STUDIES ON THE PARAMETERS THAT
AFFECT THE PROPERTIES OF
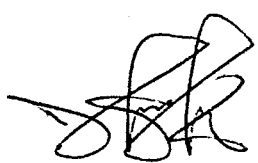## TRIPLE NICKEL ELECTROPLATING

by

OOI CHEE HENG

Thesis submitted in fulfillment of the
requirements for the degree
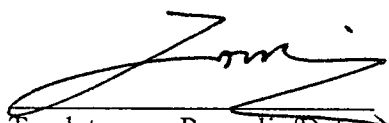of Master of Science

June 2003

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I declare that the content which is presented in this thesis is my own work which was done at Universiti Sains Malaysia unless informed otherwise. The thesis has not been previously submitted for any other degree.

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DEDICATION

This work is dedicated to my wife – Fong Won Ho for her full support and understanding of the importance of my studies i.e. to acquire additional knowledge in the field of electroplating and a springboard for my future career development.

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ABSTRACT

The triple nickel electroplating consists of three layers of nickel deposits with different sulphur content, i.e. the first layer plated on the substrate is semi-bright, followed by high sulphur and bright nickel. This research is aimed at studying the parameters that affect the various properties of triple nickel deposits such as cathode current efficiency, thickness distribution, brightness and leveling, co-deposited sulphur content, electrode potential differences and the corrosion resistance performance. The parameters being studied are the distance between cathode and anode, current density, plating time and the combination of different layers of nickel deposits.

All the test panels plated with bright nickel at the outer layer exhibited good brightness and leveling, and these effects are dependent on the plating time and current density. In addition, brighter appearance has shown finer gain structure. The cathode current efficiency is dependent on the cathode and anode distances, i.e. tends to be higher at shorter distances (7cm > 10cm > 14cm), but is not influenced much by the current density. The thickness values tend to be higher at shorter distances, and when the current density is increasing (4 A/dm^2 > 3 A/dm^2 > 2 A/dm^2). The thickness distribution has shown a consistent pattern, i.e. always thicker at the edges (high current areas) as compared to the areas in the middle of the panel (low current areas).

The electrode potential differences measurement between triple nickel layers have shown that the electrode potential for all the different nickel layers is not similar, i.e. the semi-bright is always more positive (noble) than high sulphur and bright nickel

layers, and high sulphur is more negative (active) as compared to bright nickel layer. Although sulphur was not detected in all the different nickel deposits, however, the differences in the electrode potential results have indicated on the possibility of sulphur co-deposition in different percentage onto each layer of triple nickel deposits.

The CASS test results have shown that triple nickel deposits have better corrosion resistance performance as compared to duplex and single nickel deposits with similar total plating time (or thickness). In addition, both duplex and triple nickel deposits with thicker semi-bright layer out-performed those with thicker bright nickel layer.

By optimizing the plating parameters such as cathode and anode distance, current density, plating time and the combination of different layers of nickel deposits, we are able to produce plated components that can be accepted by commercial application in terms of cost, appearance and corrosion resistance performance.

PENYELIDIKAN TERHADAP PARAMETER-PARAMETER YANG MEMPENGARUHI SIFAT-SIFAT SADURAN TRIPLE NIKEL

ABSTRAK

Proses pengelektrosaduran triple nikel melibatkan tiga lapisan nikel dengan kandungan sulfur yang berbeza, iaitu lapisan pertama disadurkan dengan nikel separa cerah, kemudian dengan nikel sulfur tinggi dan seterusnya dengan lapisan nikel cerah. Penyelidikan ini bertujuan untuk mengkaji parameter-parameter yang mempengaruhi pelbagai sifat saduran triple nikel seperti kecekapan arus pada katod, pengagihan ketebalan, kesan kecerahan dan kerataan, kandungan sulfur, perbezaan potensi elektrod dan prestasi ketahanan terhadap kakisannya. Parameter-parameter pengelektrosaduran yang diselidik ialah jarak di antara katod dan anod, ketumpatan arus, masa saduran dan dengan kombinasi pelbagai gabungan lapisan nikel yang berbeza.

Kesemua plat-plat kajian yang disadurkan dengan nickel cerah sebagai lapisan luar mempamerkan kesan kecerahan dan kerataan yang bagus, dan kesan-kesan ini adalah bergantung kepada masa dan ketumpatan arus saduran. Tambahan pula, saduran yang cerah akan memberikan struktur yang lebih halus. Keputusan-keputusan ujikaji telah menunjukkan bahawa kecekapan arus pada katod adalah bergantung kepada jarak di antara katod dan anod, iaitu lebih tinggi pada jarak yang lebih dekat (7cm > 10cm > 14cm), tetapi tidak banyak dipengaruhi oleh ketumpatan arus. Nilai-nilai ketebalan akan bertambah apabila jaraknya semakin dekat, dan apabila ketumpatan arus meningkat ($4 A/dm^2 > 3 A/dm^2 > 2 A/dm^2$). Pangagihan ketebalan telah menunjukkan sesuatu paten yang tertentu, iaitu sentiasa lebih tinggi pada sekitar penjuru plat

(kawasan berarus tinggi) jika dibandingkan dengan di tengah plat (kawasan berarus rendah).

Pengukuran potensi elektrod telah menunjukkan nilai-nilai potensi yang berbeza di antara ketiga-tiga lapisan nikel, iaitu nikel separa cerah adalah lebih positif (lengai) berbanding dengan nikel sulfur tinggi dan nikel cerah, dan nikel sulfur tinggi adalah lebih negatif (aktif) berbanding dengan nikel cerah. Walaupun kandingan sulfur tidak dapat dikesan dalam ketiga-tiga lapisan nikel, akan tetapi, pemerhatian dari perbezaan potensi elektrod telah menunjukkan kemungkinan kehadiran sulfur yang tersadur bersamaan dengan ketiga-tiga lapisan nikel dalam peratusan yang berbeza.

Kesan ketahanan terhadap kakisan telah menunjukkan bahawa saduran triple nikel mempunyai prestasi ketahanan yang lebih baik jika dibandingkan dengan duplex nikel dan lapisan tunggal nikel cerah dengan masa saduran (atau ketebalan) yang sama. Tambahan pula, duplex nikel dan triple nikel yang mengandungi lapisan nikel separa cerah yang lebih tebal akan menunjukkan tahap ketahanan yang lebih baik berbanding dengan yang mengandungi lapisan nikel cerah yang lebih tebal.

Dengan mengoptimakan parameter-parameter seperti diatas, kita boleh menghasilkan komponen-komponen tersadur yang dapat diterima oleh pihak komersial dari segi kos, rupabentuk dan pretasi ketahanan terhadap kakisan yang amat baik.

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Principles of Electrolysis

Michael Faraday (1791 - 1867) [1], is the first scientist who studied electrolysis quantitatively. From his work on electrolysis (1832 - 33), he believed that the electrolysis process is based on charged carriers called as ions. (Ion is atom or collection of atoms and has a charge). Those carrying positive charges (metal atoms) being cations and traveling towards the cathode, and those carrying negative charges (non metallic atoms) being anions and traveling towards the anode [2].

The main results of his work on electrolysis are summed up in the following two important Laws :

(I)   The amount (or weight, W) of metal deposited by a current is proportional to the quantity of electricity (Q) passed, i.e.

$$W \propto Q$$

$$W \propto It \; [Q = Current \; (I) \times Time \; (t) \;] \; \text{----------} \; ①$$

(II)   The masses of different metals deposited or dissolved by the same quantity of electricity are proportional to its chemical equivalent weights (A/Z) at 100% current efficiency, i.e.

$$W \propto \frac{A}{Z} \qquad (A = \text{Atomic weight}, \qquad \text{---------- } ② $$
$$Z = \text{Valency no})$$

From the combination of (1) and (2) as above,

$$W \propto \frac{It A}{Z}$$

$$W = \frac{ItA}{ZF} \qquad \text{--------- } ③$$

Where F   =   Faraday constant (Quantity of Electricity)

     =   96490 coulombs (Ampere - seconds)

In accordance with Faraday's Laws, the same quantity of electricity will liberate 58.7/2 g of Nickel (from a Nickel salt solution), or 63.5/2 g of Copper (from a Copper salt solution) at the cathode.

The principles that govern the electrolysis process will firstly be initiated by conduction of electricity through a solution and, secondly, the discharge of an ion at an electrode.

1.2   Principles of Nickel Electroplating

Electroplating is a process of depositing a coating having a desirable form by means of electrolysis. Its purpose is generally to alter the characteristics of a surface so as to provide improved appearance, ability to withstand corrosive agents, resistance to abrasion, or other desired properties or a combination of them. It is carried out in a

solution of various kinds and in commercial practice it is almost invariably a water solution [3, 4].

Nickel plating is the electrolytic deposition of a layer of nickel on a substance. The process involves the dissolution of one electrode (the anode) and the deposition of metallic nickel on the other electrode (the cathode). Direct current is applied between the anode (positive) and the cathode (negative). Conductivity between the electrodes is provided by an aqueous solution of nickel salts. When nickel salts are dissolved in water, the nickel is present in solution as divalent, positively charged ions (Ni^{2+}). When current flows, divalent nickel ions react with two electrons and are converted to metallic nickel (Ni^0) at the cathode. The reverse occurs at the anode where metallic nickel dissolves to form divalent ions [5].

The electrochemical reaction in its simplest form is :

$$Ni^{2+} + 2e^- = Ni^0$$
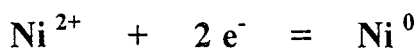
Because the nickel ions discharged at the cathode are replenished by the nickel ions formed at the anode, the nickel plating process can be operated for long periods of time without interruption.

1.3   The Nature of Nickel

Nickel is a white lustrous metal. The atomic weight is 58.71, the melting point is 1455^0C and the density at 20°C is 8.908 g/cm^3. Nickel is present in solution as

divalent, positively charged ions. The standard electrode potential, E^0 (Ni^{2+} / Ni) = -0.25 V [6, 7]. It has high mechanical strength, is fairly hard and at ordinary temperatures is ferro-magnetic. It oxidizes only with difficulty even when heated in air. A polished surface will, however, gradually corrode on atmospheric exposure. Nickel is slowly soluble in hydrochloric and also in dilute sulphuric acid. Dilute nitric acid rapidly attacks nickel, but immersion in concentrated sulphuric acid renders the surface of nickel 'passive', in which state it is not readily attacked [8].

Nickel may be deposited as a bright, semi-bright or dull coating. Although nickel is a ductile metal, the ductility of nickel coatings is very dependent upon their method of production and their purity. Many electrodeposited nickel coatings (particularly the organic bright nickels) may be brittle and have a high degree of internal stress. Similarly, chemically deposited nickel coatings have greater hardness, brittleness and different corrosion characteristics because of the incorporation of phosphorus or boron in the deposits - inherent in the method of deposition from complex solutions.

1.4   The Development of Nickel Plating

The electrodeposition of nickel was first described in 1837 by G. Bird for deposited nickel on a platinum electrode from a solution of nickel chloride or sulphate. In 1840, the first patent for commercial nickel plating was granted to J. Shore of England who specified a solution of nickel nitrate [9].

The development of the electrodeposition of nickel began in 1843 when R. Bottger described the first apparently sound nickel plate, which he obtained from a bath

containing nickel and ammonium sulphates. The solution developed by Bottger remained in commercial use for seventy years, and he is acknowledged to be the originator of nickel plating [10].

Following the lead of Roseleur in 1849, Adams in 1869 was probably the first to do nickel plating on a truly commercial basis by using both sulphate and chloride salts and was probably the first to recognize the importance of impurities in the plating bath. Dr. Isaac Adam Jr., a medical doctor was one of the first to commercialize nickel plating in the United States, and his patented process gave his company a virtual monopoly in commercial nickel plating from 1869 to 1886. His patent covered the use of pure nickel ammonium sulphate [11].

Remington was the next to commercialize nickel plating. Up to 1913 many bath compositions were proposed like Weston's introduction of boric acid into the bath, the use of chlorides by Bancroft to promote anode corrosion and the discovery that cadmium salts act as brightener about 1912 in the Elkington plant of Brimingham, England.

Since 1915, the rate of development has been quite rapid, beginning with Watts with his famous "Watts bath"; the control of quality of deposits, first emphasized by Watts and Deverton and finally maturing into ASTM - American Electroplaters' Society Specification in 1935; accurate pH control, introduced by Thomson; low - pH baths, suggested by Philips; commercial introduction of modern bright nickel plating by Schlotter and the many major improvements of it, for example, the design of automatic plating equipment for high production rates; development of bath for the ductile, low-stress, high leveling semi-bright and bright nickel coatings; the use of combination

plates of sulfur-free semi-bright nickel followed by sulfur-containing bright nickel to greatly improved outdoor corrosion protection; the use of high sulphur nickel and micro-porous nickel in combination of semi-bright and bright nickel layers to give outstanding outdoor corrosion protection with minimum thickness of total nickel deposits.

Today, nickel is one of the most important metals applied by electrodeposition which covered a broad spectrum of end uses that include decorative, engineering and electroforming applications.

Nickel plating is used principally as a bright coating underneath a chromium electroplate to provide a highly lustrous and corrosion protective finish for articles of steel, brass, zinc die castings, plastic, aluminium and magnesium alloys. In addition, thin gold or brass electroplate with a clear lacquer finish is used as a decorative coating on bright nickel deposits. Due to its mechanical properties, nickel is widely used for electroforming of moulds, dies, record stampers, seamless belts and textile printing screen.

1.5 Common Process Steps in Triple Nickel Plating

Electroplating has three major steps in sequence, which is pre-treatment, plating and post-treatment. Pre-treatment is carried out before electroplating due to the importance of perfect cleaning. After pre-treatment, it goes through plating process where the base material is deposited with the metallic coatings by electrolysis. Finally, the finished products are treated for protection purpose and drying.

The common base materials or substrates are steel, brass, copper alloy, copper, pewter, aluminium, stainless steel, zinc die-cast and plastics. No matter what materials or substrates need to be plated, they have to go through three major steps in electroplating process as outlined above.

1.5.1 Pretreatment

In general, pretreatment steps involve cleaning, descaling, degreasing, activation and other processes which prepare the basis material for plating. The purpose of the pretreatment is to produce clean, oil-free, rust-free, scale-free and active surface for subsequent plating processes [12].

The condition of substrates has a direct bearing on the properties and the performance of the deposits. Consequently, basis metals are generally prepared for plating by mechanical, chemical or electrochemical finishing. In the mechanical finishing processes of polishing, buffing [6, 13] and grinding, the surface of the work is cut or worked by abrasive which are moved over the surface of the work by rotating wheels or moving belts. Metal imperfections, scales, oils and grease must be removed from the surface if the plating process is to be successful.

Removal of scale is through mechanical means of tumbling, dry rolling, buffing, deburring, polishing, desmutting and blasting. Such mechanical treatment eliminates or minimizes the subsequent pickling applications.

The water-break test is widely used for measuring the cleanliness of metal surfaces after pretreatments. Other methods such as visual (optical, microscopical) and fluorescence contact angle are used in some cases for cleanliness measurement [14, 15].

1.5.1.1 Soak Cleaning

Soak cleaning involves the removal of oil, grease, dirt and soil from the surface of the substrate. This can be accomplished by solvent degreasing or alkaline cleaning depending on the degree of cleanliness required. The detergent nature of the cleaning solution provides the primary cleaning action [16, 17]. In general, for very heavy oil, grease, dirt and soil, pre-cleaning by means of solvent cleaner or alkaline pre-cleaner are recommended (Figure 1.1).

The alkaline cleaning normally will contain either emulsifiers or surfactants or both. The function of emulsifiers is to dissolve oil and grease through emulsifying action (Figure 1.2). The surfactants will remove oil and grease by displacement action (Figure 1.3). The dirt and soil will be removed together as well.

Incorporation of ultrasonic, spray mechanical agitation and elevated temperature will help to create mechanical and impact force by loosening the oil, grease, dirt and soil in order to further enhance the cleaning efficiency [18, 19].
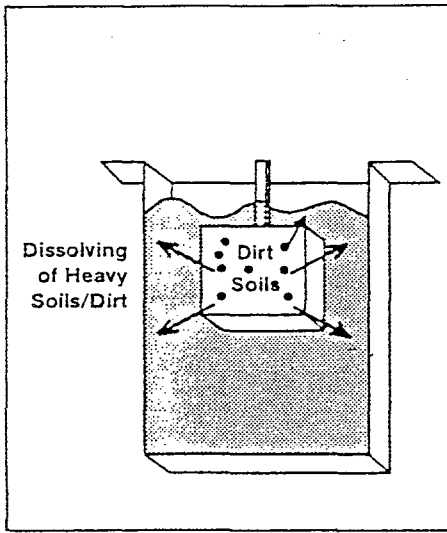
Figure 1.2 : Soak cleaning (Emulsion cleaning)
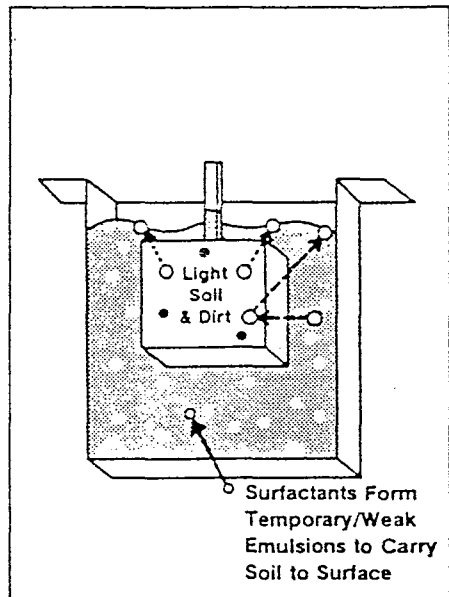
Figure 1.1 : Pre-cleaning

Figure 1.3 : Soak cleaning (Displacement Cleaning)

(Courtesy of Enthone-OMI)

1.5.1.2   Electrolytic Cleaning

Electrolytic cleaning is commonly used after alkaline cleaning. Electrolytic cleaning will remove buffing compound and some remaining oil, grease, dirt, soil and certain metal oxide from the surface of the substrate. Moreover, certain dirt particles which become electrically charged are repelled from the substrate surface.

Electrolytic cleaners are classified into 3 types, i.e. anodic, cathodic and periodic reverse [20].

(I)   Anodic cleaning involves the substrate function as anode. Oxygen gas is generated at the substrate surface. Like Hydrogen gas generated in cathodic cleaner it would provide the scrubbing action that helps to remove the soil, rust, scale and foreign inclusions (Figure 1.4).

Since the substrate will dissolved during the anodic application, there is a need to ensure that the cleaning time is not too long and the current is not too high.

(II)   Cathodic cleaning involves the substrate function as cathode during application of current. Hydrogen gas will be generated at the substrate surface and is effective in solubilizing certain metal oxides (Figure 1.5).

However, this benefit is countered by the increased potential for hydrogen embrittlement [21] of the substrate and substrate contamination by foreign inclusion which may be deposited during cathodic application. Thus, an anodic cleaner is needed after this precess.
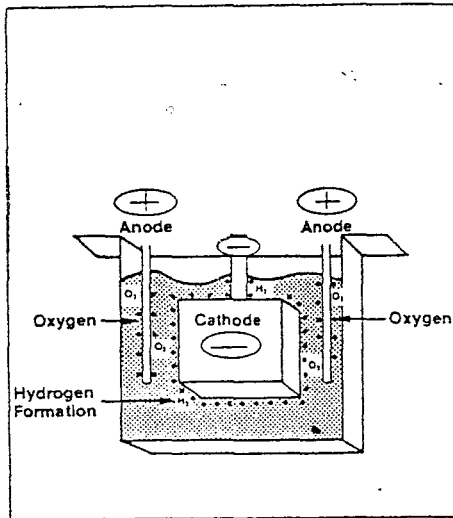
Figure 1.5 : Cathodic cleaning
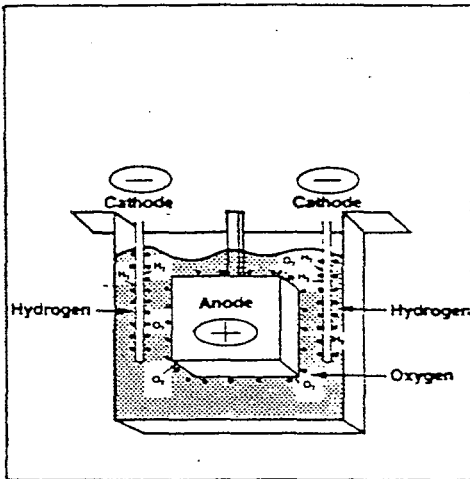
Figure 1.4 : Anodic cleaning
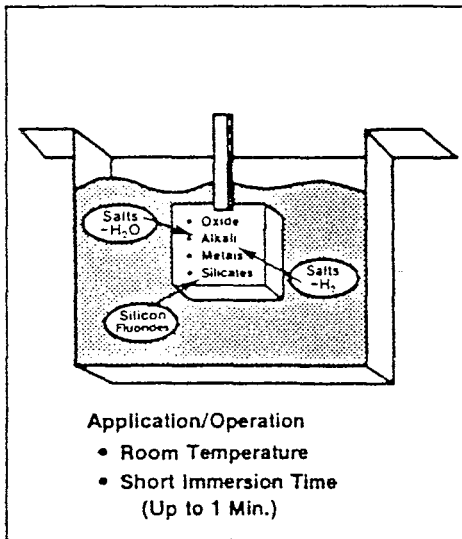
Figure 1.6 : Acid dipping

(Courtesy of Enthone-OMI)

(III)   Periodic reverse cleaning is a combination of cathodic and anodic cleaning by altering or change of the current. Both Hydrogen and oxygen gasses will be generated at certain time interval.

In order to reduce the risk of hydrogen embrittlement and contamination by foreign inclusions as highlighted in cathodic cleaner, most periodic reverse should finish when the part is anodic.

1.5.1.3   Acid Pickling

Treatment of the surface of the work pieces with acid solutions is performed for oxide and welding scale removal. The term pickling denotes the removal of relatively thick oxide films and usually includes the removal of some metal substrate [22, 23]. Acid pickling is used to remove oxide films and involves dissolution of oxide scale in an acid. A generalized reaction may be written as:

$$MO + 2\,HA \longrightarrow MA_2 + H_2O \qquad ④$$

Where   M = metal

HA = acid

Sulfuric, hydrochloric and phosphoric acid could be used in this regard. Sulfuric is most often used because it is the least expensive. The rates of reactions are increased by an increase in acid concentration, temperature and degree of agitation..

Hydrochloric acid is more costly and there is a fuming problem. Nevertheless, many small establishments use it because it works well without the addition of heat. It is also used for light acid dips before plating.

Phosphoric acid is intermediate in cost, but it forms phosphates at the surface of the basis material. This is desirable if rust resistance is needed, but not if the electroplating is to follow.

In some cases, acid electrolytic pickling cathodically is used to remove stubborn welding scale in order to achieve better plating quality.

1.5.1.4   Acid Activation

It is a final pretreatment step before plating processes. Acid activation is used to remove any flash rust and for the neutralization of the residual alkali films by dipping application (Figure 1.6). This step is to ensure clean and active surface for subsequent plating operation.

1.5.2   Triple Nickel Plating

Single and multilayer nickel coatings are used to produce decorative coatings that resist corrosion. Single-layer bright nickel deposits are specified for mildly corrosive service. Double- and triple-layer coatings are specified for use in severe corrosion service [5]. In double-layer coatings (or duplex system), the first nickel layer is

deposited from a semi-bright sulphur-free bath, and the second layer is then deposited from a conventional sulphur-containing bright bath. In triple-layer coatings, a special thin layer of bright, high-sulphur nickel is deposited between the initial layer of semi-bright nickel and the top layer of bright nickel.

1.5.2.1   Semi-Bright Nickel

Semi-bright nickel solutions contain nickel sulfate, nickel chloride, boric acid and a leveling agent [24, 25]. The original process used coumarin [9, 26] as the principal additive. Coumarin-free processes are now available. The process yields deposits that are semi-lustrous and sulfur-free (<0.005% S). The deposits are smooth and have a columnar structure unlike the banded structure or laminar characteristics of fully bright deposits.

The solution was developed to facilitate polishing and buffing; semi-bright nickel deposits are easily polished to a mirror finish. Efforts to eliminate polishing led to the combination of semi-bright and bright nickel deposits. Experience has shown that this double-layer nickel coating has greater resistance to corrosion than a single-layer coating of equivalent thickness [5, 9].

1.5.2.2   High Sulphur Nickel

High sulphur nickel solutions contain nickel sulfate, nickel chloride, boric acid and an addition agent which provides the necessary contents of sulphur in the deposits [9, 11].

In this case, a special thin layer of bright, high sulphur nickel is deposited between the initial layer of semi-bright nickel and the top layer of bright nickel. The very thin layer should comprise about 10% (about 1.2 - 2.5 microns) of the total nickel coating thickness and containing about 0.15% sulphur (as compared with 0.04% to 0.10% normally found in bright nickel deposits).

1.5.2.3   Bright Nickel

Bright nickel solutions contain nickel sulfate, nickel chloride, boric acid and at least two types of organic addition agents, which complement each other and yield fully bright nickel deposits [8, 9, 10, 11].

One type produces deposits that are mirror-bright initially, but are unable to maintain the mirror like appearance of the deposit as its thickness has increased. This class includes compounds like benzene disulfonic acid, and benzene trisulfonic acid, benzene sulfonamide and sulfonimides such as saccharin. The presence of the sulfon group and an unsaturated bond adjacent to the sulfon are critical characteristics. Adsorption of the addition agent occurs by virtue of the unsaturated bond, onto growth sites, points or edges of crystals, and at dislocations. The organic compound is reduced electrochemically at the cathode, and this is accompanied by the reduction and incorporation of sulfur (as the sulfide) in the deposit. Fully bright nickel deposits typically contain 0.04% to 0.10% sulfur. These reactions control the structure and growth of the nickel as it is deposited.

The second type may be termed leveling agents because they make the surface smoother as the thickness of the deposit has increased. They are sulfur-free, bath-soluble organic compounds containing unsaturated groups and generally introduce small amounts of carbonaceous material into the deposit. Typical examples of this second class of brighteners are formaldehyde, coumarin, ethylene cyanohydrin, and butynediol [27].

The combination of organic addition agents makes it possible to obtain smooth, brilliant, lustrous deposits over wide ranges of current density. The deposits have a banded structure consisting of closely spaced laminations, believed to be related to the co-deposition of sulfur. Certain cations, for example, zinc, selenium and cadmium, enhance the luster of electrodeposited nickel, and have been used in combination with the organic additives.

1.5.3   Post Treatment

Normally, after triple nickel plating, the top layer will be plated with decorative chromium, black chromium [29] and other finishing like hard chromium [30], brass, tin-cobalt alloy plating and etc. However, this study does not cover the top layer deposit.

Proper rinsing and drying are very important in order to make sure that any residue remaining on the surface after the plating operation is completely removed to prevent building up of the corrosion spot and staining [31].

1.6   Function of Bath Constituents

1.6.1   Nickel Sulphate

Most of the nickel ion content is contributed by nickel sulfate [7, 11]. This salt is used because it is the least expensive salt of nickel with a stable anion that is not reduced at the cathode, oxidized at the anode, or volatilized. It is also highly soluble and readily available commercially. The limiting cathode current density for sound nickel deposits is a function of the nickel ion concentration in the cathode film, which in turn depends on the metal ion concentration of the bath itself. The larger amount of nickel sulfate now used in the plating bath not only raises the limiting cathode current density but also lower the resistivity, thus improving plate distribution.

1.6.2   Nickel Chloride

A principal function of the chloride ion is to improve anode dissolution by reducing polarization. It also increases the conductivity of the bath and has marked effects at the cathode. It increases throwing power as a result of increasing cathode efficiency, electrolyte conductivity and slope of the cathode potential curve. These effects are at a maximum in the all-chloride bath studied in detail by Wesley and Carey and to a lesser degree in the high-speed bath developed by Pinner and Kinnaman which contains chloride and sulfate in about equal normalities [11]. The interesting effects of chloride ion in the cathode film have been studied though more needs to be done with brighteners present.

1.6.3 Boric Acid

Boric acid serves as a weak buffer in a nickel plating solution. Its principal effect is that of controlling the pH in the cathode film. In the absence of a buffer, nickel deposits at ordinary temperatures tend to be hard, cracked and pitted as shown by Macnaughtan.[11]. Moreover, the presence of boric acid is able to lower the overpotential of nickel deposition [32], and therefore act as a catalyst [33, 34] to facilitate faster nickel deposition. Boric acid is obtained in a very pure and inexpensive form, is nonvolatile and stable, produces whiter deposits, is helpful in its smoothing action on the deposit, and is unique in its cooperative effects with leveling agents.

1.6.4 Addition Agents (Additives / Brighteners)

The various types of additives and brighteners for semi-bright nickel, high sulfur nickel and bright nickel have been highlighted in sections 1.5.2.1, 1.5.2.2 and 1.5.2.3 respectively. Therefore, this section only covers the wetting agents.

1.6.4.1 Wetting Agents (Anti-Pitting Agents)

Although the cathode efficiency of nickel deposition is high, nevertheless sufficient hydrogen ions are discharged and cause pitted deposits during the electroplating process. Certain anionic wetting agents are used in nickel baths to prevent bubbles of hydrogen from adhering to the cathode and causing pits in the deposit [11]. They function by reducing the surface and interfacial tension, and with the correct wetting

agent the contact angle between the liberated hydrogen bubbles and cathode is reduced to zero. The bubbles are detached before they can grow to a size to cause pitting by blocking the plating at the point of contact of the bubbles.

Another value derived from the use of the wetting agents is the diminished drag-out of nickel salts because of the fast runoff from points and edges of the articles due to the low surface tension.

1.7 Effects of Plating Parameters

Beside the bath constituents as outlined above, other plating parameters also influence the nature of the cathode film and thereby the properties of the triple nickel deposits. They are distance between cathode and anode, current density, plating time (or thickness), the combination of different layers of nickel deposits, pH, temperature, degree of agitation, inorganic impurities and organic impurities. These are all interrelated [9, 10, 11].

1.7.1 Distance between Cathode and Anode

Increasing the distance between cathode and anode generally improves thickness distribution. but this effect is limited as the distance becomes large compared with the size of the cathode [35]. Shortening the distance will cause poorer thickness distribution and potential burning appearance especially at the edges of the cathode

where the nearer surfaces will receive higher current than the further surfaces as illustrated in Figure 1.7 and 1.8.

1.7.2 Current Density

The effect of current density is not marked over the range of 1 to 5 A / dm^2, but is usually in the direction of an increasing of burning appearance and poorer thickness distribution with increasing current density for all layers of nickel deposits. Although reduction in current density will improve appearance and thickness distribution, but will be in the expense of longer plating time and reduced capacity.

For high sulfur nickel, lower current density facilitates co-deposition of sulfur in the deposits and provides better corrosion resistance (Figure 1.9).

1.7.3 Plating Time

Thickness (or weight deposited) is proportional to the plating time and current density as per Equation③. In general, longer plating time will provides better appearance and enhances the corrosion resistance performance. However, most of the commercial application required as shorter plating time as possible in order to achieve higher output at lowest cost.

The "dog-bone" effect is an uneven plating condition caused by the unequal current distribution produce in an electroplating cell
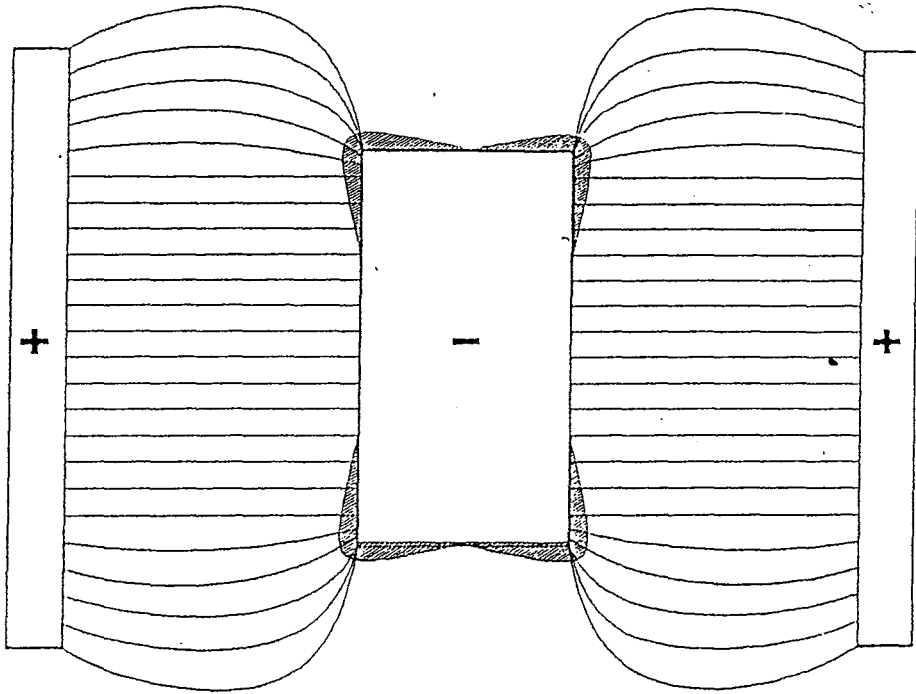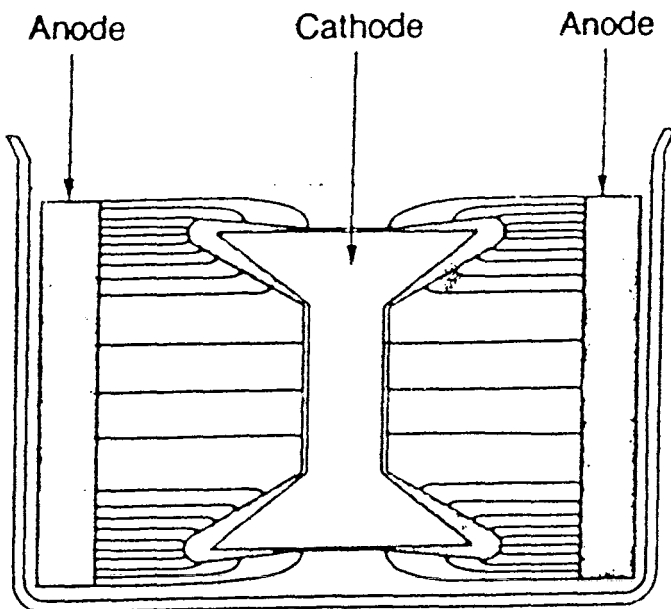

Figure 1.7 : Current distribution (The dogbone effect)
(Courtesy of Enthone-OMI)

Anode   Cathode   Anode

Areas remote from the anode receive a smaller share of the available current than areas near the anode

Figure 1.8 : Current distribution (Not uniform over a shaped article)
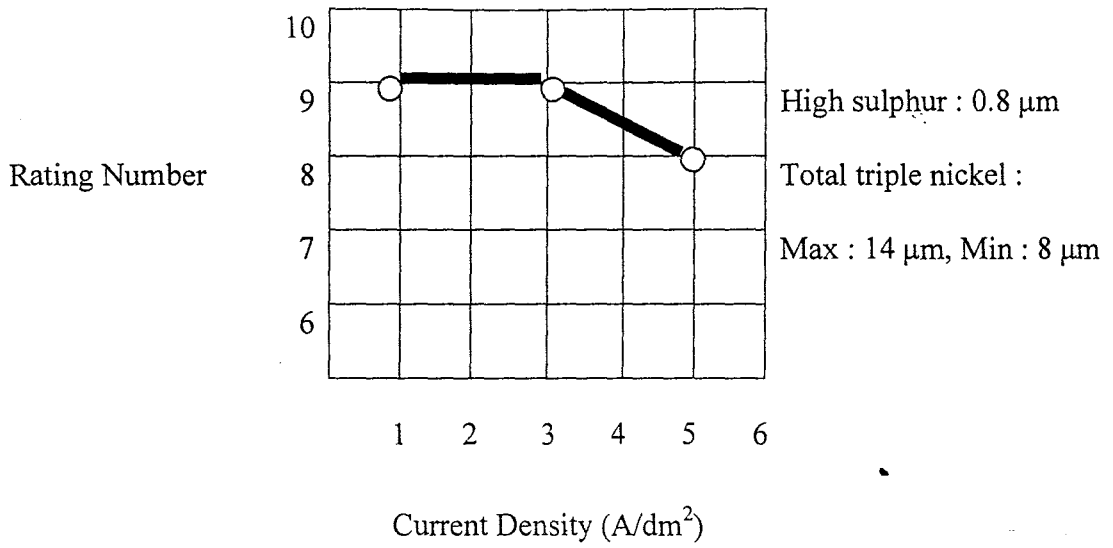(From [5])

Figure 1.9 : High sulphur nickel- Relationship between current density
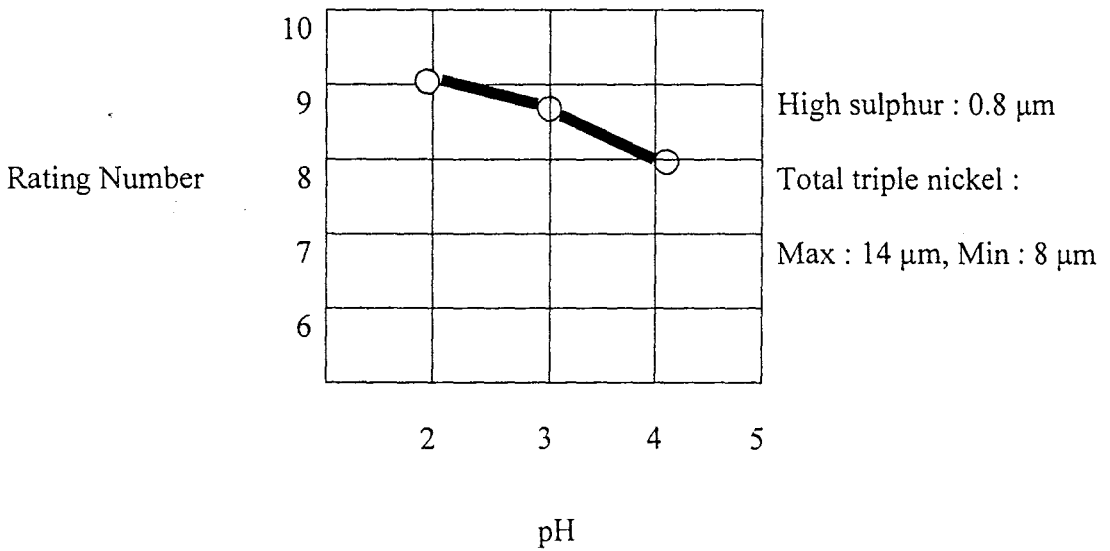and corrosion resistance (at 4 cycles CASS test)

Figure 1.10 : High sulphur nickel – Relationship between pH and
corrosion resistance (at 4 cycles CASS test)

(Courtesy of Ebara-Udylite)

1.7.4   Combination of Different Layers of Nickel Deposits

The combination of different layers of nickel deposits is able to enhance the corrosion resistance of the plated substrates by selective corrosion of the specified nickel layers because of difference in electrode potential behaviors. The selective corrosion mechanisms between different layers of nickel deposits are illustrated in section 1.5.2.4.

1.7.5   pH

The effect of pH varies with the type of the plating bath. For semi-bright and bright nickel, pH below 3.8 will cause low brightness and poor leveling; and pH above 5 will cause poor ductility and poor chromeability due to an excess of additives / brighteners in the deposits; high stress and burning will also occur because of the harmful effects of some impurities, and stress may be much more pronounced at pH above 5.

For high sulphur nickel, pH below 2.0 will cause heavy attack on the substrates such as steel and zinc die castings; pH above 3.0 will cause low co-deposition of sulfur in the deposits and subsequently causes poor corrosion resistance (Figure 1.10).

1.7.6   Temperature

The effect of bath temperature varies with the type of plating bath and the current density. For semi-bright and bright nickel, at temperature below 40 ^{0}C, burning occurs

at high current density and the brightness reduced because of the lesser amount of additives / brightness being deposited. For temperature above 70 ^{0}C, some breakdown of additives / brightness may occur and excessive electrolytes are evaporated.

1.7.7   Agitation

Agitation is accomplished by means of an air agitation, mechanical articles movement and solution circulation. The agitation helps to replenish the nickel ions and additives which are depleted during electrolysis process especially in the difficult-to-reach area or recesses. To a certain extend, moderate agitation also helps to remove hydrogen bubbles on the cathode surface to reduce pitted deposit. For high sulphur nickel, air agitation will cause decomposition of the additives, and normally only mechanical movement and solution circulation is recommended.

1.8   The Properties of Triple Nickel Deposits

In general, typical properties of triple nickel deposits such as cathode current efficiency, thickness distribution, brightness and leveling, sulphur co-deposition, electrode potential differences and the corrosion resistance performance are measured in order to control the quality of electroplated articles [5, 9, 11]. The above properties are being studied in this research. Other properties such as adhesion, ductility, roughness and pitting, internal stress and hardness are also important, but are excluded in these studies.