.40-Corrosion studies : Tafel plot of EN coated Copper plate Cu-4, in 2N H_2SO_4



4.9 CORROSION STUDIES BY WEIGHT LOSS METHOD

Weighed aluminium panels of the specific size were cleaned and immersed in the 3.5% NaCl solution,1N HCl, 2N HCl ,1N H_2SO_4 and 2N H_2SO_4 kept in a separate containers as explained in the Chapter Two. After certain time intervals these plates were removed, rinsed and weighed again. The rate of corrosion was calculated from the loss in weight. The data obtained is given in the Table 4.8.

It is observed that the corrosion resistance of EN coated plate is high in 3.5 % NaCl as compared to corrosion resistance in 1N HCl and 2N H_2SO_4. Further it is also observed that, with the increase in the thickness, the resistance to corrosion also increases. The difference in the corrosion rate between the two techniques is due to the difference in the duration of the testing period.

It was observed that in the present investigation , corrosion rate of aluminium substrate EN coated (thickness of 0.2μm) with the novel bath is 0.0245 m.p.y., which is very low as compared to the corrosion rate of aluminium substrate EN coated using sodium hypophosphite bath reported elsewhere[21].

TABLE – 4.8

Corrosion data of EN plated Aluminium panels in various environment by Weight loss method

Plate code	Immersion time days	Environment	Weight loss g	Corrosion rate mpy
S-1	07	3.5%NaCl	0.0007	0.0000157
S-2	07	3.5%NaCl	0.0005	0.0000112
S-3	07	1N HCl	0.1700	0.003832
S-4	07	1N HCl	0.1751	0.003947
S-5	01	2N HCl	0.2200	0.02770
S-6	01	2N HCl	0.1516	0.02024
S-7	07	1N H_2SO_4	0.0820	0.001848
S-8	07	1N H_2SO_4	0.0826	0.001862
S-9	11	2N H_2SO_4	0.1107	0.062198
S-10	11	2N H_2SO_4	0.1040	0.058434

Salt spray method was also employed to assess the corrosion susceptibility of the nickel coated aluminium plates .The plates were kept suspended for different duration in salt spray chamber in which 3.5% NaCl solution was sprayed using an atomizer .

High resolution photographs (magnification 600 X) of the coated plates before the experiment (Fig. 4.45) and after exposing to the salt spray in the chamber for 60 hours (Fig. 4.46) show distinct patches of the corroded sectors on the plates . Similarly surface morphology can be seen in Figure 4.47 (before corrosion)and Figure 4.48 after corrosion for 84 hours and in Figure 4.49(before corrosion) Figure 4.50 after corrosion for 98 hours.

Fig. 4.45: Photograph (before corrosion) of EN Coated Aluminium Plate, Magnification 600 X

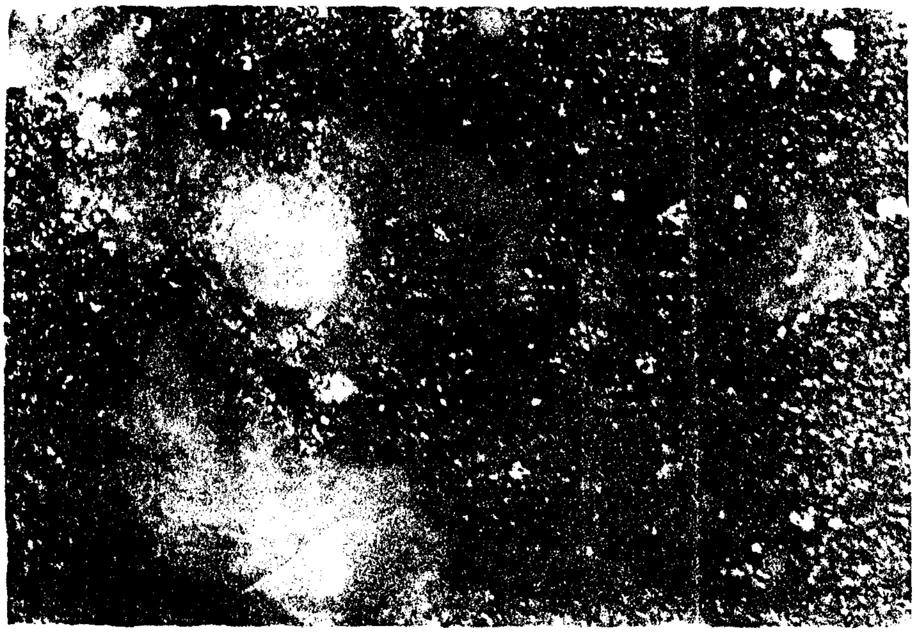


Fig. 4.46: Photograph (after corrosion) of above EN Coated Aluminium Plate, kept in 3.5% NaCl Salt spray chamber for 60 hrs, Magnification 600 X

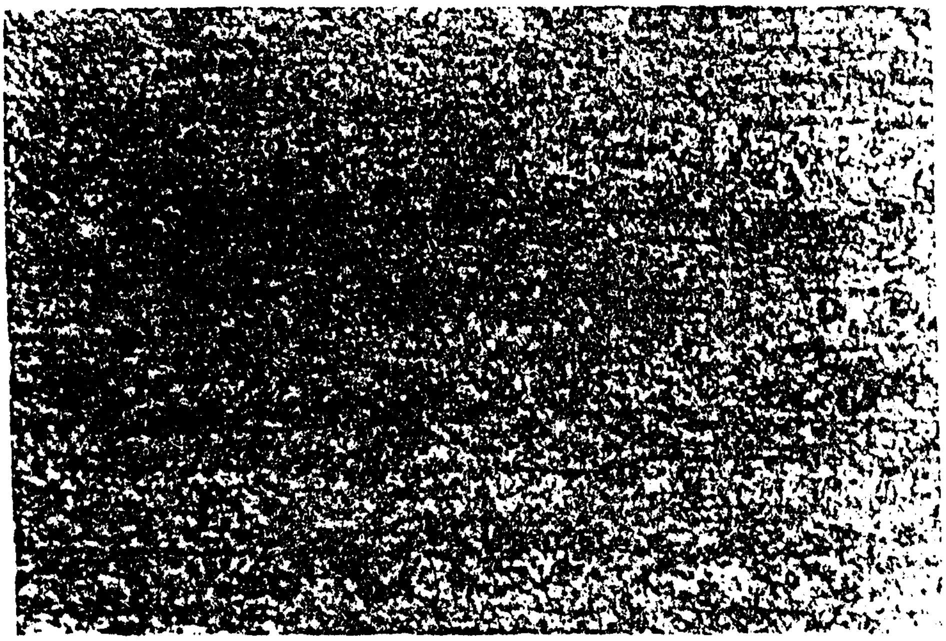


Fig. 4.47: Photograph (before corrosion) of EN Coated Aluminium Plate, Magnification 600 X

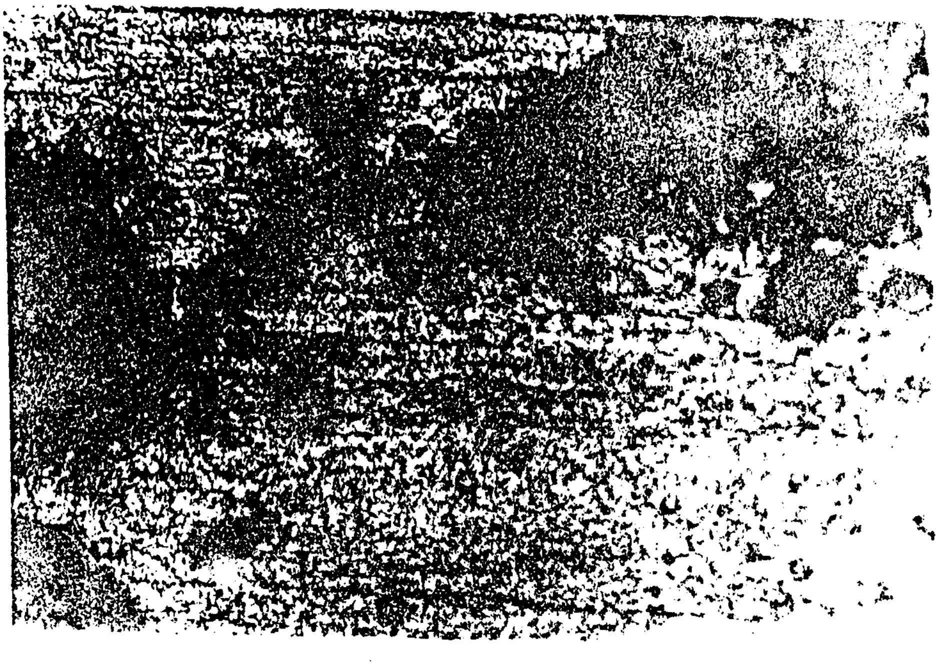


Fig. 4.48: Photograph (after corrosion) of above EN Coated Aluminium Plate, kept in 3.5% NaCl Salt spray chamber for 84 hrs, Magnification 600 X

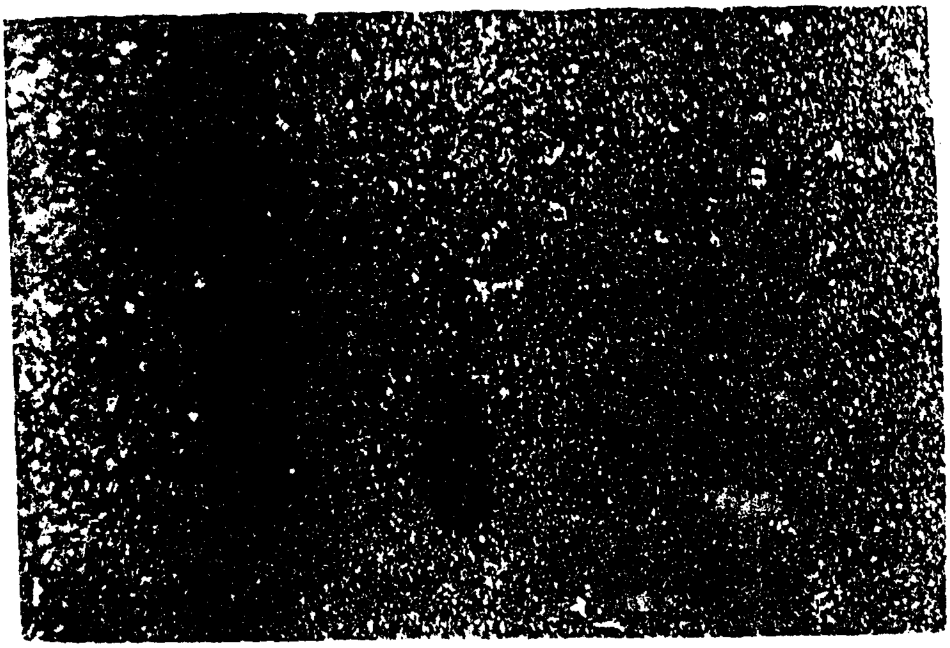


Fig. 4.49: Photograph (before corrosion) of EN Coated Aluminium Plate,
Magnification 600 X

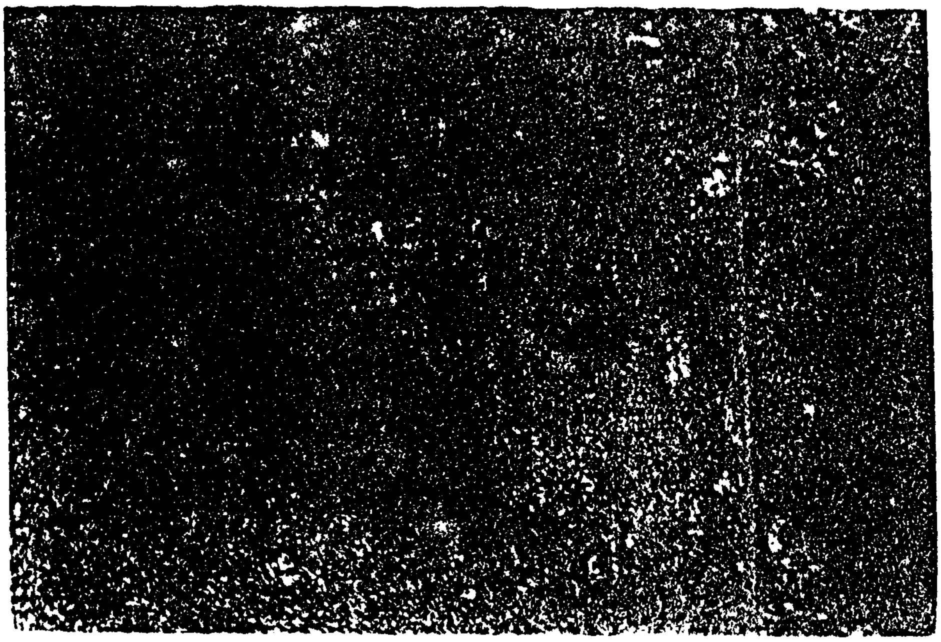


Fig. 4.50: Photograph (after corrosion) of above EN Coated Aluminium Plate, kept in
3.5% NaCl Salt spray chamber for 96 hrs, Magnification 600 X

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CHAPTER FIVE

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CHAPTER FIVE

RESULTS AND DISCUSSION

For faultless production and regulation of the *chemical or electroless*[1-3] *nickel plating*, it is necessary to control the basic components of the bath solution. Therefore, in order to standardize the bath formulation and to ensure the desired quality of an electroless nickel deposit, the following parameters of the deposition process must be monitored and optimized.

1. Pre-plate treatment of the substrate material,
2. nickel content from the chosen salt,
3. reducing agent concentration,
4. pH of the bath solution,
5. temperature of the bath solution,
6. selection of the complexing agent and its concentration.

This work was undertaken to study the use of nitrilotriacetic[4-10] acid as a complexing agent in electroless plating bath in which hydrazine[11-14] is used as a chemical reducing agent. The study involves continuous monitoring of the parameters which are mentioned above, since these parameters undergo continuous change, sometimes quickly, during the deposition process. To maintain the continuity of deposition process, it is therefore essential to make up for the spent component at regular intervals and this is accomplished by strict adherence to timely

i) replenishment of the solvent,

ii) replenishment of the reducing agent,

iii) replenishment of the metal ion, and

iv) maintaining of the bath pH at a constant value.

And it is also important to know the rate of deposition and the thickness of deposition in the plating process. Any study in this field of surface technology, therefore, involves systematic and stepwise approach to obtain desired coating for specific applications.

5.1 ZINCATING AS PRE-PLATE STEP

Type of zincating solution used in the surface preparation[15-18] of the aluminium substrate govern the nature of coating. It was observed in this study that highly alkaline zincating solution containing ZnO and NaOH mixture used in the pre-treatment of aluminium plates does not give a good adherence to the nickel deposited from the bath. Whereas newly formulated and less alkaline zincating solution containing ZnO and Na-K tartarate salt, not only gives a good adherent but also, matt finish nickel coating.

Along with the composition of the zincating solution, the immersion time in this solution in the pre-plate process also plays an important role in the nature of the final coated product. Prolonged immersion in the zincating solution for 30 seconds instead of 10 seconds, yields a black nickel coating on aluminium surface. This black nickel coating obtained by using new zincating solution containing tartarate salt, probably can be employed as solar absorber and in such related applications. It has been observed that, different type of zincating solution gives coating which vary in texture, colour and surface finish. In the present investigation with new zincating solution and with appropriate immersion time of about 10 seconds at room temperature, however, it was possible to get desired matt finish of electroless nickel on the aluminium base metal.

5.2 BATH COMPONENTS AND NICKEL DEPOSITION

All the EN plating baths, reported or patented in the literature, consist of nickel salts in the form of chloride or sulphate or nitrate along with the appropriate complexing and reducing agent. In the present study a single nickel salt[19] in aqueous medium, containing in it a source of the metal ion, the reducing agent and the complexing agent, has been tried as a source for all the three important components in electroless nickel plating bath. This way it is possible to eliminate the undesirable effects of adding many components / ingradients separately. In this method, the salt is dissolved in de-ionized water and the pH is adjusted to the required value to yield a bath. Two such methods have been developed and standardized in this study.

Basic nickel carbonate has been used to prepare nitrilotriacetate salt in order to avoid the presence, and the effects of chloride and sulfate ions in the electroless plating bath, which is essential for specific applications. Such a combination of nickel ion and nitrilotriacete ion in this plating bath is reported for the first time through this study. Another important property of this bath is that it can be kept stable for a longer duration by suppressing the formation (Chapter Three) of free insoluble nitrilotriacetic acid with timely addition of hydrazine hydrate. Addition of hydrazine also ensures replenishing of the reducing agent hydrazine and longer life of the plating bath.

An uniform and thin layer (about 0.23 µm thick) nickel is successfully deposited on aluminium substrate from this novel bath solution,which is maintained at a temperature of 348 K, and contains 0.01 M Ni^{+2} ions. The pH of the bath solution is also an important factor in the deposition process. Since the hydrazine based electroless plating baths operate in alkaline medium, in this study, it is found that the optimum bath pH of 10.75 should be maintained for continuous deposition of the metal. It is also observed here that ammonia is the most suitable pH regulator in this bath.

Although the rate of deposition of nickel metal from this bath is fairly low, (about 0.25 µm / hour), due to the enhanced stability of the bath it is possible to obtain the required thickness of the deposited layer by prolonged plating. The rate of deposition of nickel from this bath is found to improve largely with increase in the concentration of the Ni^{+2} ion. However, the nature and the texture of the deposits are not of the desirable quality. Most of the hydrazine based electroless plating baths are known to give nitrogen embrittlement to the base metal, which is due to the formation of this gas as one of the product during reduction. However, this nitrogen embrittlement can be largely reduced by increased agitation of the bath solution during deposition and also by proper heat treatment after deposition.

Proposed mechanism for the electroless plating of nickel from the solution containing hydrazine as a reducing agent and nitrilotriacetic acid as a complexing agent is similar to the one proposed by Wiese and Weil [20] for copper deposition in presence of EDTA complexing agent. This mechanism is based on experimental observation of regeneration (Chapter Three) of the complexing agent NTA. In addition, it is also observed that the deposition becomes a continuous process once requisite quantity of hydrazine hydrate is added to the bath to dissolve this acid. Thus thickness of the deposited layer can be increased by timely addition or replenishment of reducing agent and the metal ion source.

Hydrazine based electroless plating bath with nitrilotriacetic acid complexing agent was also successfully tried for the deposition of nickel on copper substrate. Pure nickel metal deposition can be obtained by using this bath. However, an improved rate of deposition of 0.46 μm /hour is observed for copper substrate in comparison to 0.25 μm/hour for Al substrate. This could be due to a better catalytic activity of copper metal than that of aluminium in the deposition process.

High resolution photography as well as scanning electron microscope (SEM) data of the coated plates reveal continuity in the deposited layer. The elemental analysis with the help of an X-ray energy – dispersive spectrometer attachment to the SEM studies confirm the presence of pure nickel metal on the plated surface. The coated plates are found to be fairly resistant when subjected to accelerated oxidation.

During this study, some experiments were carried out with hypophosphite as reducing agent instead of hydrazine, and nitrilotriacetic acid as the complexing agent.

Here again a good, adherent nickel deposition is obtained with better deposition rate. But the bath is highly unstable, and decomposes within one and half hour, especially at high temperature (about 343 K).

5.3 SURFACE PROPERTIES OF THE COATED NICKEL FILM.

In addition to the Scanning Electron Microscope, the X-ray Diffraction[21] patterns of the coated plates were taken in order to investigate the nature of the thin film deposits. The d-values calculated from the diffraction pattern (θ values) show the presence of pure nickel (d = 2.033). However, the peak in the diffraction pattern appears as a shoulder to another peak of metal aluminium. Some d-values of Al and Ni are almost identical.

One of the important applications of the electroless plating method has been for corrosion protection. Consequently, primary test for the coated plate is to assess its corrosion resistivity.

The electrochemical corrosion experiments were carried out (Chapter Four) with aluminium plates coated with thin film of electroless nickel in various environments. The corrosion rates of these plates in 3.5 % NaCl solutions, 1 N HCl and 2 N H_2SO_4 are highly encouraging. Although the thickness of the coated nickel film is as low as 0.25 μm, interestingly, its resistance to corrosion is high. The lower corrosion rates of 0.023 - 0.027 mpy are probably due to the compactness of the metallic atoms in the deposits. Table 5.1 gives the summary of the corrosion rate of the coated plates in different media.

Table 5.1 Summary of corrosion rates of coated plates

FOR ALUMINIUM SUBSTRATE			
ENVIRONMENT	PLATING BATH	CORROSION RATE m py	METHOD USED
3.5% NaCl	Standard	0.02455	Electrochemical
3.5% NaCl	Standard	0.0000157	Weight loss method
1N HCl	Standard	0.0277	Electrochemical
1N HCl	Standard	0.003832	Weight loss method
2N HCl	Standard	0.02770	Weight loss method
2N H_2SO_4	Standard	0.0239	Electrochemical
1N H_2SO_4	Standard	0.01848	Weight loss method
2N H_2SO_4	Standard	0.05843	Weight loss method
FOR COPPER SUBSTRATE			
3.5%NaCl	Standard	0.03390	Electrochemical
1N HCl	Standard	8.670	Electrochemical
2N H_2SO_4	Standard	1.608	Electrochemical

It is also observed that the rate of corrosion increases considerably when the plates are heated to about 723K as a post-treatment process. As is revealed from the SEM photographs that the heated panels develop cracks in the coated layers. And initiation of the corrosion attack of the base metal in various environment begins from these sites, thereby enhancing the corrosion rate.

Reflectance measurements of the aluminium plates, coated with black nickel were carried out by using UV- Visible Spectrophotometer. This black nickel coating was obtained with excessive zincating of the aluminium plates in the pre-plate step. The solar absorptance (α) of these plates is found to be about 0.85 .

5.4 APPLICATIONS OF THE NOVEL EN PLATING BATH

It can be concluded that the newly formulated electroless plating bath with nitrilotriacetic acid and hydrazine as complexing and reducing agent respectively, gives nickel deposition as a highly protective coating which is resistant to corrosion. Its application as a suitable chemical plating bath for protective coating of aluminium substrate with nickel is proposed. In aerospace industries[22] , where several light weight aluminium parts or plates are required to be protected from polluting environments, this bath formulation can be suitably used.

Another important application of this bath is its use in developing solar absorber coating [23-24] on low cost aluminium substrate. Although ideally 0.90 – 0.95 absorptance(α) would be most suitable for this application, the absorptivity exhibited by the plates obtained from novel bath developed in the present investigation, is quite encouraging. Similar study with copper as base metal will be useful in other applications such as memory disc, EMI sheilding etc where thin layer deposit of the metal or alloys is desirable.

A thin flim coating of variety of pure metal and their alloys with wide range of surface properties and engineering applications can be developed with this novel electroless bath system .

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