DETERMINATION OF THE PLATING PARAMETERS AND CORROSION CHARACTERISTICS OF COPPER PLATED STEEL IN CORROSIVE MEDIA.

BY

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CERTIFICATION

I certify that this work was carried out by Egunlae Olawale Olarewaju and was supervised by me and submitted to the Department of Metallurgical and Materials Engineering, Federal University of Technology, Akure.

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DEDICATION

This work is dedicated the **Almighty God**

And to

Dad and **Mum**

ABSTRACT

Locally produced steels (NST60Mn and NST50-2) were electroplated with copper to determine the optimum electroplating parameters in an acid-sulphate bath. The corrosion characteristics of copper-electroplated steels in six media 0.1M NaOH, 3.5M NaCl, 0.1M H_2SO_4, tap water, well water and rainwater were used to study the integrity of the coating. The results obtained from the copper- plating and corrosion tests were used to develop a computer program in V-Basic language to simulate the coating thickness required to protect any given size of steel work piece. The results show that steel could be best plated in acid–sulphate bath at 2V applied voltage, 200g/l $CuSO_4.5H_2O$ electrolyte concentration, 120mm anode-cathode minimum separation, on 600μm surface finishing grades using 0.5g/l saccharin as brightening agent. The results of corrosion for 30days revealed that copper coated steels have lower corrosion rates than as-received steels in the six media. From the computer programming results, a copper film of not less than 3.1μm thickness will be required to protect a 40mm x 15mm x 5.5mm steel for 1year in the least corrosive medium (well water) when a perfect adhesion of Cu film to steel surface at constant room temperature is maintained.

Table of Content

Chapter Five

List of Tables

List of Figures

Page

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND STUDY

Among the metals and alloys, steels have found very wide applications in engineering construction and machine parts fabrications (Young, 1980). With exception of a few noble metals, such as silver, gold and platinum, metals in general are susceptible to corrosion (Denny, 1982; Bastidas et. al, 2000). Therefore the choice of production methods including the surface finishing is very vital for the engineering component and service.

A variety of low carbon steels (such as ST30-LC, NST44) and mild steels medium (NST50-2), medium carbon steels (NST60Mn) and high carbon steel are produced in Nigeria. These are used in many areas such as wire drawing, steel rolling, automobile (car) and machine parts and machine tools fabrication to mention a few. Steels are characterized by high strength and high workability, but are like other metals susceptible to corrosion when used. The improved service requirement of steel can be achieved by the measures such as heat treatment (ASM, 1986); coating such as painting, metallising and electroplating (Bolton, 1998); regular lubrication and so on which offer a long lasting protective measure on the machine part under services (Liucien, 1985; Higgin, 1993; Ashby and David, 1986).

Coating and plating as finishing operations are carried out to obtain a good characterized surface finish of the materials (Serope, 1997; Higgins, 1993) for effective corrosion resistance, heat reflection, wear resistance and decorative value. There are different methods of metal coating, which include electroplating, hot dipping, cladding, electroless plating and auto catalytic plating. Electroplating involves the deposition of a metal on another metallic surface by the passage of electric current through solution of the metal to be deposited. The commonest materials for electroplating are Au, Ag, Cu, Zn, Cr, Ni and Cd (Blick, 1982). The process is performed in most cases at room temperature and it can be used for low melting pure and alloyed soldered joint. In other case, nickel, copper and some other metals could be deposited by electroless plating and auto catalytic plating methods that do not require external potential (Baudrand et al, 1986). The coating thickness and adhesion are very important. The thickness varies from hundredth of micron to millimetres. There is control of the uniformity in the coating thickness. Copper is

commonly used in coating of steel surface for use as the earthen rod due to its high conductivity and adhesion to the steel surface. The shape of the work piece and the bath throwing power determine the plate thickness. For this purpose, a few micron thickness layers is necessary. (Smithell, 1978; SIRI, 1989; Niebel et al, 1990).

In recent years, many engineering production are based on computer aided design CAD, computer aided manufacturing CAM and other newly computer programming languages. The use of computer software in production helps in simulation of products for various applications. The protection of metal surface against corrosion by coating is such of the many areas where computer simulation programs become relevant. The choice of computer programming language needs to be simple, flexible, user friendly and interactive such as the V-BASIC applications.

1.2 Aim and Objectives

The aim is to develop electroplating procedure of copper on steel substrates for industrial applications.

The objectives of this research are:

- To coat steel using copper by electroplating process
- To determine the optimum plating parameters for copper plating on steel substrates,
- To determine the corrosion resistant characteristics of plated steels in active corrosive media
- To develop a computer program in V-BASIC language
- To use the developed computer program to predict the film thickness required for plated steels.

1.3 Statement of Problem

The local manufacturing (engineering) industries make use of variety of steels in the production of machine parts for both industrial and domestic applications. These machine parts are used under different working environment such as very severe or fairly hostile (corrosive) environments in which heat treatment does not fully eliminate the steel surface susceptibility to corrosion. With the use of electroplating, very thin film of metal (copper) of relatively high chemical resistance to corrosive environment could be enhanced with improved aesthetic value and abrasion resistance of the steel surface. The application of computer programming shall go along way in

simulating the film thickness that may be required to protect a given steel work piece in a corrosive media.

1.4 Scope of Study

The optimum plating parameters (such as the applied voltage, surface finishing grade SFG of steel, cathode-anode separation distance, film thickness and film weight gain) of locally made steels in an acid sulphate bath were determined. The effects of organic additives (saccharin, dextrin, milk and lactic acid) on the brightening property of copper plate were also studied on the acid-sulphate bath. The work extends to the study of the viability of copper plated steels in six media; brine, caustic soda, sulphuric acid, processed water, well water and rainwater. The final aspect of the work entails the development of a computer program (in V-BASIC) to simulate the film thickness required to protect a given size of steel substrate for any length of time under a given corrosive environment.

1.5 Justification of the Study

The expected contribution to knowledge and potential benefit of the research are:

- To formulate standard (optimum) metal finishing procedure for electroplating of copper on steel substrates.
- The computer program developed will be useful in simulating film thickness of copper coatings
- It will also be useful tool for both laboratory work and steel plating industries in designing electrolytic baths for copper coating.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Metals and alloys as engineering materials.

The diverse engineering materials are made into components or machine parts that perform certain functions either singly or in conjunction with other components in the engineering designs. To this effect, specific choices of materials whose properties and processes of fabrication have been defined are needed to be chosen for application. Metals and alloys are the most widely used (Askeland, 1985).

Metals and their alloys are the backbone of all engineering and technological development. They possess very important properties that make them useful. Such properties include adequate strength, hardness, corrosion resistance, work-ability, magnetic properties (Higgins, 1993). There are two broad classes of ferrous metals/alloy metals viz ferrous and non-ferrous. Ferrous metals are those whose major component is made up of iron. On the other hand, non-ferrous metals are metals and alloys without iron in the composition, such include: Al, Mg, Pb, Zn, Sn, Ti, Cu, Ni, Ag, Au, Si, Co, Mo, Cr, Te and alloys brass, bronze. They possess low strength but are superior in corrosion resistance as compared with ferrous metals. Some are more expensive and are applied for very special purposes e.g surgical tool, aircraft body (Denny,1982; Trentheway, 1995).

2.2 Metal Corrosion, prevention and control

Corrosion can be defined as the gradual deterioration and surface wastage of a metal due to its reaction with its environment (Pletcher, 1982). Corrosion is a major material problem usually facing the oil, chemical, small and big engineering industries and domestic (homes) and it requires greater attention. Corrosion is caused by many factors but the major causes of it are the material properties, nature and aggressiveness of the environment (Rieger, 1986).

With the exception of few noble metals, metals and alloys are susceptible to corrosion. So much importance is attached to its prevention and control due to its unbearable wastage and losses that may occur whenever corrosion problem strikes. Hence, corrosion in metals are monitored, measured, prevented and controlled by different methods such as metal coating, painting, anodic protection and inhibition. Different works by Jope et al, 1995; Wu et al, 1993 and Ghandhi, 1983 have reported the effective use of inhibitors on copper corrosion control.

Corrosion control is a complex science, requiring considerable knowledge of corrosion chemistry and of the system being evaluated. (www.aces.edu/pubs/docs). The corrosion process is an oxidation/reduction reaction that returns refined or processed metal to their more stable ore state. (JAIC, 1986). Nearly all metals will corrode to some degree. The rate and extent of the corrosion depends on the physical and chemical characteristics of the media, metal, and environment. (http://www.water-research.net/corrosion.html)

Metal Coating Processes

There diverse methods of metal coating or plating process. These include processes like hot dipping (Niebel et al, 1993), anodising, (Pletcher, 1982) electroplating, (Schlesinger and Paunovic, 2000), electroless plating, (Baudrand et al, 1986) autocatalytic plating, (Gabe, 1984), cladding, Parkerizing (Beranger, 1996) and galvanising (Karlson,1989, Sullivan and Worsely, 2002).

2.3 Development on electrodeposition

Today, with the impressive progress and deeper understanding of the underlying electrochemical principles of Electrodeposition, sophisticated plating baths formulae have been developed and are being routinely employed (Beranger et al, 1996; Karlson 1989; Li, 2001; Perderson, 2005). Film thickness and performance of electroplated finishes are among the attributes that have been brought under strict control. New developments enable greater plating speed, better throwing power : that is, the ability of a plating solution to produce a relatively uniform distribution of metal upon a cathode of irregular shape (Alber, 1989), as well as reliable plated finishes. In addition, electroplating of materials such as platinum, osmium, and ruthenium are now broadly used in electronics for connectors, circuit boards, contacts etc. Some writers (Gray, 1989; Schlesinger, 2002) believe that new and innovative electroplating technology will facilitate the rapid expansion of the telecommunication industry.

Electroplating Process

Electroplating is often also called "electrodeposition", and the two terms are used interchangeably. Electrodeposition is the process of producing a coating, usually metallic, on a surface by the action of electric current. The deposition of a metallic coating onto an object is achieved by putting a negative charge on the object to be coated and immersing it into a solution which contains a salt of the metal to be

deposited. In other words, the object to be plated is made the cathode of an electrolytic cell (Schlesinger, 1998 and 2002).

The metallic ions of the salt carry a positive charge and are thus attracted to the object. When they reach the negatively charged object (that is to be electroplated), it provides electrons to reduce the positively charged ions to metallic form.

The purpose of such process may be to enhance or change the substrate's appearance and/or attributes such as corrosion resistance obtained in gold or silver coating on jewellery and utensils, and of chrome on automobile parts (Gabe, 1984; Li et al, 2001).

2.4 Electrolytic circuit

As explained by Perderson (2005), electroplating is performed in a liquid solution called an electrolyte, or referred to as the "plating bath". The bath is a specially designed chemical solution that contains the desired coating metal of positively charged ions. In addition, various substances (additives) are introduced into the bath to obtain smooth and bright deposits. The object that is to be plated is submerged into the electrolyte (plating bath), and acts as a negatively charged cathode (Olatuja, 1992; Naran, 1999; Ted-Mooney, 2000). The positively charged anode(s) completes the electric circuit at opposite edges of the plating tank, thus causing film deposit on the cathode. A power source in the form of a battery (Crumpton, 1982) or rectifier (which converts ac electricity to regulated low voltage dc current) provides the necessary required current. This type of circuit arrangement directs electrons (negative charge carriers) into a path from the power supply (rectifier) to the cathode (the object to be plated). In the bath the electric current is carried largely by the positively charged ions from the anode(s) toward the negatively charged cathode. This movement makes the metal ions in the bath to migrate toward extra electrons that are located at or near the cathode's surface outer layer. Finally, by way of electrolysis the metal ions are removed from the solution and are deposited on the surface of the object as a thin layer. (Paunovic and Schlesinger, 1998).

Electrolysis

Electrolysis is the decomposition of a compound (solid or liquid) by the passage through it of an electric current. An electrolyte is a compound in solution or molten compound (Gill, 1980; Blick, 1982; Lukasko and Murphy, 1992) that will conduct electric current with decomposition at the electrodes as it does so. A non-electrolyte is

a compound, which cannot be decomposed by an electric current. The electrodes are two poles of carbon or metal by which the current enters or leaves an electrolyte. The anode is the positive electrode by which the current enters. The cathode is the negative electrode by which the current leaves. (Theraja and Theraja, 1999)

Laws of electrolysis

The theories of process of electro-deposition are based on the previous works done by Michael Faraday in 1833 on electrolysis (Schlesinger, 2002). The first law states that the mass of the material (m) liberated during electrolysis is proportional to the quantity of electricity (q) that passed through the solution, which is mathematically expressed as

$$m/q = \text{constant.} \quad \text{---------- (2.1)}$$

It has been known from the Coulomb's law that **q = it**, where i = current and t = time.

Also the second law states that, the amount of a given element liberated during electrolysis is proportional to its equivalent weight. This means that one can determine the amount of other metals that can be deposited from the same quantity of electricity if the quantity of one metal that is liberated by a given quantity of electricity is known. These two theories remains unmodified and among the foundation of the physical sciences. And in case more than one substances are deposited as in the co deposition of hydrogen or in alloy plating, Faraday's law apply to the total number of equivalents of all substances, but do not specify the proportions. This law is mathematically represented as

$$m/e = \text{constant} \quad \text{---------- (2.2)}$$

Electro-deposition theories

In the concentrated solution, the ions do not exist independently of each other due to the fact that their action is being hindered by inter-ionic attraction and by formation of ion pairs or other structured configurations. The activities of the ions determine their influence on potential conductivity, diffusion process and so on. (Askeland, 1985). When a current source is used, there is imposition of the potential difference that makes electrons to be surplus at the cathode above the quantity available when there is no external current source is applied. That is, cathode becomes more negative, and on this fact positive metal ions are attached and deposited as neutral metal atoms (Ted-Mooney, 2000).

Electrochemical deposition

Electrochemical deposition (of metals or alloys) involves the reduction of metal ions from aqueous, organic, or fused salt electrolytes. In it's simplest form the reaction in aqueous medium at the cathode follows the equation

$$M^{n+} + ne^- = M \quad \text{---------- (2.3)}$$

$$M = M^{n+} + ne^- \quad \text{---------- (2.4)}$$

with a corresponding anodic reaction. The anode material can be the metal to be deposited and in this case the electrode reaction is electro-dissolution that continuously supplies the metal ions (Silberberg, 1996).

The deposition reaction presented in Equation (2.3) is a reaction of charged particles at the interface between a metal (electrode) and a liquid solution. The two types of charged particles that can cross the interface are metal ions "M^{n+}" and electrons "e^-".

The reduction of a metal, which occurs during the plating process, has been generalized as Equation (2.3) for a single metallic ion. To reduce one mole of a given metal "n" moles of electrons are required. That is, the total cathodic charge used in the deposition Q (coulomb) is the product of the number of gram moles of the metal deposited "m", the number of electrons taking part in the reduction "n", Avogadro's number "Na" (the number of atoms in a mole), and the electrical charge per electron "Qe" (coulomb). Thus, the following equation gives the charge required to reduce "m" mole of metal:

$$Q = m\ n\ 'Na'\ 'Qe' \quad \text{---------- (2.5)}$$

The product of the last two terms in this equation is the Faraday constant "F".

$$Na\ Qe = F \quad \text{---------- (2.6)}$$

The number of moles of metal reduced by charge Q can be obtained as:

$$m = Q / (n F) \text{ or } It / nF \quad \text{---------- (2.7)}$$

$$Q = It \quad \text{or} \quad Q = I_{vary}\, t \quad \text{---------- (2.8)}$$

Since the total charge used in the deposition can be obtained as the product of current "I" (A) and time of deposition "t" (s) if the deposition current is held constant.

$$m = Q / (n F) \quad \text{or} \quad m = It / nF. \quad \text{---------- (2.9)}$$

The weight of the deposit "w" (gram) can be obtained by multiplying Equation (2.9) with the atomic weight "Mw" of the deposited metal.

Finally, to calculate the thickness of the deposit, the density of the metal "ρ_m" (g/cm^3) is used according to Schlesinger and Paunovic, (2000).

$$\rho_m = w / V = w / (A\ T). \quad \text{---------- (2.10)}$$

where "V" is the volume of the deposited metal in cm^3, "A" is the area of the deposit in cm^2, and "T" is its thickness in cm. Using equations (9) and (10), we have

$$T = QMw / \rho_m\ AnF. \quad \text{---------- (2.11)}$$

From the above it means that the thickness of the electroplated layer on the substrate is determined by the time duration of the plating. In other words, the longer the time the object remains in the operating plating bath, the thicker will be the resulting electroplated layer. (Pedersen, 2005). The electro-deposition (film) thickness has also been determined from the equation below

$$T = (CD \times W \times CE) / 235 \times \rho_m \quad \text{---------- (2.12)}$$

Where CD = current density, W = weight of metal deposited, CE = current efficiency and ρ_m = metal density (Smithells, 1978).

Electrode Potentials

When a metal is dipped into a solution containing its own ions, the surface of the metal lattice become hydrated and dissolves into the solution. Simultaneously, some ions in solution are attached to the metal surface and are deposited (Hilbert and James, 1984). This exchange rate depends on the potential difference between the metal-solution interface (Vogt, 1998). If no side reaction takes place, and no external potential is imposed, then at a given temperature, there is a specific potential at which the two rates are equal. This is referred to as the equilibrium potential. It is dependent on the temperature, concentration or activity of ions in the solution. Only the relative potentials with respect to hydrogen ion activity (pH = 0) can be determined since the measurement of the potential requires two electrodes (Ted-Mooney, 1995 and 2000).

2.5 Plating Variations

There are some factors that determine the properties of the plating. Generally, the properties of the coating will vary with the factors such as the electrolyte composition, current density, agitation, solution pH, temperature, throwing power and conductivity (SIRI, 1990; Schlesinger, 1998). The three properties usually sought when specifying an electroplate are the hardness value, corrosion resistance and the appearance in terms of the brightness of the finishing coat. The current density c.d is the amount of current passing through the cross sectional area of electrode in the plating cell (Gadshov, 1989). Diverse materials have different c.d values, depending on the bath composition, there are c.d $\approx$ 1~20 A/dm^2 for copper plating in acid bath, c.d $\approx$

0.5~1.0 A/dm^2 in copper cyanide bath, and c.d ≈ 2.0~6.0 A/dm^2 in other cyanide baths (Amstead et al, 1990).

Agitation. It is at times important to find a possible way of increasing the rate of anodic dissolution because in the immediate surrounding of the cathode, diffusion is the principal mode of transport. Therefore, the baths are agitated mechanically by stirring and forced air.

Solution pH shows the level of acidity or alkalinity strength of the bath composition. As external potential is applied to the cell, there is dissolution and deposition of metals through ion exchange; some metals are readily attacked by the acidic medium after their deposition (Dickson and Wilson, 1991).

Temperature effect: From the kinetic theory of matters, an increase in temperature increases the agitation and movement within the (liquid) electrolyte, which affects the overall behaviour of the plating cell. Conductivity is increased while anode-cathode polarisation is reduced. Different temperatures are operated for different cells depending on the composition (Rieger, 1986).

Plating time does not affect the adhesion, brightness, colour and texture except when the electrolyte is abnormally acidic and then attacking the plating. The cathode weight gain increases with increasing plating time. This is obvious since m α q (Faraday's law).

Surface pre-treatment by chemical and/or mechanical means is important in all the cases of preparations for electroplating. These methods are designed to ensure good adhesion of the coating to the surface. Usually, this includes employing of solvents, alkaline cleaners, acid cleaners, abrasive materials and/or water (Gabe, 1984).

Success of metal-plating or surface conversion depends on removing contaminants and films from the substrate. Organic and non-metallic films interfere with bonding by causing poor adhesion (Silberberg, 1996; Higgins, 1993) and even preventing deposition. Specific residues include lubricants, phosphate coating, quenching oils, rust proofing oils, drawing compounds, and stamping lubricants (Liucien, 1985; Amstead et al, 1990).

2.6 Cleaning processes and surface Pre-treatment Operations

These are the various forms of preliminary operations that must be performed to prepare the surface of the metal for proper and adequate coating.

Cleaning processes are based on two approaches. In physical cleaning, mechanical energy is introduced to release both extrinsic and intrinsic contaminants from the (metal) surface, such as ultrasonic agitation and brush abrasion. In chemical cleaning contaminant films are removed by active materials, dissolved or emulsified in the cleaning solution (Li et al, 2001; Schlesinger, 2000).

Degreasing is done to remove dirt, oil and other foreign materials that might have adhered to the surface of the metal in course of manufacture, transport and storage. For subsequent coating to be done successfully, one or more of these cleaning process such as alkaline cleaning, Emulsifying agent degreasing , Sodium Silicate or caustic soda, sulphonated castor oil with water or soap and an organic solvent such as Kerosene, vapour degreasing can be used. Rinsing in water follows after degreasing so as to prevent contamination of the baths (Gadshov, 1989).

Pickling is another pre-coating process applied after rinsing. The metal piece is lowered into the pickling baths that contains sodium hydroxide. The purpose of the treatment process is to remove the oxide film form on the surface of the metal and to remove scratches and marks on the metal surface (Smithells, 1978).

Desmulting: The active chemical in this bath is nitric acid or any dilute acid. Its purpose is to neutralize the action of sodium hydroxide used in the pickling. The operation occurs at room temperature.

2.7 Bath composition and Additives used in plating baths

Salts have different effects on the plating behaviour of the bath. Although, the anion does not enter directly into the plating process, it may have profound effect on the deposition such as the structure of the deposit, if strongly absorbed on the cathode.

Promotion of conductivity

In a copper acid-sulphate bath (Alber, 1989), H_2SO_4 is added to increase conductivity of the solution; hence, increasing ionic activity, chlorides (up to 15ppm) is added to a through hole copper sulphate plating bath as a deposit modifiers. Wetting agents are added to some baths such as bright Ni bath to promote detachment of bubbles and eliminate pitting. (Baudrand et al, 1986).

Promotion of anode corrosion

Additions are made to promote anode corrosion as chlorides are used in Nickel sulphate baths, tartarate and carbonates are added in cyanide copper plating bath.

They have the power to dissolve the NiO and CuCN films that passivates the normal dissolution of anode.(Olatuja, 1992)

Levelling and brightening agents

Some salts are added to increase the brightening and levelling of electroplate, thereby improving the porosity and appearance such as dextrin, lactic acid and saccharin are added to cadmium on steel plating baths (Mayana et al, 1989).

Conducting salts and buffer

Buffers and catalysts do not take part in chemical reaction but shift the state of equilibrium of the reaction, such as the addition of H_2SO_4 increases the conductivity of copper sulphate bath and the addition of NaOH to cyanide bath prevent the hydrolysis. Boric acid is used in Nickel bath at pH of 5.6 (Baudrand et al, 1986).

2.8 Electroplating of steels

Steel machine parts and structures are prevented from environmental attack in various ways such as organic and inorganic coating such as painting and plating et.c. This attack may be due to oxidation at high temperature or its contact with water and from rust. Other properties usually sought for in steel plating include hardness (for wear resistance) and improved appearance. Depending on the choice of the plating electrode material, (Baudrand et al, 1986) various baths are used in the steel plating and these baths are considered to be factors that determine the plating behaviours of steel (Schlesinger 2002). The set of the most commonly used plating metals include Cr, Ni, Cu, Cd, Zn, Ag and Au (Amstead et al, 1990).

Copper plating on steel.

It is often applied for good adhesion and improved appearance. (Niebel et al, 1993; Ted-Mooney, 1995) Though copper coating on steel have good resistance to corrosion, but once the base metal is exposed by a pin hole or scratch, a strong voltaic effect is set up at the breaks beneath the coating and this results in peeling away of the coat. Copper coating for a decorative reason is always prevented from oxidation by top coating with clear lacquer. High throwing power baths are often used such as sulphate and fluoborate-acid baths, cyanide and pyrophosphate alkaline baths (Alber, 1989).

Copper plating baths

A typical Acid sulphate bath by SIRI, (1990) consists of 200~500g/l copper sulphate $CuSO_4.5H_2O$, sulphuric acid 20~60g/l, and phenol 1g/l acting as inhibitor.

The plating conditions involves 16~50°C, c.d = 1~20 A/dm^2, CE = 95~97% at 1~3V applied voltage. The solution pH is insignificant on the deposition. The anode consists of pure copper metal in a rubber or lead lined wood or steel Vat. The throwing power is high enough while the deposit has pronounced excellent adhesion on the material. (Mayana et al, 1989). The phenol is sulphonated by heating with its own equivalent weight of sulphuric acid at 120°C for about an hour (SIRI, 1990). Agitation and filtration are also necessary at higher current density.

Influence of electrolyte concentration on copper plating bath.

Alber, (1989) carried out studies on low concentrated acid sulphate solution with respect to the influence of $CuSO_4$ on the throwing power, current efficiency, conductivity, current density range and polarisation characteristics (Askeland and Wilson 1991). At the initial stage of immersing the steel into the acid copper sulphate bath when V = 0, the deposition is due to or driven by the potential difference between the steel surface and the solution; and thin layers of copper is deposited since there is no imposition of external current. The chemistry of the reaction can be represented as

$$Cu^{2+} + Fe = Cu + Fe^{2+} \quad \text{..... (2.13)}$$

2.9 Areas of copper plating application

Copper electroplating has been of much interest for the interconnection of printed circuit boards (PCBs) and ultra large scale integration (ULSI). (Shuhei and Hideo, 2003) Soft coatings are used to provide lower electrical contact resistance, an important consideration in some electrical and electronic applications. Ferrous metals like low carbon steels are often copper-electroplated for improved electrical conduction of surface and hence used as earthen rod and cable. (www.sciencedirect.com). Copper alloys are so widely used, many in complex applications, that there are over 370 commercial copper and copper alloy grades. The Copper family includes coppers, high-copper alloys, brasses, leaded brasses, bronzes, aluminium bronzes, silicon bronzes, copper nickels, and nickel silvers.

Electrodeposited Copper Bellows and custom Copper Electroforms for a variety of special applications can be designed and produced using a servomotor. Servomotor electrodeposited copper is non-magnetic and acts as a natural EMI shield. Copper plating is used in making water-cooling components. Zak Inc. (USA) specializes in

the design and manufacture of copper-coated water cooling components used for water cooling titanium and high temperature alloys in the melting process.

2.10 Future trend of copper and cu-alloys electroplating

The trend in the growth of copper and copper alloys electroplating industries will of no doubt, and in nearest future over take other methods of copper coating and provide superior service in many of the applications included in the following general classifications:

- Applications requiring resistance to atmospheric exposure, such as roofing and other architectural uses, hardware, grille work, hand rails, lock bodies, doorknobs, and kick plates
- Freshwater supply lines and plumbing fittings, for which superior resistance to corrosion by various types of waters and soils is important
- Marine applications - most often freshwater and seawater supply lines, heat exchangers, condensers, shafting, valve stems, and marine hardware - in which resistance to seawater, hydrated salt deposits, and biofouling from marine organisms is important
- Heat exchangers and condensers in marine service, steam power plants, and chemical process applications, as well as liquid-to-gas or gas-to-gas heat exchangers in which either process stream may contain a corrosive contaminant
- Industrial and chemical plant process equipment involving exposure to a wide variety of organic and inorganic chemicals.

Electrical wiring, hardware, and connectors; printed circuit boards; and electronic applications that require demanding combinations of electrical, thermal, and mechanical properties, such as semiconductor packages, lead frames, and connectors

2.11 Corrosion of copper in aqueous solutions

The copper plated steel has the lower values of weight loss or corrosion rate in brine as compared with the uncoated steel in the same medium. This is because copper ions (copper I and copper II) form complexes, which are more stable chloride solution. Hence copper plated steel is more protected in brine than the uncoated steel. To enhanced lower rate of weight loss of copper coated steel in brine, inhibitors can also be used . It has been reported by the Institute of Technology, Banaras Hindus

University India. (www.itbhu.com), that use could be made diphenylamine to enhance corrosion inhibition of copper plate in brine.

The characteristics of copper coated steels actually demonstrated the corrosion of copper in the media. The mode of the reaction can be represented as in equation (2.14)

$$Cu = Cu^{+2} + 2e \text{ ---------- (2.14)}$$

The report of different experiment on NaCl, H_2SO_4 and NaOH tend to show further the behaviour of copper corrosion in various environment including alkali and sodium and potassium salts as established in previous works of some authors such as Villamil et al, (1999); Bastidas et al, (2000); Cano et al , (2001); Martens et al, (2003); Vogt et al, (1998); Jope et al, (1995); Feng et al, (1997). Other reports of investigation include the use of inhibitors to enhance reduction in copper corrosion by Wu et al; (1993), Talati and Ghandi, (1983); Singh and Singh (1995).

2.12 Computer programming and programming languages.

Computer programming (often simply programming or coding) is the craft of implementing one or more interrelated abstract algorithms using a particular programming language to produce a concrete computer program (Drury,1998). Programming has elements of science, mathematics, and engineering. Software engineering regards programming (implementation) as just one phase in a software development process. A computer program is usually written by a programmer. A programmer writes source code in a particular programming language. (Lester, 1998)

Different programming languages support different styles of programming (called programming paradigms). Part of the art of programming is selecting one of the programming languages best suited for the task at hand. Different programming languages require different levels of detail to be handled by the programmer when implementing algorithms, often resulting in a compromise between ease of use and performance. Computer software could be defined as set of program, instructions, procedures and documentation that directs the operation of a computer system (Weinberg and Geller, 1989). It is also essentially a computer program encoded in such a fashion that the program (the instruction set) contents can be changed with minimal effort. Software and hardware are inseparably linked and they are always developed together. Computer software is used to describe all programs used by the computer system. The three types of software are: System software, Programming

software and Application software System software help to run the computer hardware and computer system. It includes operating system, devices drivers, diagnostic tools, services windowing systems utilities and more (Amdahl, 1999. High level languages are symbolic. This language is designed / developed to a level of sophistication that makes it similar to human language. The language is English like and allows the use of mathematical terms and symbols. The time and efforts needed to write a program in high level language are reduced and the programmes are easier to correct and modify.

There are many high-level languages, designed for a variety of applications (Anderson et al, 1999). The following are few of the high-level language used in business world today:

ALGOL: An abbreviation for algorithmic oriented language. It is used internationally as procedure oriented program.

COBOL: an abbreviation for Common Business Oriented Languages. It is a coding system, with business data processing procedures may be precisely described in a standard form.

FORTRAN: An abbreviation for Formula Translation. This is a Programming Language Designed for Problem that can be expressed in algebraic notations, allowing for experimentation and up to three sub-scripts. (Oyenuga, 1996)

R P G: It is a high-level program generator and acronym for Report Program Generator, most suitable for printing simple reports. It handles alphabetic information easily.

PASCAL: This language is named after Blase Pascal, the French mathematician who developed digital calculation. A programming language has the purpose of allowing data processing program to be written with a minimum of burden on the programmer and a maximum of burden in the computer. (Bertram, 1994).

BASIC: an abbreviation for Beginners All Purpose Symbolic Instruction Code. It is very simple mathematical problem-oriented programming language.(Falodi and Adedara, 2005)

QBASIC is an abbreviation for Quick Beginners All Purpose Symbolic Instruction Code. It is a typical Basic programming language. VBASIC (Visual Beginners All purpose Symbolic Instructional Code) is a programming language which is used for the task at hand.

2.13 Why visual basic programming language?

This Windows graphic user-interface presents before a computer user, a desktop filled with icons and programs that use mice (pointing devices) and menus. This makes computer looks more fascinating and easier to use. Perhaps even more importantly, than the look is the feel that the applications developed for Windows generally have a consistence user interface. This implies the user can spend more time to master the application and less time to worry about which keystroke do one thing or the other within the menu and dialog boxes. The Visual BASIC is an easy but yet powerful tool for developing Windows applications in Basic. Visual basic let you add menus, text boxes, command buttons, option buttons, (for making exclusive choices), check boxes (for non-exclusive choices), list boxes, scroll bars, files and directory boxes to blank Windows. In this application, one can agree to handle tabular data and can also communicate with other Windows applications (unlike the Quick-Basic), and easy method to let the user control and access data bases, which if all these will be accomplished in other programming language will require extra thousands of codes (Okunola, 2006).

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 Materials

Materials for plating include two steel samples to be plated (NST50-2 and NST60Mn), initial electrolyte (H_2SO_4, $CuSO_4.5H_2O$ and phenol). The additives (brightening agents) used include milk powder, saccharin 550, dextrin and lactic acid. Other materials are electrolytic cell, hand files, polishing machine, sand papers of 60μm, 120μm, 320μm, 400μm and 600μm fineness and pure copper electrode (anode) rod, HCl and NaOH. Materials used for corrosion tests are weight meter, analytical grade of NaCl, H_2SO_4, NaOH, Rain water, well water and tap water samples were sourced and collected from three different locations within Ado-Ekiti town namely; Federal Polytechnic main-campus, Omisanjana Area, and Ekiti State Ministry of Water Resource Ireje Scheme, Ado-Ekiti respectively. The analysis of water samples are shown in Table 3.1.

3.2 Methodology

3.2.1 Copper plating on steel

Steel samples were collected from Osogbo Steel Rolling Mill, Osogbo and were cut length (40mm) x width (15mm) x thickness (5.5mm). The samples surface were manually smoothened by filing with 0.8mm, 0.6mm and 0.4mm hand files and finally polished on the ELE polishing machine (EL 78/260) using five grades of sand papers (60μm, 120μm, 320μm, 400μm and 600μm). The final stage of surface cleaning were carried out by brush cleaning and washing in emulsifying solution made from 1:1 kerosene and detergent at 50°C for 10mins, followed by water rinsing for 1mins at 70°C, alkaline-washing in 1% NaOH solution operating at 45°C for 2mins to degrease the surface, followed by acid-washing in 13% HCl at 50 °C for 1min with intermittent water rinsing at 27°C between every stage. The initial weight of the specimen was determined on weight meter. The copper electroplating bath (Fig. 3.1) was set up under the following conditions; the acid sulphate bath comprises of three initial plating solutions: 200g/l $CuSO_4.5H_2O$, 50g/l H_2SO_4, 1.0g/l phenol as inhibitor, operated at 50°C bath temperature, current density (c.d) = $1A/dm^2$, 95% current efficiency.

The optimum plating characteristics of NST50-2 steel were determined by varying the applied voltage from 1V to 5V, concentration of $CuSO_4$ from 200g/l to

250g/l, electrode distance from 60 to 140mm, plating time from 5 to 25min and surface finishing: 60-600μm. Four organic additives (brightening agents) were tested on the acid-copper sulphate bath. The saccharin concentration was varied from 0.1g/l to 0.5g/l to determine the effect of increasing additive concentration on the plating. After which 0.5g/l concentration of each of other additives (dextrin, milk and lactic acid) was tested. The obtained optimum values were used to plate NST60Mn steel substrate.

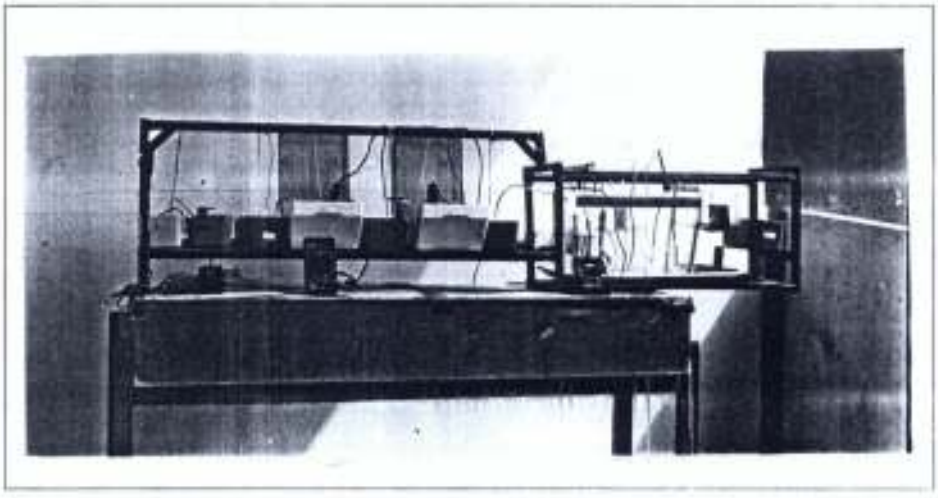

Figure 3.1: Laboratory set up for copper plating experiment

The plated steel was seal rinsed in water at 80°C for 1min. The material is dried in air and the final weight is measured. The copper film weight-gain is determined from the difference in the final and initial weights. The thickness of the metallic Cu-film was measured using micrometer screw gauge and while powdery film thickness was calculated by using Equation (2.12)

3.2.2 Corrosion tests.

The obtained optimum values were used to plate steel substrate used for corrosion tests. All copper-plated samples used for the corrosion tests were plated for about 30mins to obtain thicker films suitable for corrosion experiment.

Four substrates used were: 2 of as-received samples (NST50-2 and NST60Mn) and 2 of Cu-coated steel samples (NST50-2 and NST60Mn). 500ml of each of the corrosive media used for corrosion tests were prepared. These include: 3.5M NaCl, 0.1M H_2SO_4, 0.1M NaOH, Processed Water, Well water and Rainwater. Each of the four steel samples was fully immersed into the six media for 30days. The method of

measurement is by taken the weight loss (mg) as a measure of corrosion at every 2days interval of immersion period.

Table 3.1: Chemical analysis of water samples

Source	Rainwater	Well water	Processed water
Location	Fed. Poly	Omisanjana	ESMWR, Ado
PH	7.78	9.6	7.1
Total hardness	176.11	230	220.5
Chloride	18.05	20.1	45.6
Sulphate	42	124	272
Nitrate	12	17.3	58.67
Alkalinity	261	156	56.2
Acidity	1.49	1.48	0.31
Total dissolved solid	76.3	68.21	71.6
Sodium	65	71	78

3.3.3 Development of computer program 'COSEP' in V-BASIC language.

The whole process is summarised as chart in Fig. 3.2. A computer program in V-Basic language was developed based on the pre-determined optimum plating parameters and corrosion characteristics of steels in the six media used. The model equations (2.12, 4.1 through 4.13) were used to generate a program that is capable of determining or simulating the thickness of copper coat required to protect any size of a steel material in any of the six media; 0.1M NaOH, 3.5M NaCl and 0.1M H_2SO_4, rainwater, well-water and processed water.

The following inputs were used in the development of the computer programming for plating copper on steel.

1. Plating parameters:

   Voltage (V), Electrode separation distance (mm), Concentration of $CuSO_4$ electrolyte (g/l), Plating time (min), Surface finishing grade (μm)

2. a) Corrosion rate

   Weight loss (mg), Exposure time (day), Surface area (mm^2)

   b) Media/environments

   NaCl, H_2SO_4, NaOH, Tap water, Well water, Rainwater

3. Design of VBASIC forms and program code writing

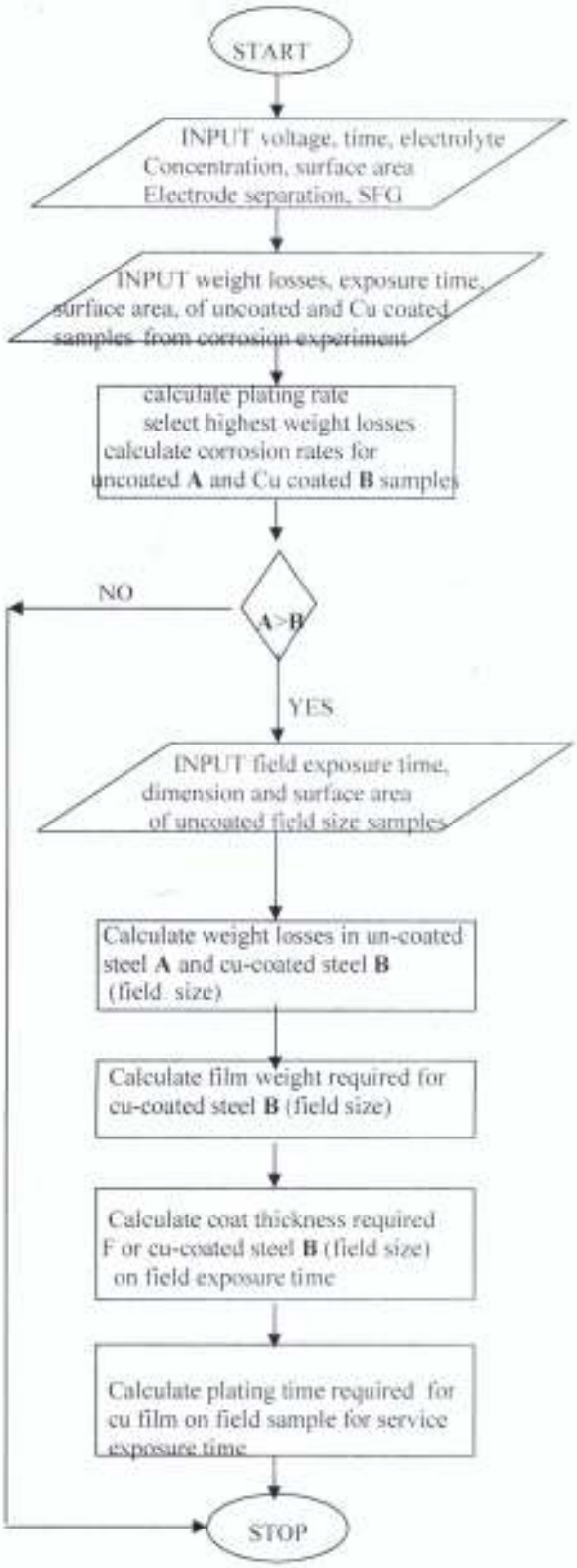

Figure 3.2: Flow sheet for COSEP Development

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Copper plating

The determination of the optimum plating parameters of copper deposition on steel in an acid-sulphate plating bath was determined and the results presented in Figures 4.1 through 4.14.

4.1.1 Effect of voltage variation on plating

The Figures 4.1 and 4.2 show the plot of applied voltage increased from 1V to 5V against copper film weight gain and thickness on steel surface respectively. Observation shows that some amount of copper is deposited on steel immediately the steel is immersed into copper-sulphate solution even when no external source of voltage (V = 0) was applied. With the application of external voltage, the results show that the Cu-deposition increased with increasing applied voltage. Figure 4.1 shows a linear curve for applied voltages ranging between 1-2V. At these voltages, the plating was stable, bright and protective. As 3V is exceeded, there was a drastic increase in the film weight and thickness, thus causing a sharp change in the gradient of the curve. Hence the overall trend of curve obtained from the weight gain-voltage curve is defined by equation (4.1).

$$W_{gv} = 0.0413V^2 - 0.1507V + 0.147 \quad \text{----------} \quad (4.1)$$

Where W_{gv} = weight of copper deposited at voltage V

Observation shows that the best plating appearance was obtained at 2V while above 3V, the deposit become rough-looking, peeling, porous and powdery with colour changing from red to brown. It was also observed that the adhesion, brightness, texture became worse as the voltage was increased, while Cu deposition at 4-5V are very poor and not protective but become spongy. Smithell, (1978) suggested that good copper (Cu) on steel plating from acid sulphate bath could be obtained within the range of 1-3V applied voltage. Also observation shows that though higher film thickness values were obtained above 3V, the films are not protective, but become powdery.

4.1.2 Effect of plating time variation

The result of the increasing effect of plating time is shown in Fig 4.3 and 4.4. The results in figures 4.3 and 4.4 show that the film weight-gain and thickness increase with increasing plating time. Figures 4.3 and 4.4 show linear curves for plating time

ranging between 0-10mins. Above this plating time, the trend of increase in the film weight-gain is small. Hence the curves become parabolic. The trend of the curve is defined by the equation (4.2) obtained as;

$$W_{gt} = -0.0273t^2 + 0.2904t - 0.247 \quad \text{---------- (4.2)}$$

Where W_{gt} = weight of copper deposited at time t

Observation shows that the plating time did not affect the adhesion, brightness, colour and texture of the plating.

4.1.3 Effect of $CuSO_4$ electrolyte concentration.

The effect of increasing $CuSO_4$ electrolyte concentration on film weight and thickness is shown in Fig 4.5 and 4.6. The trends of the curves show that the film weight (Fig 4.5) and thickness (Fig.4.6) increase with increasing $CuSO_4$ electrolyte concentration from 200 to 250g/l.

From the result, only 200g/l $CuSO_4.5H_2O$ gave very reliable and protective plating, while observation shows that there was evolution of gas at the cathode, and spontaneous increase in the current drawn into the circuit at 220g/l$CuSO_4.5H_2O$ and higher value of electrolyte concentration. The physical appearance and colour show that the best plating was obtained from 200g/l $CuSO_4.5H_2O$ solution, while at higher concentration above 200g/l produced un-stable copper plating.

4.1.4 Effect of electrode separation

Figure 4.7 shows the result of effect of increase in electrodes (anode-cathode) separation distance on copper film weight and film thickness on steel. In figure 4.7, the curves show that, increasing the electrode separation resulted in corresponding decrease in the copper film weight and film thickness. The reduction in the distance available between anode and cathode shows corresponding increase in weight of Cu deposited and coating thickness.

This increases the porosity of the coating and reduces the adhesion on steel surface. The reduction in separation adversely affected the physical appearance of Cu plate obtained, though larger quantity (in gram) of Cu deposition was obtained. The most stable and good-looking plating were obtained at 140mm separation distance. Further observation shows that, as the electrode separation is reduced below 100mm, the plating characteristics (adhesion, porosity, colour, brightness and texture) became worse, while the evolution of gas increased at the cathode as the two electrodes approached each other (because of increased current density across cathode V = IR).

4.1.5 Effect of surface finishing grade with and without additives.

(i) Effect of surface finishing grade without additives

In Fig 4.8, the effects of five surface-finishing grades of steel samples were studied on the copper film weight and film thickness in sulphate bath. Fig 4.8 shows copper-plating on steel using improving surface finishes ranging from 60 to 600μm grades. No additive was used. From the result, the film weight gain and the film thickness reduce as the surface-finishing grades increased. The physical appearance (colour, porosity, lustre and adhesion) improves as the surface improves.

Observation shows that the most stable plating was obtained from the 600μm surface finishing grade. There were unstable, rough deposits on the 320, 120μm and 60μm grades, while the deposition on 400μm and 600μm finishes were of metallic lustre and better adhesion characteristics. The result shows that a very thin layer (μm) of copper film was deposited on the steel cathode.

(ii) Effect of surface finishing grade with additives

The results of the effect of four different organic brightening agents (saccharin 500, dextrin, lactic acid and milk) on the film weight gain and the film thickness using five surface finishing grades are presented in Figures 4.9 through 4.12. These organic additives are used to improve on the throwing power of acid-sulphate electrolyte and the brightening of the copper plating.

(a). Effect of increasing concentration of saccharin 550

Fig. 4.9 and 4.10 show the results of increasing the concentration of saccharin 550 additives used as organic brightener on copper-plating on five surface finishing grades of steels in an acid-sulphate bath. There was reduction in film weight gain and thickness as the surface finishing grades SFG increased. Observation shows that, the increasing saccharin-550 concentration from 0.1g/l to 0.5g/l shows improvement on the physical appearance of the plating. At lower concentrations 0.1g/l saccharin-550, there was a high film weight and thickness value but poor brightening characteristic of the plating. The addition 0.5g/l saccharin 550 to the bath gave stable plating on all the surface finish grades. The trend of curves in Fig. 4.9 and 4.10 revealed that there was reduction in copper film weight for all surface-finishing grades used as the concentration of saccharin 550 increased. The deposition on the 600μm finish grade was very thin, bright, protective and stable. Thus, the combination of 600μm SFG and 0.5g/l saccharin produced the most stable plating.

(b). Effects of four organic additives

In Fig. 4.11 and 4.12, four organic additives (Saccharin 550, milk dextrin and lactic acid) were used as brightening agents on copper plating in the acid-sulphate bath. The effect of 0.5g/l saccharin 550 was first tested on the bath, followed by milk, dextrin and finally, the lactic acid. Copper film weight (Fig 4.11) and thickness (Fig 4.12) are plotted against five surface finishing grades SFG for each of the organic additive. The surface finish grade was varied from 60 to 600 μm.

The addition of 0.5g/l of each organic additive shows that there were improvement on the physical appearance of the plating. The copper film weight (g) reduces in all cases of brighteners as the surface-finishing grade increased. Close values of copper deposition (weight gain) were obtained from the use of 0.5g/l saccharin on 120~600μm finish grades.

The saccharin and lactic acid additive curves show decrease in copper film weight (Fig 4.11) and thickness (Fig 4.12) as the surface-finishing grade increased. In the saccharin and lactic acid based electrolytes, the plating stability increased with increasing SFG.

The milk gave the most stable plating on 60μm SFG. Saccharin and milk have similar plating film weight (Fig 4.11) and thickness (Fig 4.12) on 320μm and 400μm SFG. The curve shows that milk gave increase in the film weight and thickness as the SFG increased from 400 to 600μm. The physical observation shows that, with exception of milk, other three organic additives gave stable plating with lower film thickness values on 600μm SFG. Good plating were obtained on the 600μm finish grade by adding equal concentration of milk, dextrin and lactic acid, whereby dextrin gave the least brightening effect of plating on the 600μm surface finish grade among the three other brighteners tested.

Using the 600μm surface-finishing grade, saccharin produced the least copper film weight (Fig 4.11) and thickness (Fig 4.12) with best physical appearance and plating stability, followed by lactic acid while the highest film weight (Fig 4.11) were gotten from both milk and dextrin additives.

Generally, all the organic additives used yielded better and improved results in terms of brightness of colour and adhesion, though less quantities of film weight (Fig 4.11) and thickness (Fig 4.12) were produced. Hence, the overall results shows that with the use of 0.5g/l saccharin 550, very thin film could be obtained from 120 ~

600μm SFG while 400– 600μm SFG are workable for other brightening agents (milk, dextrin and lactic acid).

The trends of the curves are defined by the equations (4.3) through (4.6) obtained as;

Saccharin additive:

$W_g = 3E\text{-}07G^2 - 0.0003G + 0.0911$ ---------- (4.3)

Milk additive:

$W_g = 3E\text{-}07G^2 - 0.0003G + 0.0969$ ---------- (4.4)

Dextrin additive:

$W_g = 2E\text{-}07G^2 - 0.0002G + 0.1137$ ---------- (4.5)

Lactic acid additive:

$W_g = 1E\text{-}07G^2 - 0.0002G + 0.0944$ ---------- (4.6)

Where W_g = weight gain, G = surface finishing grade

4.1.6 Copper- plating on two steel types

The results of copper film weight and film thickness on five surface finishing grades of NST50-2 and NST60Mn steels are compared in Fig. 4.13 and 4.14 respectively. The plating was done using the optimum plating values of V=2V, S= 140mm, 200g/l $CuSO_4$ electrolyte for 10minutes. For both of the NST50-2 and NST60Mn, the trend of curves obtained from the film weight versus surface finishing grades plot are the same as illustrated in Fig. 4.13 which equations are given by equation.

$Wg = 0.0057G^2 - 0.0503G + 0.132$ ---------- (4.7)

Where Wg = weight gain, G = surface finishing grade

The trend of both NST50-2 and NST60Mn curves show that the film weight and film thickness decrease with increasing SFG from 60-600μm while observation revealed that plating become more stable from 400 to 600μm SFG. Both curves show a decrease in film weight and thickness for SFG from 60 to 320μm and from 400 to 600μm. From 320 to 400μm, NST50-2 maintained a constant film weight and thickness values while on the NST60Mn curve, the film weight and thickness increased with SFG.

The little difference in Cu-deposition on the steel surfaces might have been influenced by some other imperfections (scratches etc) rather than the composition of the steel. Hence, it is evident that the level (degree) of surface smoothness has more pronounced influence on deposition rather than the steel types. Best Cu-plating was

obtained for the two types of steels when 400 and 600μm grades were used. The plating is sufficient enough to offer protection against corrosion.

4.2 Result of corrosion tests

The result of immersion test of as-received steels (NST60Mn and NST50-2) and Cu–coated steels (Cu– coated NST60Mn and Cu– coated NST50-2) for 30 days in NaCl, H_2SO_4, NaOH, tap water, well water and rainwater are presented in figures 4.15, 4.16, 4.17, 4.148, 4.19 and 4.20 respectively. The trends of the corrosion rate curves obtained (from copper-film) in the six media are defined by the equations (4.8) through (4.13).

4.2.1 Copper corrosion in aqueous solutions of NaCl

Fig 4.15 shows the weight loss vs. exposure time curve of four samples (A = as-received NST60Mn, B = NST50-2, C = Cu– coated NST50-2 and D = Cu– coated NST60Mn) in 3.5M NaCl. The weight loss increased with exposure time at almost same rate for all the four samples in the first twelve days. The weight loss rates are small with gentle slopes. The as-received NST60Mn showed a sharp rise in weight loss rate between the 12th and 28th day after which the weight loss rate becomes constant until 30th day. The as-received NST50-2 also showed a sharp rise in weight loss rate between the 12th and 26th day after which the weight loss rate becomes constant until 30th day. The as-received NST60Mn steel has the highest level of weight loss in 3.5M NaCl for the period of the 30 days. The weight loss in of as-received steels increased tremendously after 12 days. Figure 4.15 shows that the coated steels have lower weight losses in the brine solution than the uncoated (as-received) steel samples. The Cu– coated NST50-2 showed higher weight loss rate between the 16th and 26th day after which the weight loss rate becomes constant until 30th day. The weight loss rate of cu coated NST60Mn increased with gentle slope until the 28th day. The weight losses remain constant between 28th and 30th for the coated samples. Comparatively, the highest values of 392mg, 247mg, 169mg, and 152mg, weight loses were measured for as-received steels (A and B) and cu-coated steels (C and D) respectively within the 30days of immersion in 3.5M NaCl. The trend of the corrosion rate curve obtained (from copper-film) in NaCl is given by

$$Wl = 5.0541t - 1.919 \quad \text{----------} \quad (4.8)$$

Where Wl = weight loss (mg), t = time (day)

4.2.2 Copper corrosion in aqueous solutions of H_2SO_4

Fig 4.16 shows the weight loss vs exposure time curve of four samples (A = as-received NST60Mn, B = NST50-2, C = Cu- coated NST50-2 and D = Cu- coated NST60Mn) in 0.1M H_2SO_4. The weight loss increased with exposure time at almost same rate for all the four samples in the first 6 days and at very close rate between 6th and 12th day. For sample A, the weight loss increases with exposure time for the 30 days of immersion except for the period of 2days (between 20th and 22nd day). Fig. 4.16 shows a drop in weight loss in sample B the 12th and 14th day after which there was a rise in the weight loss value until the 26th day. The weight loss was also constant between 26th and 28th after which there was a drop in weight loss until the 30th day. Figure 4.16 shows that the coated steels have lower weight losses in the H_2SO_4 solution than the uncoated (as-received) steel samples. The weight losses increased with exposure time at almost same rate for the two coated-steel samples within the 30 days of immersion. Comparatively, the highest values of 94mg, 80mg, 31mg, and 34mg, weight loses were measured for as-received steels (A and B) and cu-coated steels (C and D) respectively within the 30days of immersion in 0.1M H_2SO_4. The trend of the corrosion rate curve obtained (from copper-film) in H_2SO_4 is given by

$$Wl = 0.6814t + 15.717 \quad (4.9)$$

Wl = weight loss (mg), t = time (day)

4.2.3 Copper corrosion in aqueous solutions of NaOH

Fig 4.17 shows the weight loss vs exposure time curve of four samples (A = as-received NST60Mn, B = NST50-2, C = Cu- coated NST50-2 and D = Cu- coated NST60Mn) in 0.1M NaOH. In fig. 4.17, the weight loss increased with exposure time at almost same rate and at very close values for all the four samples in the first 8days and for three samples A, B and C extends to the 12th day. There was a drop in the weight loss in sample A between the 12th and 14th day after which there was an increase in the weight loss of the sample as the exposure time increased.

For sample B, the weight loss increases with exposure time for the 30 days of immersion except for the period of 2days (between 20th and 22nd day). Sample B shows the highest weight loss of the four samples in NaOH solution.

Sample C shows a drop in the weight loss between the 14th and 20th day after which there was rise in the weight loss of the sample as the exposure time increased until the 26th day when the weight loss become constant until the 30th day.

Comparatively, the highest values of 85mg, 96mg, 57mg, and 58mg, weight loses were measured for as-received steels (A and B) and cu-coated steels (C and D) respectively within the 30days of immersion in 0.1M NaOH. The trend of the corrosion rate curve obtained (from copper-film) in NaOH is given by

$$Wl = 1.7484t + 4.9657 \quad (4.10)$$

Wl = weight loss (mg), t = time (day)

4.2.4 Copper corrosion in aqueous solutions of Tap water

Fig 4.18 shows the weight loss vs exposure time curve of four samples (A = as-received NST60Mn, B = NST50-2, C = Cu– coated NST50-2 and D = Cu– coated NST60Mn) in tap water. The weight losses in the four increased with the increasing exposure time. The weight losses in the two as-received samples A and B are very close while the coated samples C and D have almost the same values with the increasing exposure time. The weight loss in Sample A increased until the 26th day after which the weight loss becomes constant. The weight loss in sample B becomes constant after the 28th day of exposure. Comparatively, sample A has higher weight loss values than sample B in the tap water. Also, the highest values of 52.2mg, 61mg, 32.2mg, and 31mg, weight loses were measured for as-received steels (A and B) and cu-coated steels (C and D) respectively within the 30days of immersion in the tap water. The trend of the corrosion rate curve obtained (from copper-film) in tap water is given by

$$Wl = 1.7484t + 4.9657 \quad (4.11)$$

Wl = weight loss (mg), t = time (day)

4.2.5 Copper corrosion in aqueous solutions of well water

Fig 4.19 shows the weight loss vs exposure time curve of four samples (A = as-received NST60Mn, B = NST50-2, C = Cu– coated NST50-2 and D = Cu– coated NST60Mn) in well water. The weight losses in the four samples are almost the same and very close the first 8 days after which the weight losses increased with the increasing exposure time. Samples A and B have similar trend of weight losses after 8days while weight losses in C and D are also similar.

The weight loss in Sample A increased until the 28th day after which the weight loss becomes constant. The weight loss in sample B is constant between 26th and 30th day of exposure. The weight loss in sample C remains constant between 22nd and 28th day while sample D showed constant weight loss between 20th and 26th day of exposure. Comparatively, sample A and B have higher weight loss values than sample C and D in the well water for the period of 30days exposure. The highest values of 54.6mg, 51.1mg, 30mg, and 29mg, weight loses were measured for as-received steels (A and B) and cu-coated steels (C and D) respectively within the 30days of immersion in the well water. The trend of the corrosion rate curve obtained (from copper-film) in well water is given by

$$WI = 0.9273t + 7.9362 \quad (4.12)$$

WI = weight loss (mg), t = time (day)

4.2.6 Copper corrosion in aqueous solutions of rainwater

Fig 4.20 shows the weight loss vs exposure time curve of four samples (A = as-received NST60Mn, B = NST50-2, C = Cu– coated NST50-2 and D = Cu– coated NST60Mn) in rainwater. The weight losses in the four increased with the increasing exposure time. The weight losses in samples A and B are very close in the first 10days after which the weight losses increased at different trends with the increasing exposure time. The weight losses in Sample A and B increased until the 28th day after which the trends of weight losses become constant. The coated samples C and D have almost the same values and trend of weight loss with the increasing exposure time. Comparatively, sample B has higher weight loss values than sample A in the rainwater. The weight loss in sample C remains constant between 22nd and 26th day while sample D showed constant weight loss between 24th and 26th day of exposure. Both samples recorded higher values of increase in weight losses between from 26th to 28th day after which both samples showed a small level of reduction in the weight losses until the 30th day of exposure. The highest values of 79.2mg, 82.7mg, 21mg, and 24mg, weight loses were measured for as-received steels (A and B) and cu-coated steels (C and D) respectively within the 30days of immersion in the rainwater. The trend of the corrosion rate curve obtained (from copper-film) in rainwater is given by

$$WI = 0.5282t + 5.6952 \quad 4.13$$

WI = weight loss (mg), t = time (day).

Comparing the result of copper corrosion in Fig. 4.18 through Fig. 4.20, observation shows that Cu – plated steels corrode with increase in exposure time. Tap water contains active reagents such as chlorine and hypochlorous, Na^+, K^+, Mg^+ salts which are used in water treatment to make it portable. These reagents actively react with Cu to promote the corrosion. Comparison shows that as received sample A and B have greater level of corrosion than the copper coated steels (sample C and D) in six environments examined for 30days.

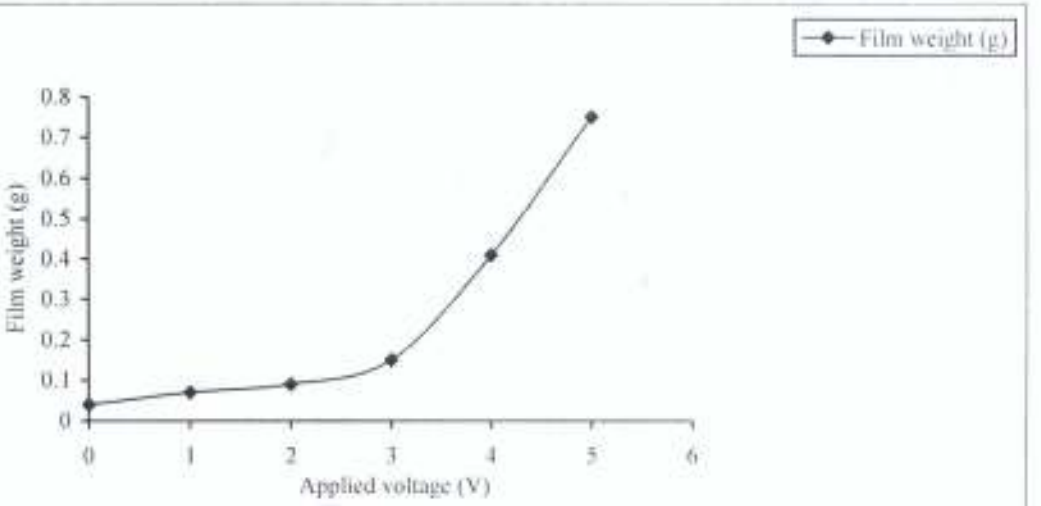

Fig4.1: Plot of applied voltage against copper film weight

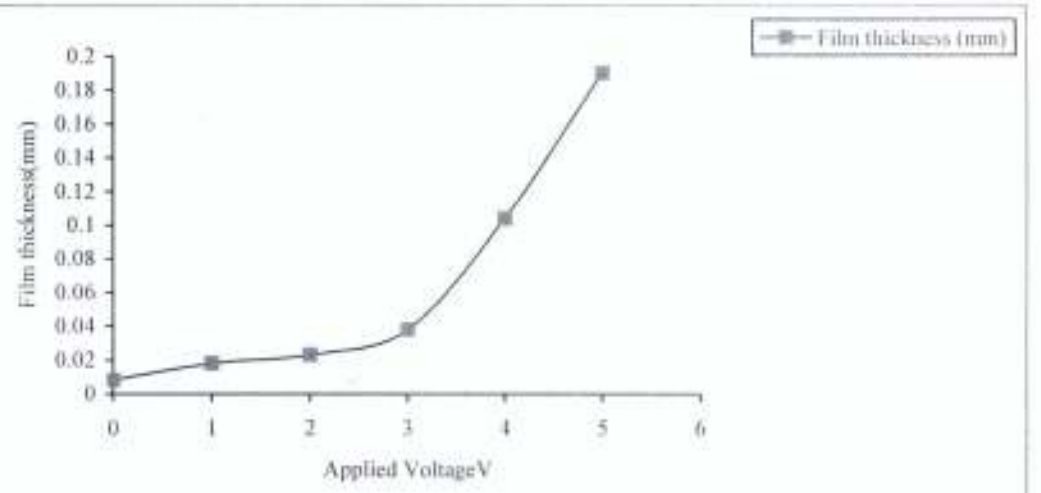

Fig 4.2:Plot of voltage against copper film thickness

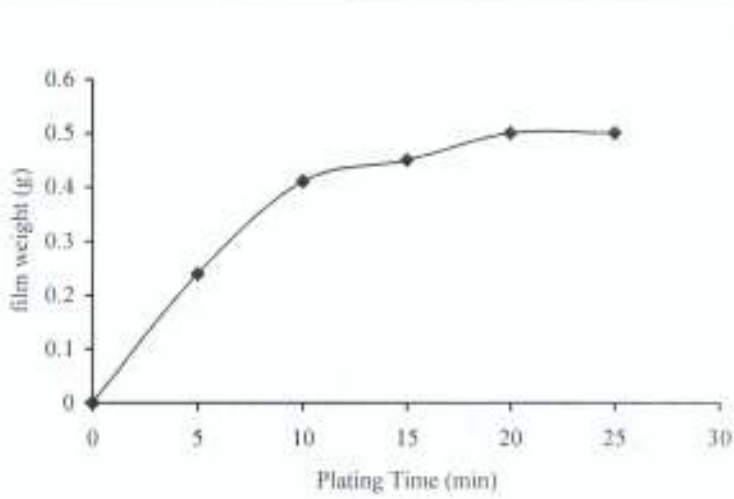

Fig4.3:Plot of plating time against copper film weight

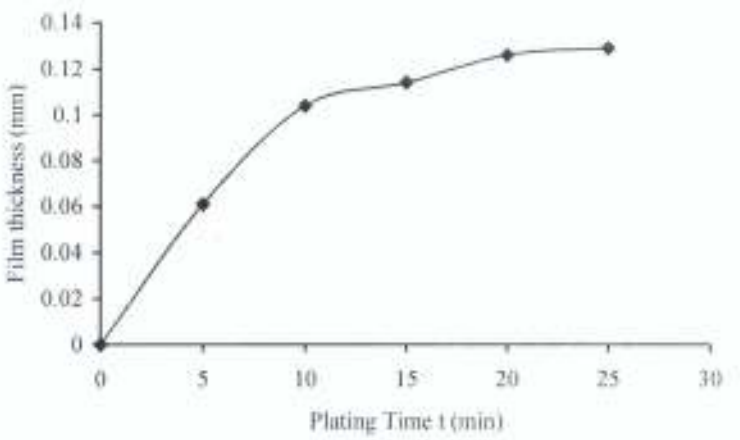

Fig4.4: Plot of plating time against copper film thickness

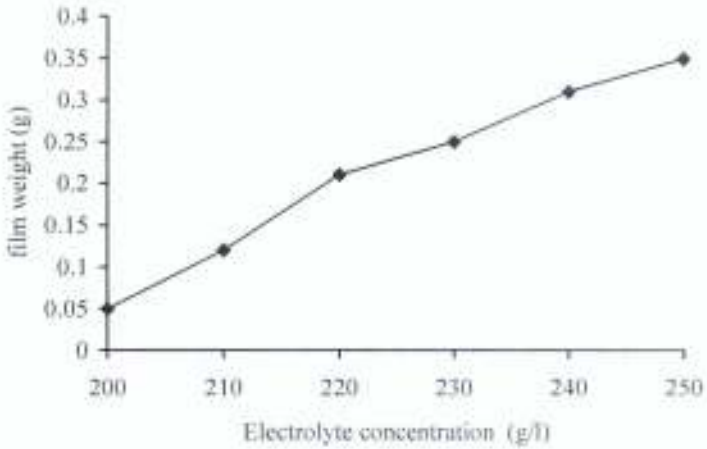

Fig4.5:Plot of electrolyte concentration against copper film weight

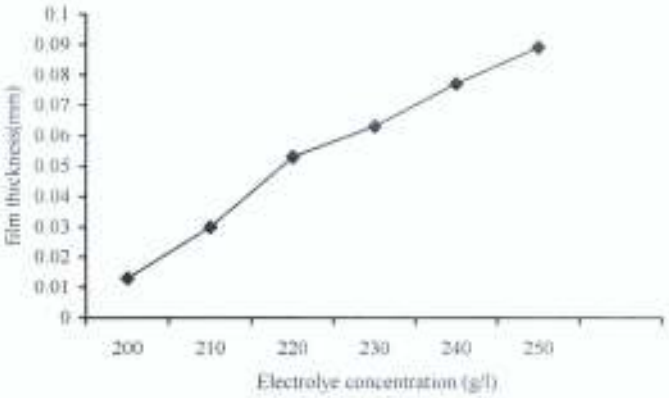

Fig4.6:Plot of electrolyte concentration against copper film thickness

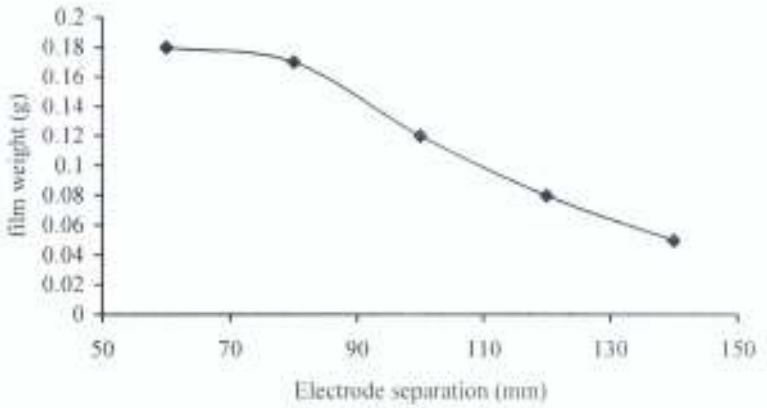

Fig 4.7a: Plot of electrode separation against copper film weight

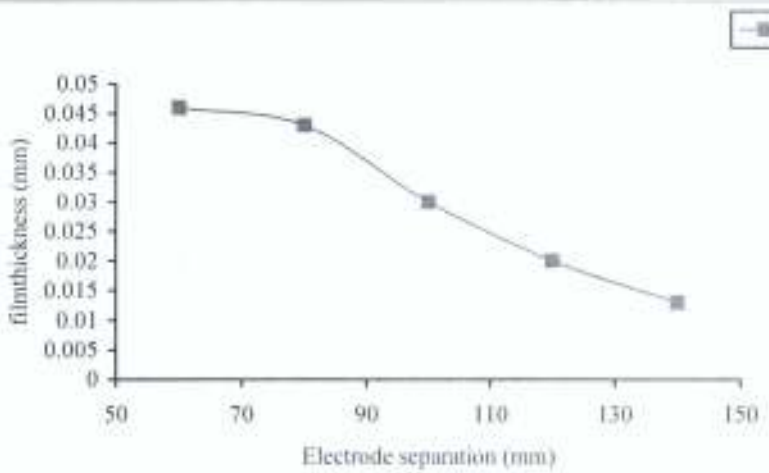

Fig 4.7b: Plot of electrode separation against copper film thickness

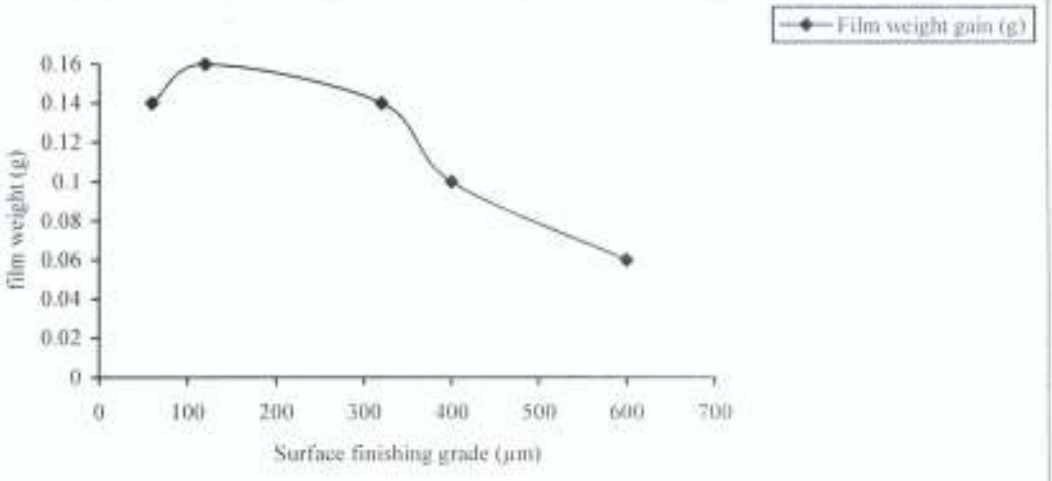

Fig 4.8a: Plot of surface finishing grade against Cu film weight (without additive)

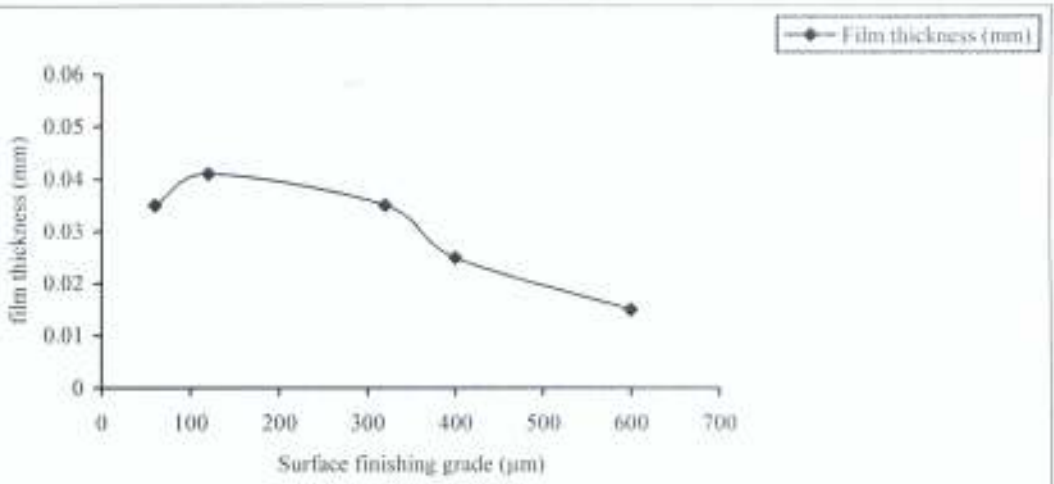

Fig 4.8b: Plot of surface finishing grade against Cu film thickness (without additive)

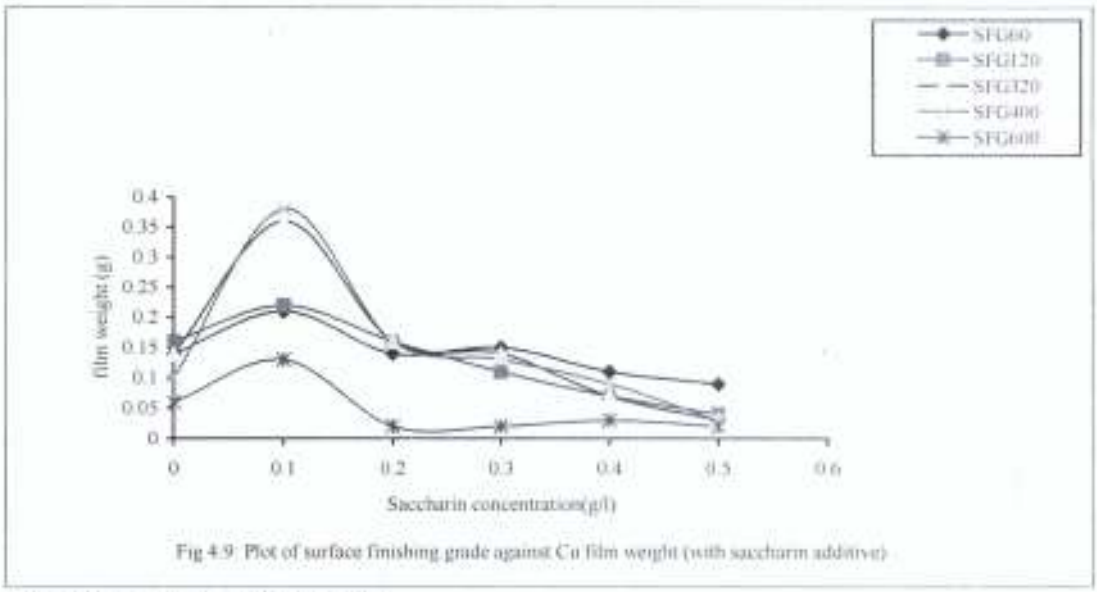

Fig 4.9 Plot of surface finishing grade against Cu film weight (with saccharin additive)

SFG = Surface Finishing Grade (μm)

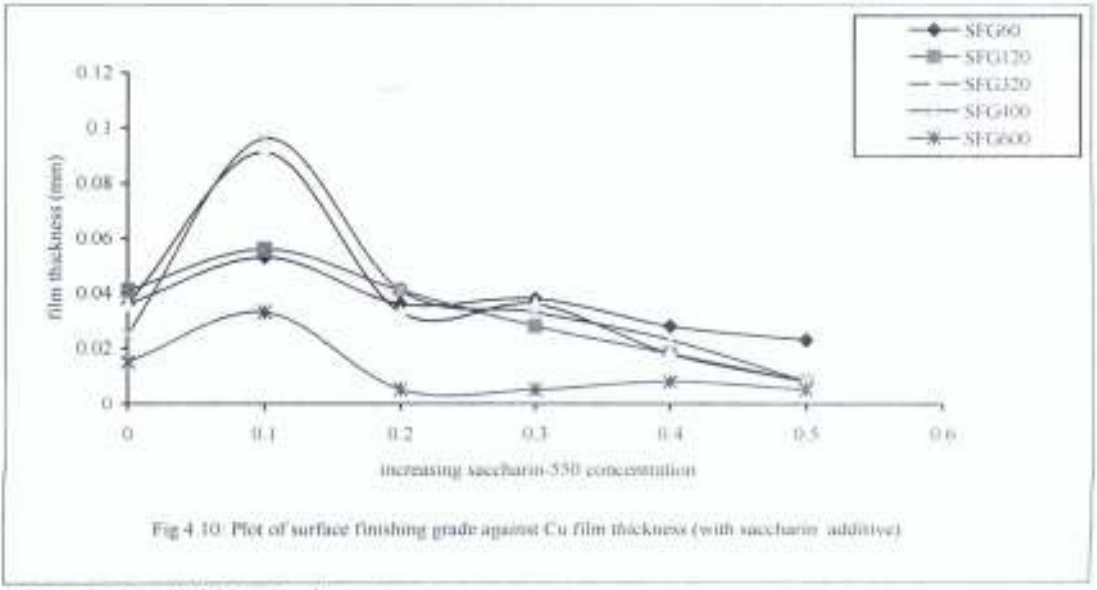

Fig 4.10 Plot of surface finishing grade against Cu film thickness (with saccharin additive)

SFG = Surface Finishing Grade (μm)

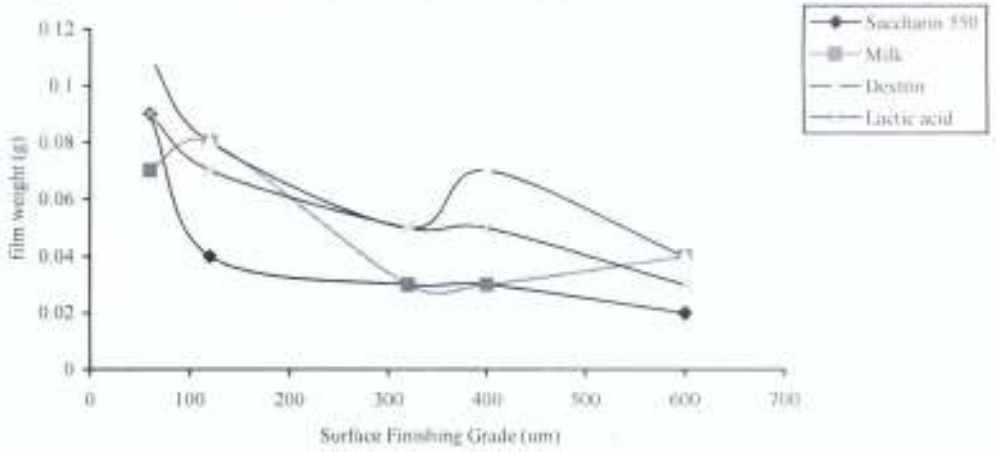

Fig 4.11: Plot of surface finishing grade against Cu film weight (using four additives)

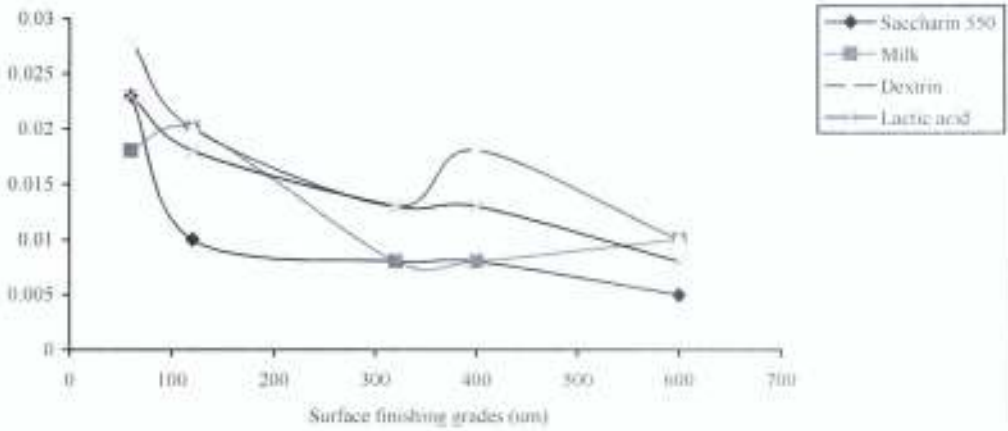

Fig 4.12: Plot of surface finishing grade against Cu film thickness (using four additives)

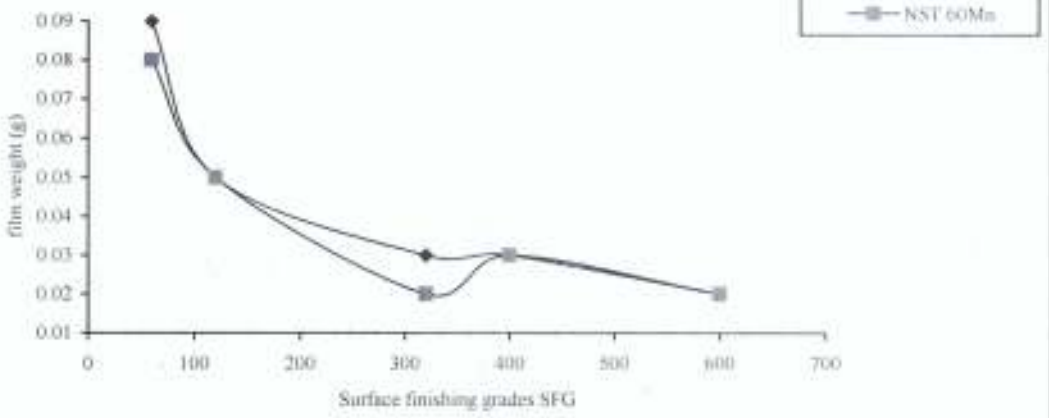

Figure 4.13: Comparison of surface finishing grades and Cu film weight on NST50-2 and NST60Mn steels

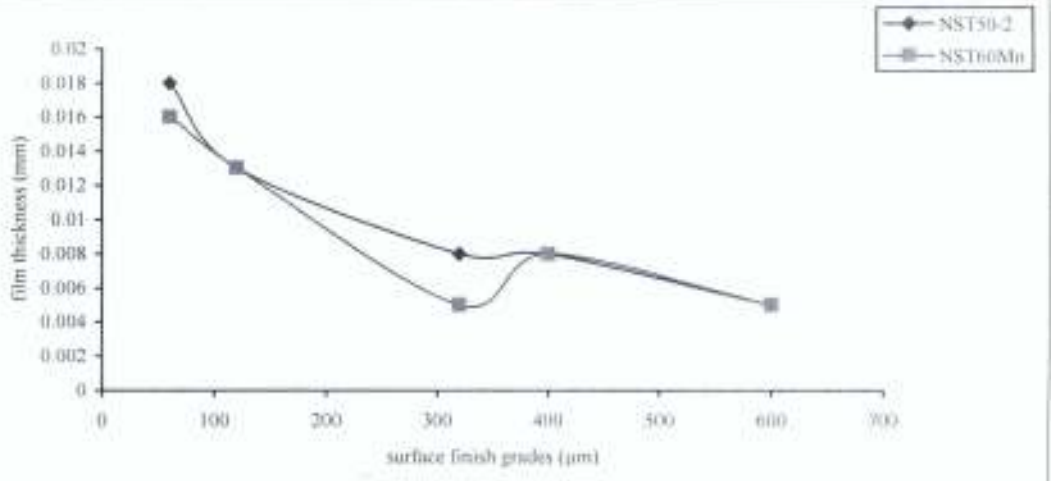

Fig.4.14: Comparison of surface finishing grades and Cu film thickness on NST50-2 and NST60Mn steels

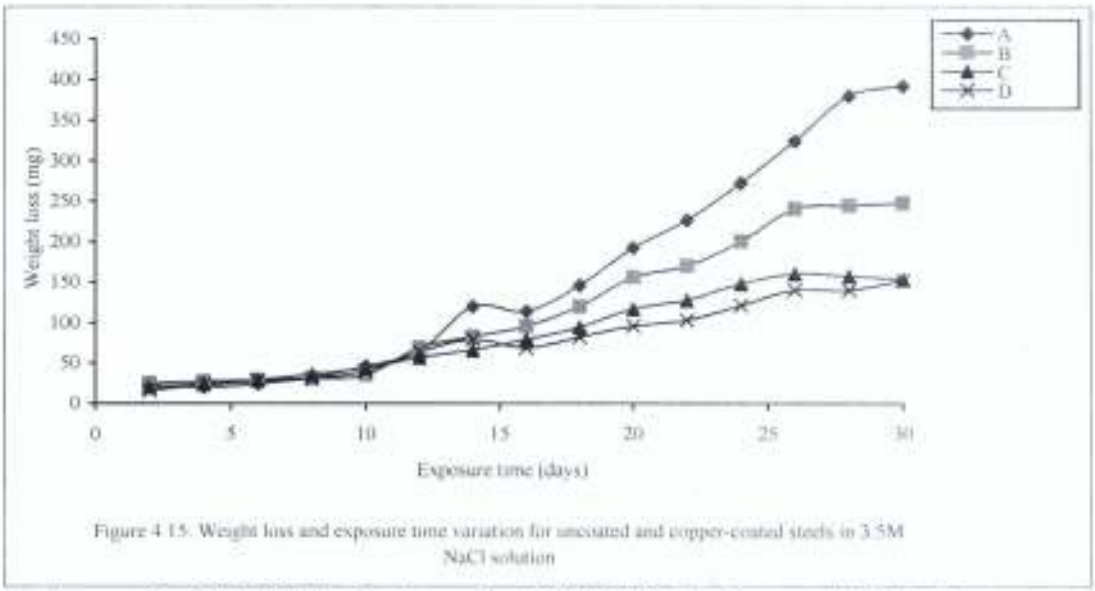

Figure 4.15: Weight loss and exposure time variation for uncoated and copper-coated steels in 3.5M NaCl solution

A= As-received NST60Mn, B= As-received NST50-2, C= Cu coated NST50-2, D= Cu coated-NST60Mn

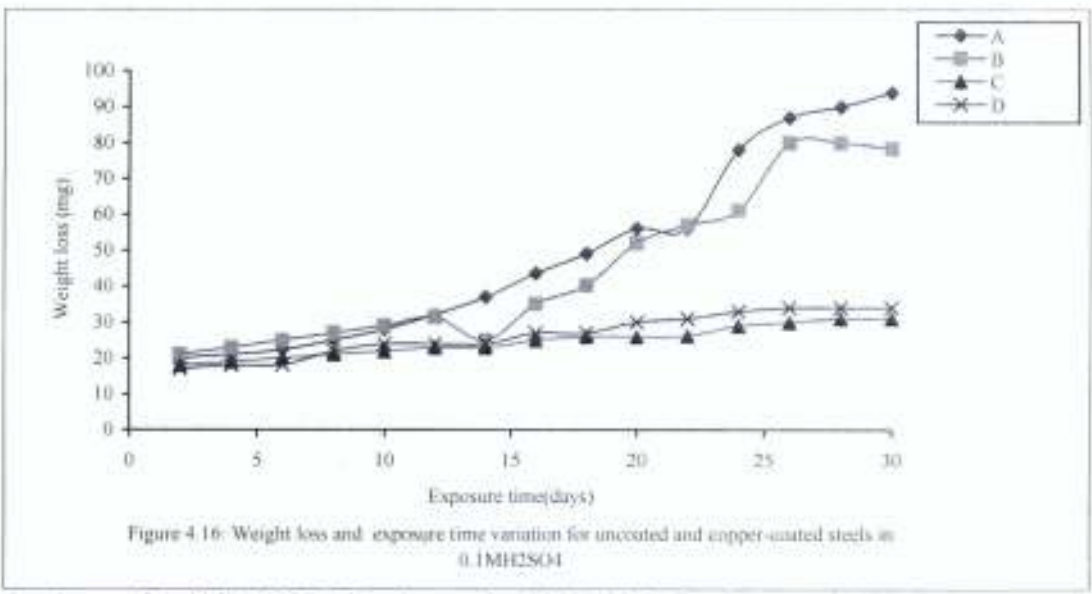

Figure 4.16: Weight loss and exposure time variation for uncoated and copper-coated steels in 0.1MH2SO4

A= As-received NST60Mn, B= As-received NST50-2, C= Cu coated NST50-2, D= Cu coated-NST60Mn

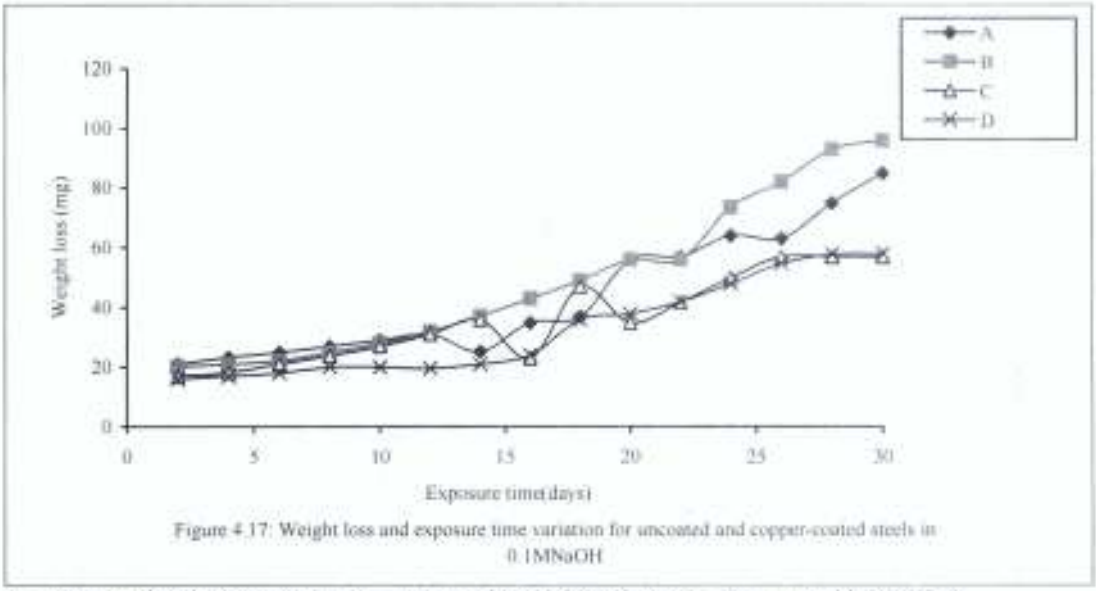

Figure 4.17: Weight loss and exposure time variation for uncoated and copper-coated steels in 0.1MNaOH

A= As-received NST60Mn, B= As-received NST50-2, C= Cu coated NST50-2, D= Cu coated-NST60Mn

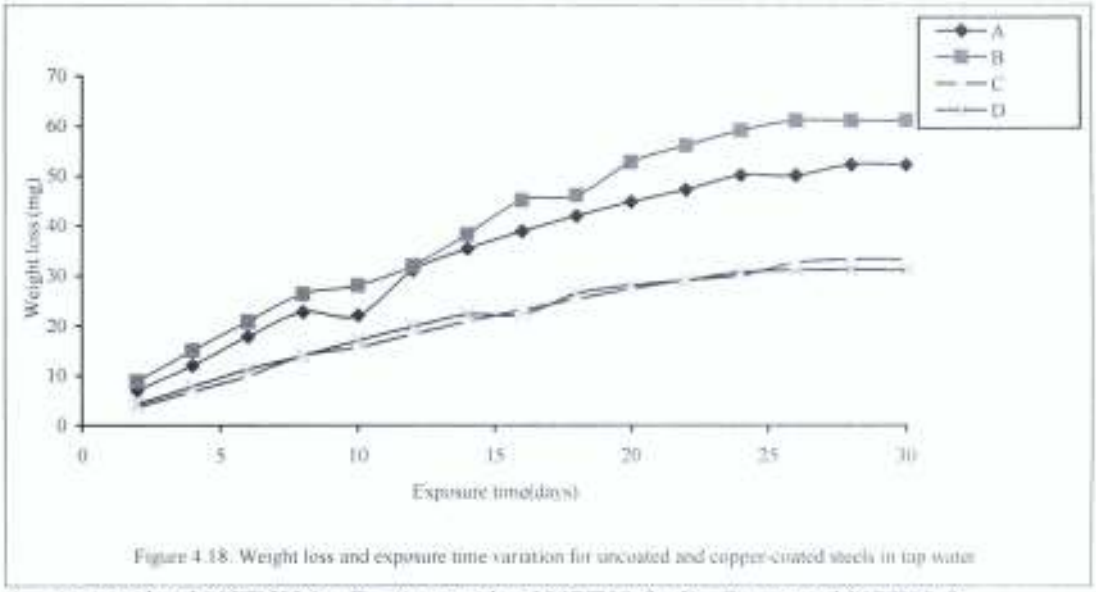

Figure 4.18: Weight loss and exposure time variation for uncoated and copper-coated steels in tap water

A= As-received NST60Mn, B= As-received NST50-2, C= Cu coated NST50-2, D= Cu coated-NST60Mn

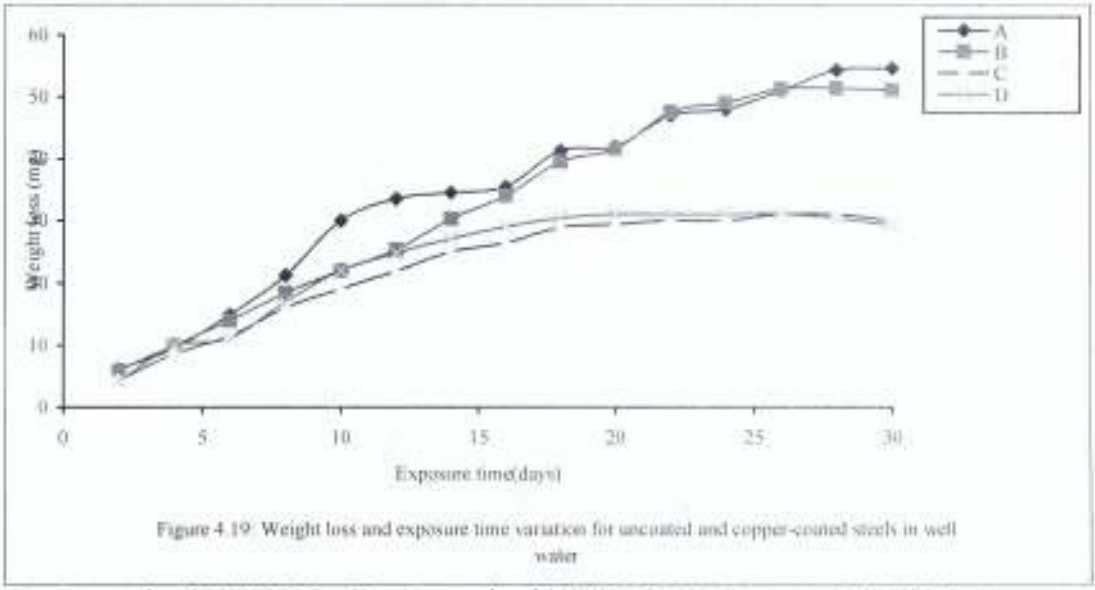

Figure 4.19: Weight loss and exposure time variation for uncoated and copper-coated steels in well water

A= As-received NST60Mn, B= As-received NST50-2, C= Cu coated NST50-2, D= Cu coated-NST60Mn

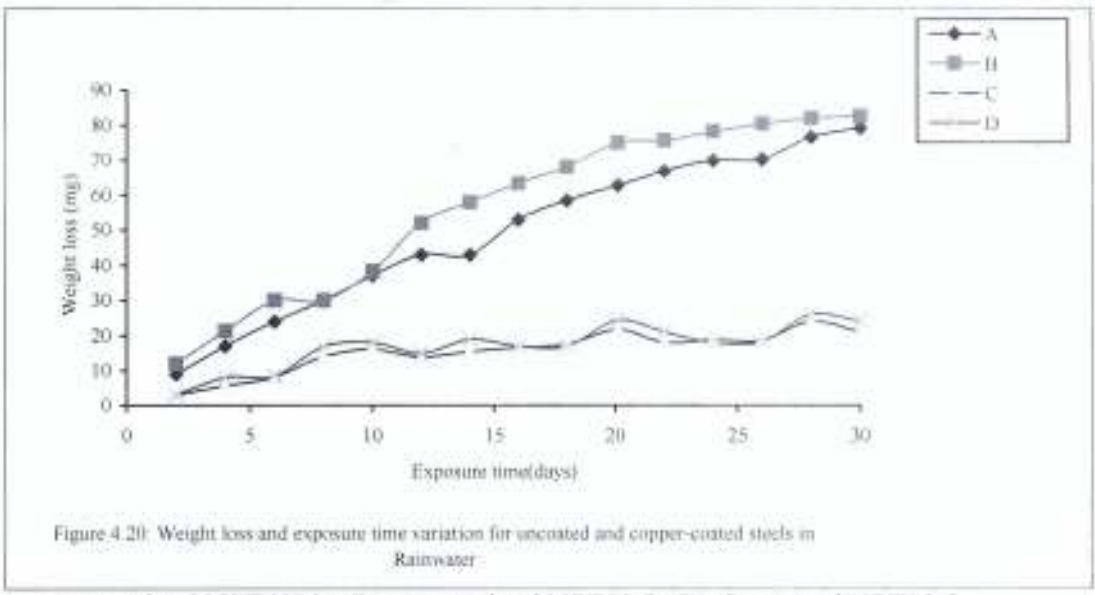

Figure 4.20: Weight loss and exposure time variation for uncoated and copper-coated steels in Rainwater

A= As-received NST60Mn, B= As-received NST50-2, C= Cu coated NST50-2, D= Cu coated-NST60Mn

4.3 Determination of corrosion rates of as-received steel and Cu-coated steel.

The corrosion rate of immersed samples (as-received steel and copper coated steels) in the six media for 30 days is presented in Table 4.1.

Table 4.1: Corrosion rate of as-received steels and Copper-coated steels in six media

Media	Total Exposure time (days)	Corrosion rate of as-received steel **A** ($mgmm^{-2}day^{-1}$)	Corrosion rate of Cu-coated steel **B** ($mgmm^{-2}day^{-1}$)
3.5M NaCl	30	$7.23x10^{-3}$	$3.06x10^{-3}$
0.1 M H_2SO_4	30	$2.01x10^{-3}$	$6.46x10^{-4}$
0.1M NaOH	30	$1.93x10^{-3}$	$1.2x10^{-3}$
Processed water	30	$1.21x10^{-3}$	$6.5x10^{-4}$
Well water	30	$9.97x10^{-4}$	$5.72x10^{-4}$
Rainwater	30	$1.51x10^{-3}$	$3.47x10^{-4}$

The corrosion rates of as-received and Cu-coated steels in Table 4.1 serve as the basis for determining the program continuity when running the program.

4.4 Results of computed Cu film weight, thickness and plating time

The program is written and run in the VBASIC program codes (Appendix C.2) to compute the required Cu film thickness (Figure 4.21) and required plating time (Figure 4.22) needed to coat steel surface for 365days application in six media (Table 4.2).

Table 4.2: Results of computation of Cu film weight, film thickness for 365 days and plating time

Media	Film weight (mg) 365days	Required. thickness (μm) 365days	Required. plating time (min)
3.5MNaCl	2.15899	29.11	385.5
0.1MH_2SO_4	0.455	6.1	79
0.1MNaOH	0.83	11.2	148
Tap water	0.455	6.3	80.5
Rainwater	0.230	5.4	41
Well water	0.4	3.1	71.5

Table 4.2, Figures 4.21 and 4.22 show that for a given size of 40mm x15mm x 5.5mm steel specimens to be used for 365days in NaCl, H_2SO_4, NaOH, Tap water, Well water and Rainwater, a total of 29.11 μm, 6.1 μm, 11.2 μm, 6.3 μm, 5.4 μm, and 3.1 μm of Cu film thickness will be required and also; it will take about 385.5 mins, 79 mins, 148 mins, 80.5 mins, 41 mins and 71.5 mins to electroplate the samples to be used in each of the media respectively.

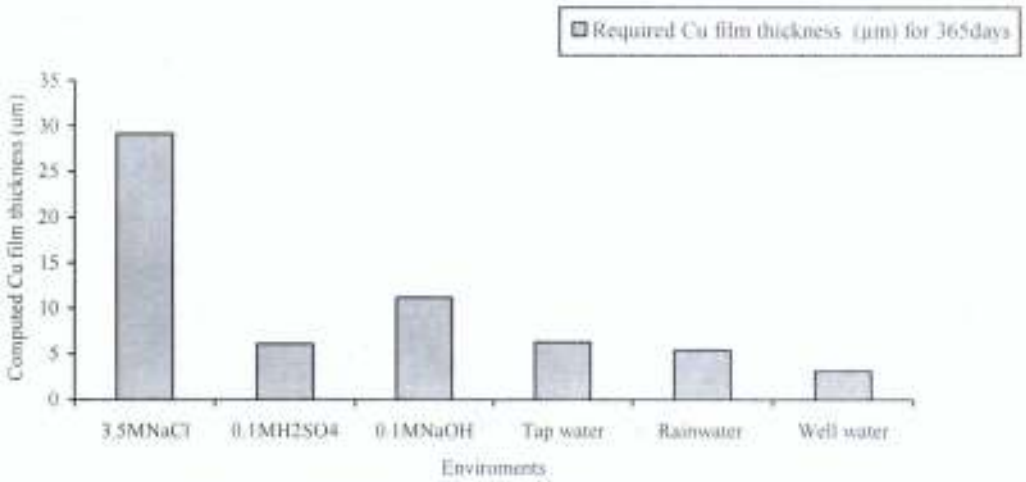

Figure 4.21: Computed Cu film thickness needed for 365 days.

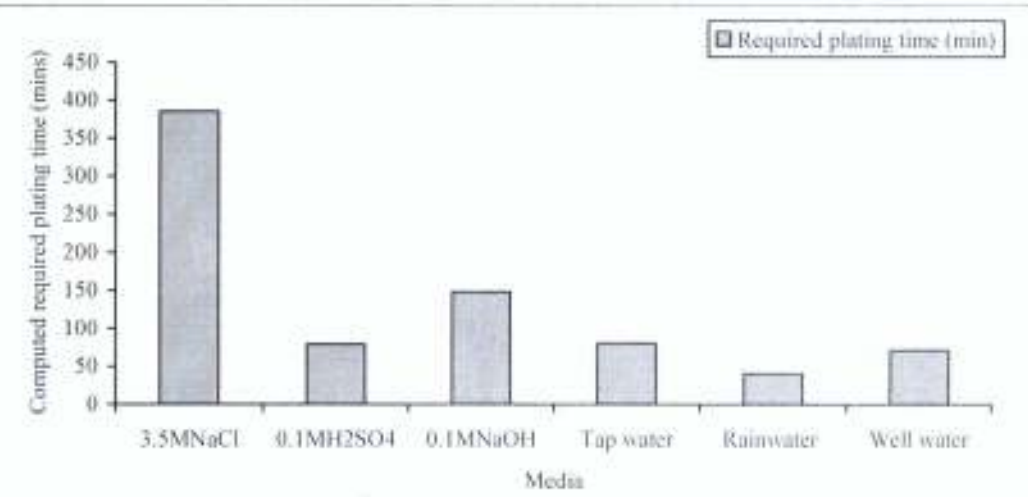

Figure 4.22: Computed required plating time of Cu film thickness needed for 365 days.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Based on the result of this experiment, the following conclusions could be drawn that:

1. Steels were coated using copper by electroplating process. The optimum plating parameters for copper plating on steel substrates were obtained at 2V applied voltage, 200g/l $CuSO_4$. H_2O electrolyte concentration, 120mm minimum electrodes separation, 600μm surface finishing grade and 0.5g/l saccharin concentration (used as organic brightening agent). The types of steel used do not show much pronounced effect on Cu-deposition but rather by the grade of smoothness of surface finishing of steel material. The use of 0.5g/l of other brightening agents such as dextrin, milk and lactic acid also will improve deposition characteristics of copper on steel surface.
2. The corrosion resistant characteristics of plated steels in active corrosive media were determined. Copper coated steels resisted corrosion more than un-coated samples in all media tested. The Cu-coated samples show very close similar trend of weight loss per exposure time in all media.
3. A computer program in V-Basic language was developed. The V-basic program codes were used to simulate the required copper film thickness to protect steel surface for 1year in the six environments. With the evolution of many small-scale foundry and machine shops, which make use of steels in the production of both domestic and machine parts such as electrical earthen rod, copper can be effectively used on steel surfaces.

5.2 RECOMMENDATIONS

The following recommendations are suggested:

1. A standard electroplating laboratory and workshop equipped with adequate facilities should be established in the department to enhance further researches on the application of computer programming on electroplating practices.
2. The use of COSEP is recommended for the local plating industries. It will in many ways save materials and production cost.

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APPENDIX A

A1. Determination of optimum plating parameters of copper on steel.

Table A1: Chemical composition (%) of as-received steel.

Elements	Fe	C	Si	Mn	P	S	Cu	V	Ni	N_2
NST50	98.3	0.24	0.18	0.40	0.40	0.04	-	-	-	0.01
NST60 Mn	97.7	0.35	0.3	0.9	0.04	0.25	-	-	0.10	-

Table A2: Chemical Analysis showing metal content in the milk.

Ca^{+}	**P**	**K**	**Cl^{-}**	**Na^{+}**	**Mg^{+}**	**Zn^{+}**
0.94	0.76g	1213mg	758 µg	344 µg	96 µg	310 µg
Selenium	**Cu^{++}**	**F^{-}**	**Cr**	**Mn**	**Fe^{++}**	**I**
10 mg	0.02 mg	0.02 mg	12 mg	0.02 mg	0.17 mg	25 mg

Table A3: Plot of voltage against copper film weight and film thickness

Applied voltage (V)	Film weight (g)	Film thickness (mm)	Appearance of plating
1	0.07	0.018	Pink colouration
2	0.09	0.023	Red and transparent
3	0.15	0.038	Red and smooth
4	0.41	0.104	Deep red colour and rough
5	0.75	0.190	Brownish red and powdery

Table A4: Plot of plating time against copper film weight and film thickness

Plating time (mins)	Film weight (g)	Film thickness (mm)	Appearance of plating
0	0.00	0.00	
5	0.24	0.061	Red and smooth
10	0.41	0.104	Red and smooth
15	0.45	0.114	Red and smooth
20	0.50	0.126	Red and smooth
25	0.53	0.134	Red and smooth

Table A5: Plot of electrolyte concentration against copper film weight and thickness

Concentration (g/l)	Film weight (g)	Film thickness (mm)	Appearance of plating
200	0.05	0.013	Red and smooth
210	0.12	0.030	Red and rough
220	0.21	0.053	Red and rough
230	0.25	0.063	Deep red colour and rough
240	0.31	0.077	Deep red colour and rough
250	0.35	0.089	Deep red colour, rough and porous

Table A6: Plot of electrode separation against copper film weight and film Thickness

Electrode separation mm	Film weight (g)	Film thickness (mm)	Appearance of plating
140	0.05	0.013	Red and smooth
120	0.08	0.020	Red and fairly smooth
100	0.12	0.030	Red and fairly smooth
80	0.17	0.043	Deep red colour and rough
60	0.18	0.046	Rough and powdery

Table A7: Plot of surface finishing grade against Cu film weight and film thickness (without additive)

Polishing grade (μm)	Film weight (g)	Film thickness (mm)	Appearance of plating
60	0.14	0.035	Deep red colour and rough
120	0.16	0.041	Deep red colour and rough
320	0.14	0.035	Deep red colour
400	0.10	0.025	Red colour
600	0.06	0.015	Bright red colouration

A2. Determination of effect of organic additives on copper plating characteristics

Table A8: Plot of surface finishing grade against Cu film weight (with saccharin additive)

Concentration (g/l)	Film weight (g) using				
	60μmSFG	120μmSFG	320μmSFG	400μmSFG	600μmSFG
0.0	0.14	0.16	0.14	0.10	0.06
0.1	0.21	0.22	0.36	0.38	0.13
0.2	0.14	0.16	0.16	0.16	0.02
0.3	0.15	0.11	0.14	0.13	0.02
0.4	0.11	0.07	0.07	0.09	0.03
0.5	0.09	0.04	0.03	0.03	0.02

Table A9: Plot of surface finishing grade against Cu film thickness (with saccharin additive)

Saccharin Concn (g/l)	Film thickness (mm) using				
	60μmSFG	120μmSFG	320μmSFG	400μmSFG	600μmSFG
0.0	0.036	0.041	0.036	0.025	0.015
0.1	0.053	0.056	0.091	0.096	0.033
0.2	0.036	0.041	0.033	0.041	0.005
0.3	0.038	0.028	0.036	0.033	0.005
0.4	0.028	0.018	0.018	0.023	0.008
0.5	0.023	0.041	0.008	0.008	0.005

Table A10: Plot of surface finishing grade against Cu film weight (using four additives)

0.5g/l Additives	Film weight (g) using				
	60μmSFG	120μmSFG	320μmSFG	400μmSFG	600μmSFG
Saccharin 550	0.09	0.04	0.03	0.03	0.02
Milk	0.07	0.08	0.02	0.03	0.04
Dextrin	0.11	0.08	0.05	0.07	0.04
Lactic acid	0.09	0.07	0.05	0.05	0.03

Table A11: Plot of surface finishing grade against Cu film thickness (using four additives)

0.5g/l Additives	Film thickness(mm) using				
	60μmSFG	120μmSFG	320μmSFG	400μmSFG	600μmSFG
Saccharin 550	0.023	0.010	0.008	0.008	0.005
Milk	0.018	0.020	0.005	0.008	0.010
Dextrin	0.028	0.020	0.013	0.018	0.010
Lactic acid	0.023	0.018	0.013	0.013	0.008

Table A12: Plot of surface finishing grade against Cu film weight on NST50-2 and NST60Mn steels

Steel type	Film weight (g) using					Appearance of plate
	60μm	120μm	320μm	400μm	600μm	
NST50-2	0.09	0.05	0.03	0.03	0.02	Good as from 120μm
NST60Mn	0.08	0.05	0.02	0.03	0.02	All good

Table A13: Plot of surface finishing grade against Cu film thickness on NST50-2 and NST60Mn steels

Steel type	Coat thickness (mm) using surface finish grades				
	60μm	120μm	320μm	400μm	600μm
NST50-2	0.018	0.013	0.008	0.008	0.005
NST60Mn	0.016	0.013	0.005	0.008	0.005

APPENDIX B

B1 Corrosion tests.

Table B1: Weight loss versus exposure time for uncoated and copper-coated steels in 3.5M NaCl solution

Exposure time (days)	Wt loss of as-received NST60Mn A (mg)	Wt loss of as-received NST50-2 B (mg)	Wt loss of Cu-coated NST50-2 C (mg)	Wt loss of Cu coated-NST60Mn D (mg)
2	22	25	20	16
4	20	27.2	24	23.2
6	24	29	29	28
8	32	31	36.2	31
10	46	35	44	40
12	64.7	69	57	64
14	120	83	66	79
16	114	95.6	79	68.7
18	146	120	94.4	82
20	192	156	136	96
22	226.1	170	128	103
24	272	200	148	121
26	324	240.1	169	140.3
28	380	244	145	140
30	392	256	166	152

Table B2: Weight loss versus exposure time for uncoated and copper-coated steels in $0.1MH_2SO_4$

Exposure time (days)	Wt loss of as-received NST60Mn A (mg)	Wt loss of as-received NST50-2 B (mg)	Wt loss of Cu-coated NST50-2 C (mg)	Wt loss of Cu coated-NST60Mn D (mg)
2	20	21	18	17
4	21	23	19	18
6	22.3	25	20	18.1
8	25	27	21	22
10	28	29	22	24
12	32	31.4	23	24.3
14	37	25	23.1	24
16	43.5	35	25	27.2
18	49	40.2	26	27.7
20	56	52	26	30
22	56	57	26.2	31
24	78	61.1	29	33
26	87	73	30	34
28	98	85.7	31	34
30	109	95	32	35

Table B3: Weight loss versus exposure time for uncoated and copper-coated steels in 0.1MNaOH

Exposure time (days)	Wt loss of as-received NST60Mn A (mg)	Wt loss of as-received NST50-2 B (mg)	Wt loss of Cu-coated NST50-2 C (mg)	Wt loss of Cu coated-NST60Mn D (mg)
2	21	20	17	16
4	23.2	21	18.2	17
6	25	22.1	21	18
8	27	25	23.7	20
10	29	28	27	20
12	31	32	31	19.6
14	25.3	37.2	36	21
16	35	43	23	24
18	37	49	57	36
20	56	56	35	38
22	57	56	41.8	42
24	64	73.4	50	48
26	63.1	82	57	54.7
28	75	93	60	58.8
30	85	104	65	61

Table B4: Weight loss versus exposure time for uncoated and copper-coated steels in tap water

Exposure time (days)	Wt loss of as-received NST60Mn A (mg)	Wt loss of as-received NST50-2 B (mg)	Wt loss of Cu-coated NST50-2 C (mg)	Wt loss of Cu coated-NST60Mn D (mg)
2	7.0	8.9	3.6	4.2
4	12.6	15.0	6.8	7.8
6	17.8	20.8	9.9	11.2
8	22.7	26.3	12.9	14
10	27	31	15.6	17
12	31	36	18.3	19.8
14	35.3	40.9	20.8	22.2
16	38.8	45	23.1	24.4
18	41.9	49	25.3	26.3
20	44.7	52.7	27.3	28
22	47.1	56	29	29
24	49.1	59	30	30.6
26	50.8	61.	32.5	31
28	52.2	64.	33.9	32.2
30	53.2	66.3	35.2	32.7

Table B5: Weight loss versus exposure time for uncoated and copper-coated steels in well water

Exposure time (days)	Wt loss of as-received NST60Mn A (mg)	Wt loss of as-received NST50-2 B (mg)	Wt loss of Cu-coated NST50-2 C (mg)	Wt loss of Cu coated-NST60Mn D (mg)
2	2.1	5.9	4.3	6.2
4	3.5	10	8.6	10.9
6	14.9	14	12.5	15.1
8	21.2	18.4	16	18
10	22.4	22.0	19.1	22.0
12	33.5	25.3	21.9	24.8
14	34.5	30.3	24.3	27.1
16	35.5	34.0	26.4	29.0
18	41.3	39.5	28.1	30.4
20	42	39.6	29.4	31
22	47	47.5	30	31
24	48	49.1	30	31
26	48	50.4	31	31.3
28	54.3	51.4	31	30.4
30	54.6	52.1	30	29.0

Table B6: Weight loss versus exposure time for uncoated and copper-coated steels in Rainwater

Exposure time (days)	Wt loss of as-received NST60Mn A (mg)	Wt loss of as-received NST50-2 B (mg)	Wt loss of Cu-coated NST50-2 C (mg)	Wt loss of Cu coated-NST60Mn D (mg)
2	9.5	12	2.9	3.0
4	17	21.3	5.6	5.9
6	24	30.0	8.1	8.4
8	30	38.0	10.3	10.7
10	37.1	45.3	12.2	12.8
12	43	52.0	13.9	14.5
14	48.5	58.0	15.4	15.9
16	53	63.4	16.6	17.0
18	58.5	68.1	17.5	17
20	62.9	72.2	18	18.4
22	66.9	75.6	18	18.7
24	70	78.3	18.8	18.7
26	73.8	80.4	18.7	18.3
28	76.7	81.9	18.4	17.7
30	79.2	82.7	17.8	16.8

APPENDIX C

C.1 VBASIC forms designs

The program user's interfaces are presented in Figures 4.21 through 4.32.

Figure C1: COSEP welcome screen

Figure C2: COSEP Materials and Bath composition

Figure C3: COSEP Optimum plating parameters

Figure C4: COSEP laboratory corrosion experiment table and analyses

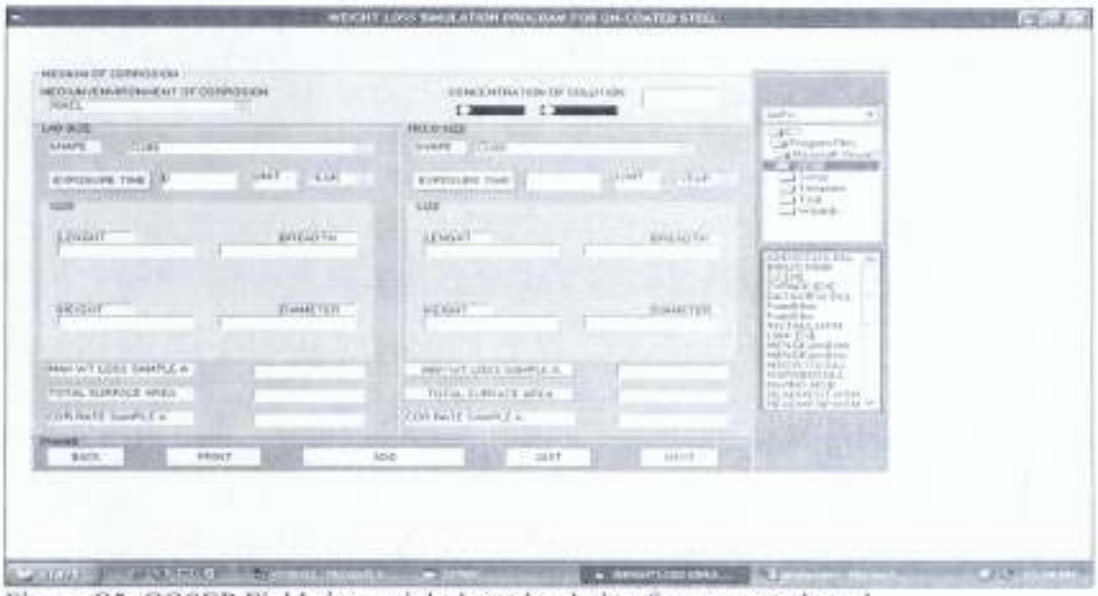

Figure C5: COSEP Field size weight loss simulation for un-coated steel.

Figure C6: Field size weight loss simulation for copper-coated steel.

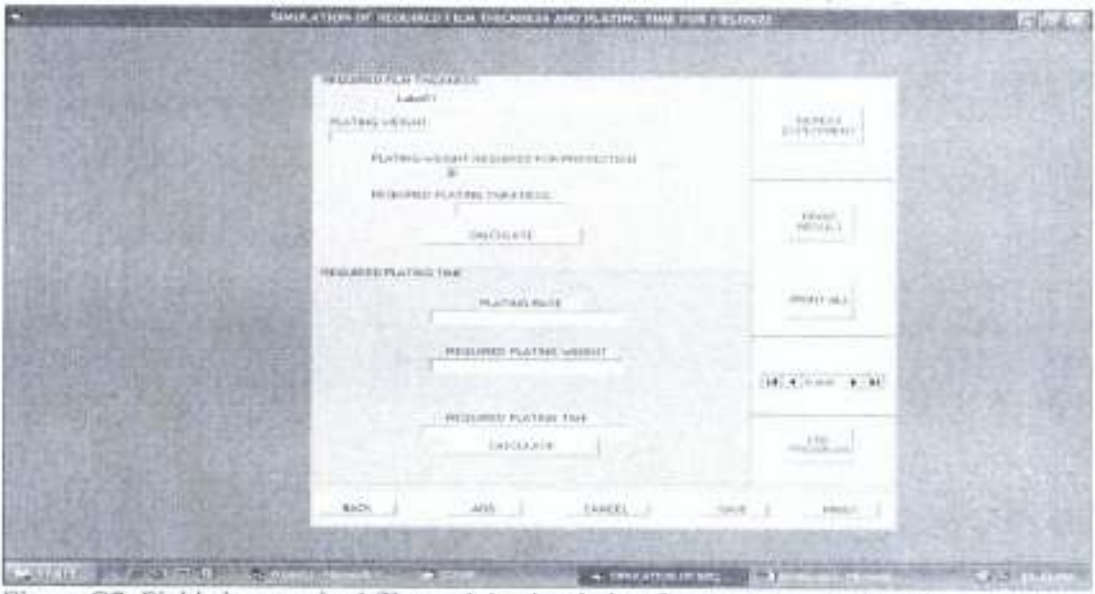

Figure C7: Field size required film weight simulation for copper-coated steel.

C.2 VBASIC program codes

```
Private Sub CONTINUE_Click()
 MDIForm1.Show
 End Sub
Private Sub Command4_Click()
   Dim CD, CE, W, CUDENS As String
      THICKNSS = Val(Text17.Text)
      CD = Val(Text8.Text), CE = Val(Text9.Text),      CUDENS = Val(Text10.Text)
      W = Val(Text12.Text)
      Text17.Text = (CD * CE * W / 235 * CUDENS)
End Sub
Private Sub Command5_Click()
 'To calculate the plating rate with the given values
   Dim WeigthGain, SurfaceArea, PLATTIM As String
   WeigthGain = Val(Text12.Text)
   SurfaceArea = Val(Text19.Text)
   PLATINGTIME = Val(Text11.Text),    LENGHT = Val(Text13.Text)
      BREADTH = Val(Text14.Text),      Height = Val(Text11.Text)
      DIAMETER = Val(Text13.Text),      BREADTH = Val(Text14.Text)
      Height = Val(Text11.Text)
   'Accepting the condition in the laboratory tests before proceeding
      If Text1.Text > 0 And Text1.Text <= 2 Then
     Text18.Text = WeigthGain / (SurfaceArea * PLATTIM)
   Else
     MsgBox "Enter the right Values for Voltage"
           End If
     If Text2.Text = 200 Then
     Text18.Text = WeigthGain / (SurfaceArea * PLATTIM)
   Else
     MsgBox "Enter the right Values for CuSO4 concentration"
```

```
    End If
    If Text3.Text > 0 Then
  Else
    MsgBox "Enter the right Values for current"
      End If
    If Text4.Text >= 400 And Text4.Text <= 600 Then
      Else
    MsgBox "Enter the right Values for Surface finishing grade"
      End If
  'Electrode separation
  If Text5.Text >= 100 And Text5.Text <= 140 Then
    Text18.Text = WeigthGain / (SurfaceArea * PLATTIM)
  Else
    MsgBox "Enter the right Values for Electrode separation"
    End If
  If List1 = "saccharin" Or "dextrin " Or "lactic acid" Or "milk" Then
      Text18.Text = WeigthGain / (SurfaceArea * PLATTIM)
  Else
    MsgBox "Enter the right CHOISE of ADDITIVE"
      End If
  If Text7.Text >= 0.5 Then
    Text18.Text = WeigthGain / (SurfaceArea * PLATTIM)
  Else
    MsgBox "Enter the right Values for Surface finishing grade"
      End If
    If Text8.Text >= 0 And Text8.Text <= 20 Then
    Text18.Text = WeigthGain / (SurfaceArea * PLATTIM)
  Else
    MsgBox "Enter the right Values for Current Density"
      End If
  If Text9.Text >= 95 And Text8.Text <= 97 Then
    Text18.Text = WeigthGain / (SurfaceArea * PLATTIM)
  Else
    MsgBox "Enter the right Values for Current Density"
  If Text22.Text = 1 Then
  Dim STEEL As String
 If Text24.Text = STEEL Then
    Text18.Text = WeigthGain / (SurfaceArea * PLATTIM)
  Else
    MsgBox "Enter STEEL"
      End If
End Sub
Private Sub Command6_Click()
Dim L, B, H, D, TOTAREA As String
L = Val(Text13.Text), B = Val(Text14.Text), H = Val(Text15.Text),
D = Val(Text16.Text)
TOTAREA = Val(Text19.Text)
Text19.Text = 2 * ((L * B) + (L * H) + (B * H))
End Sub
Private Sub Form_Load()
```

```
For i = 1 To 30
    Next i
Private Sub Text11_Change()
Dim PLATINGTIME As String
PLATINGTIME = Val(Text11.Text)
End Sub
Dim temp As Single
Private Sub Command1_Click()
   temp = CSng(Text2(0).Text)
   For i = 1 To 30
    If (CSng(Text2(i).Text) > CSng(Text2(j).Text)) Then temp = CSng(Text2(i).Text)
    Next i
   Text4.Text = CStr(temp)
  End Sub
Private Sub Command10_Click()
  'To calculate the TOTAL SURFCAE AREA of UNCOATED sample A
   Dim CUBE, CUBOID, ROUNDBAR, L, B, H As String
L = Val(Text17.Text), B = Val(Text16.Text), H = Val(Text15.Text)
D = Val(Text14.Text)
constpie = 3.142
      Text26.Text = 2 * ((L * B) + (L * H) + (B * H))
 End Sub
Private Sub Command11_Click()
   'To calculate the TOTAL SURFCAE AREA of CU-COATED sample B
   L = Val(Text18.Text), B = Val(Text19.Text), H = Val(Text20.Text)
D = Val(Text21.Text)
Private Sub Command13_Click()
Text10.Text = Text4.Text / (Text26.Text * Text1(30).Text)
End Sub
Private Sub Command2_Click()
temp = CSng(Text3(0).Text)
   For i = 1 To 30
      If (CSng(Text3(i).Text) > CSng(Text3(i - 1).Text)) Then temp =
CSng(Text3(i).Text)
   Next i
   Text5.Text = CStr(temp)
End Sub
Private Sub Command3_Click()
 Text6.Text = (1 / Text26.Text) * (CStr(CSng(Text4.Text) / CSng(Text1(30).Text)))
  Text7.Text = (1 / Text27.Text) * (CStr(CSng(Text5.Text) / CSng(Text1(30).Text)))
End Sub
Private Sub Command8_Click()
'If A > B Then
   If Text6.Text > Text7.Text Then
   Text8.Text = "you can apply copper for plating in the choised environment"
Else
   Text8.Text = "you cannot apply copper for plating in the choised environment"
   mgsbox = "to go back to laboratory again, click quit"
   End If
End Sub
```

```
Private Sub Form_Load()
   For i = 0 To 30
      Text1(i).Text = 0
      Text2(i).Text = 0
      Text3(i).Text = 0
 Next i
   End Sub
Private Sub Command1_Click()
        Dim MXWTLOSS, CORRATE, EXTIME, TAREA As String
        CORRATE Val(Text19.Text),        EXTIME = Val(Text20.Text)
        TAREA = Val(Text9.Text),         MXWTLOSS = Text8.Text
End Sub
        List4.AddItem "DAY"
Private Sub Text21_Change()
Text21.Text = CorrosionRate * (TotalSurfaceArea * EXPOSURETIME)
End Sub
Private Sub Text30_Change()
Dim TOTAREA, L, B, H As String
TOTAREA = Val(Text30.Text)
L = Val(Text25.Text), B = Val(Text26.Text), H = Val(Text27.Text)
D = Val(Text28.Text)
Text30.Text = 2 * ((L * B) + (L * H) + (B * H))
End Sub
Private Sub Text32_Change()
Dim EXPOSURETIME As String
EXPOSURETIME = Val(Text32.Text)
End Sub
Private Sub Command1_Click()
Dim RQPLTWT, MXWTLOSS, CD, CE, CUDENSE, RQPLTHICK, PLTRATE As
String
CD = Val(Form4.Text8.Text),        CE = Val(Form4.Text9.Text)
CUDENSE = Val(Form4.Text20.Text)
RQPLTWT = Val(Text1.Text)
Text1.Text = MXWTLOSS + (0.05 * MXWTLOSS)
RQPLTHICK = Val(Text11.Text)
Text11.Text = (CD) * (CE) * RQPLTWT / (235 * CUDENSE)
End Sub
Private Sub Form_Load()
Dim RQPLTWT, MXWTLOSS, CD, CE, CUDENSE, RQPLTHICK, PLTRATE As
String
CD = Form4.Text8.Text
CE = Form4.Text9.Text
CUDENSE = Form4.Text20.Text
RQPLTWT = Text1.Text
Text1.Text = MXWTLOSS + (0.05 * MXWTLOSS)
RQPLTHICK = Text11.Text
End Sub
END
```

```
For i = 1 To 30
    Next i
Private Sub Text11_Change()
Dim PLATINGTIME As String
PLATINGTIME = Val(Text11.Text)
End Sub
Dim temp As Single
Private Sub Command1_Click()
   temp = CSng(Text2(0).Text)
   For i = 1 To 30
    If (CSng(Text2(i).Text) > CSng(Text2(j).Text)) Then temp = CSng(Text2(i).Text)
    Next i
   Text4.Text = CStr(temp)
  End Sub
Private Sub Command10_Click()
  'To calculate the TOTAL SURFCAE AREA of UNCOATED sample A
   Dim CUBE, CUBOID, ROUNDBAR, L, B, H As String
L = Val(Text17.Text), B = Val(Text16.Text), H = Val(Text15.Text)
D = Val(Text14.Text)
constpie = 3.142
      Text26.Text = 2 * ((L * B) + (L * H) + (B * H))
 End Sub
Private Sub Command11_Click()
   'To calculate the TOTAL SURFCAE AREA of CU-COATED sample B
   L = Val(Text18.Text), B = Val(Text19.Text), H = Val(Text20.Text)
D = Val(Text21.Text)
Private Sub Command13_Click()
Text10.Text = Text4.Text / (Text26.Text * Text1(30).Text)
End Sub
Private Sub Command2_Click()
temp = CSng(Text3(0).Text)
   For i = 1 To 30
      If (CSng(Text3(i).Text) > CSng(Text3(i - 1).Text)) Then temp =
CSng(Text3(i).Text)
   Next i
   Text5.Text = CStr(temp)
End Sub
Private Sub Command3_Click()
 Text6.Text = (1 / Text26.Text) * (CStr(CSng(Text4.Text) / CSng(Text1(30).Text)))
  Text7.Text = (1 / Text27.Text) * (CStr(CSng(Text5.Text) / CSng(Text1(30).Text)))
End Sub
Private Sub Command8_Click()
'If A > B Then
   If Text6.Text > Text7.Text Then
   Text8.Text = "you can apply copper for plating in the choised environment"
Else
   Text8.Text = "you cannot apply copper for plating in the choised environment"
   mgsbox = "to go back to laboratory again, click quit"
   End If
End Sub
```

```
Private Sub Form_Load()
   For i = 0 To 30
      Text1(i).Text = 0
      Text2(i).Text = 0
      Text3(i).Text = 0
 Next i
   End Sub
Private Sub Command1_Click()
        Dim MXWTLOSS, CORRATE, EXTIME, TAREA As String
        CORRATE Val(Text19.Text),        EXTIME = Val(Text20.Text)
        TAREA = Val(Text9.Text),         MXWTLOSS = Text8.Text
End Sub
        List4.AddItem "DAY"
Private Sub Text21_Change()
Text21.Text = CorrosionRate * (TotalSurfaceArea * EXPOSURETIME)
End Sub
Private Sub Text30_Change()
Dim TOTAREA, L, B, H As String
TOTAREA = Val(Text30.Text)
L = Val(Text25.Text), B = Val(Text26.Text), H = Val(Text27.Text)
D = Val(Text28.Text)
Text30.Text = 2 * ((L * B) + (L * H) + (B * H))
End Sub
Private Sub Text32_Change()
Dim EXPOSURETIME As String
EXPOSURETIME = Val(Text32.Text)
End Sub
Private Sub Command1_Click()
Dim RQPLTWT, MXWTLOSS, CD, CE, CUDENSE, RQPLTHICK, PLTRATE As
String
CD = Val(Form4.Text8.Text),        CE = Val(Form4.Text9.Text)
CUDENSE = Val(Form4.Text20.Text)
RQPLTWT = Val(Text1.Text)
Text1.Text = MXWTLOSS + (0.05 * MXWTLOSS)
RQPLTHICK = Val(Text11.Text)
Text11.Text = (CD) * (CE) * RQPLTWT / (235 * CUDENSE)
End Sub
Private Sub Form_Load()
Dim RQPLTWT, MXWTLOSS, CD, CE, CUDENSE, RQPLTHICK, PLTRATE As
String
CD = Form4.Text8.Text
CE = Form4.Text9.Text
CUDENSE = Form4.Text20.Text
RQPLTWT = Text1.Text
Text1.Text = MXWTLOSS + (0.05 * MXWTLOSS)
RQPLTHICK = Text11.Text
End Sub
END
```

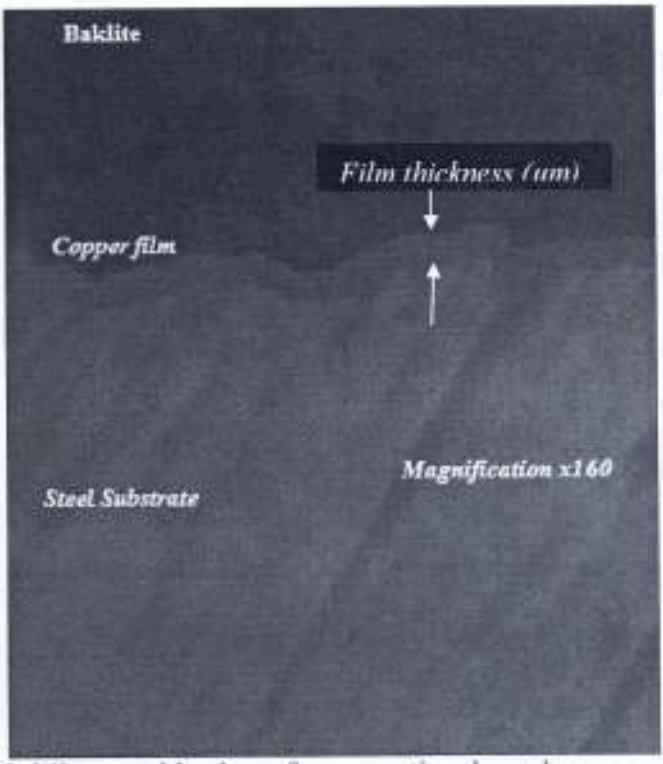

Figure C8: Micrographic view of cross section through copper-steel plating (magnification x160)

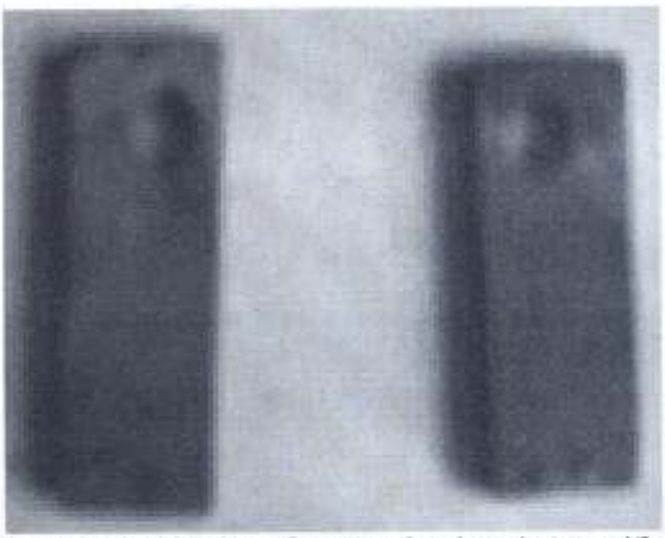

Figure C9: Photographic view of copper plated steels (magnification x2)

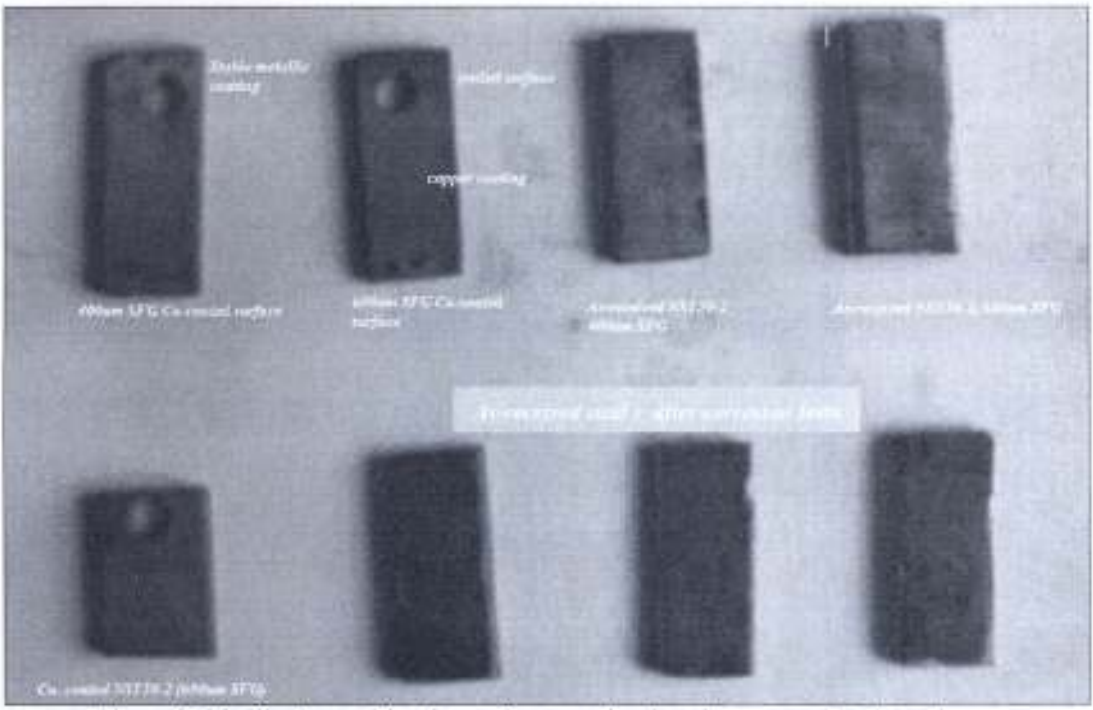

Figure C10: Photographic view of as-received and copper plated steels

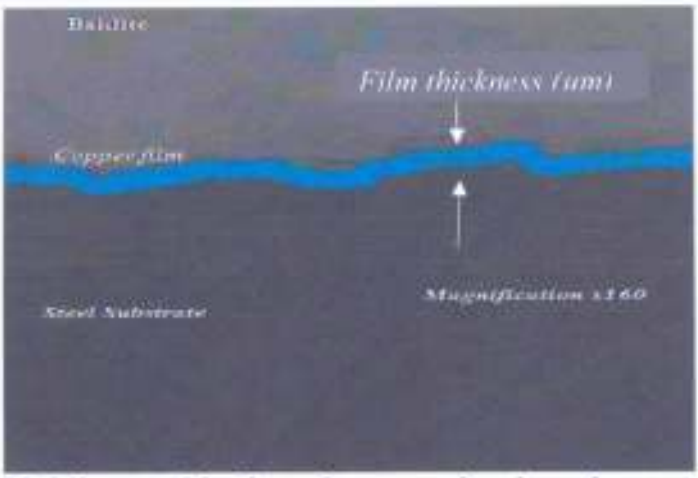

Figure C8: Micrographic view of cross section through copper-steel plating (magnification x160)

Figure C9: Photographic view of copper plated steels (magnification x2)

Figure C10: Photographic view of as-received and copper plated steels