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Developments in platinum electroplating for aero-engine applications

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
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*DEVELOPMENTS IN PLATINUM ELECTROPLATING
FOR AERO-ENGINE APPLICATIONS*

BY

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*A thesis submitted in fulfilment of
the regulations for the degree of*

*Doctor of Philosophy
of
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October 1993

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ABSTRACT

The electro-deposition of platinum on mild-steel and nimonic alloys substrates using more than twenty baths have been investigated. It has been shown that the cell efficiency can be improved markedly with lower current density , pH value and plating temperature. Distinct differences between direct and pulsed processes revealed themselves in the cathode current efficiency data. Implications of using pulse plating to control the quality of electrodeposits have been considered.

The experimental work reported in this thesis is to a large extent based on cell efficiency and potentiodynamic polarisation which is considered to be a powerful tool for evaluating potential coating solutions. The cathodic polarisation characteristics of platinum solutions has been studied quantitatively.

An excellent technique (electroless) has been developed in an attempt to successfully apply platinum deposit on commonly used mild steel or nimonic alloys using 'Q'salt manufactured by Johnson Matthey.

A series of different designed experiments were used to evaluate the high value ranges of throwing power(localised plating) capabilities and opportunities for extending that capability to replace the Brush plating. Throwing power is currently used for those blades which require the platinum/rhodium plating for RB211 Blades at concave aerofoil

sections manufactured by Rolls Royce situated at Derby in U.K. The investigation employed different size and shape of anodes/cathodes to explore the effects of various factors in the Ni-plating and then as this technique has been established using nickel rather than noble metals, it was used to implement this feature in platinum and rhodium plating.

PREFACE

The work presented in this thesis was carried out at the C.U.K Ltd's laboratory in Hatfield, Herts and Loughborough University of Technology during the period from July 1989 to October 1993. During this period the candidate has not been registered for any other university degree.

The research reported here is, as far as can be ascertained, original except where due reference has been to previous work.

I would like to thank Dr D.R.Gabe, my supervisor, for his considerable help and guidance during this project.

I would also like to express my grateful thanks to Mr M.Dean, my industrial supervisor at C.U.K Ltd, to whom I am greatly indebted for his patient supervision and encouragement. Similarly I would like to thank Mr D.Maxwell-Lyte, laboratory supervisor, Mr D.Clark, Laboratory Chemist, and all technical staff in the C.U.K Engineering company for their invaluable help, advice and constant support.

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CHAPTER 1

1.0 DEVELOPMENTS IN PLATINUM ELECTROPLATING FOR AERO-ENGINE APPLICATIONS

1.1 SUMMARY

The plan of the research embodied in this thesis can be summarized as:

(a) To investigate the relationship between the processing conditions in platinum plating bath .ie, Diammino-dinitrite [$\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$] or known as 'p'salt, which currently being used, compared with other electrolytes.

(b) To establish the parameters controlling the formation of high cell-efficiencies and coherent alloy platings of predetermined composition.

(c) To investigate the electrochemical properties of the platinum plating in terms of thermodynamic equilibrium conditions.

A plating unit has been designed and constructed and electrodeposits were formed using a D.C power supply having a variable current output to 10 Amp and Amp-hour meter to determine the cell-efficiency of plating electrolytes.

The conditions of thermodynamic equilibrium of all the reactions that can occur when a metal is in contact with an aqueous solution at a given temperature..will be expressed on potential-pH diagrams in which the equilibrium

potential will be plotted against pH for each reaction. Therefore, cathodic and anodic polarizations were measured.

1.2 HISTORY OF PLATINUM

Platinum, discovered in the sixteenth century in the Choco district of Columbia, was originally called 'platina del pinto' or 'little silver of the pinto river',⁽¹⁾. Charles Wood, an Assay Master of Jamaica, brought it to Europe in 1741 and passed the specimen by way of William Brownrigg FRS to Sir William Watson FRS who described it to the Royal Society in 1750⁽¹⁾. A fairly definitive account of platinum was published in 1766 and 1757 by William Lewis FRS, a medical practitioner of Kingston-Upon-Thames⁽¹⁾.

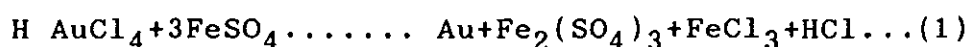
1.2.1 OCCURRENCE

Platinum occurs as metal, and before 1914 most of it come from Russia and Columbia; today the sources of native platinum are Alaska and Columbia, but their contribution represents only a very minor part of world production. Nearly all platinum is derived from the copper-nickel ores of Canada, South Africa and Russia, and they contain less than an ounce of platinum per ton.

1.2.2 EXTRACTION

The Platinum and palladium in cupronickel ores are recovered along with other noble metals from the anode slimes

produced in the electrolytic recovery of the copper and nickel or from the involatile residues from the Mond carbonyl process for refining nickel. Figure 1 outlines the treatment of the concentrates⁽¹⁾. This begins with aqua-regia which is used to dissolve the platinum, palladium and gold. Because platinum is more easily oxidised than palladium, the former reaches the +4 and the latter only the +2 oxidation state. This solution is treated with either ferrous sulphate or chloride which reduces chloroauric acid to gold, leaving platinum and palladium in solution (equation 1).



The addition of ammonium chloride precipitates orange-yellow ammonium hexachloroplatinate(IV), which is filtered off and ignited to give an improved platinum sponge. This crude sponge is dissolved in aqua-regia, filtered and evaporated with sodium chloride and hydrochloric acid to remove nitric acid and nitrosyl compounds and convert the platinum to water-soluble sodium hexachloroplatinate(IV). The sodium hexachloroplatinate(IV) solution is then treated with sodium bromate to oxidise the remaining impurities (Ir, Rh and Pd) to valence states from which, by a careful addition of sodium bicarbonate the metals are quantitatively precipitated as dark slimy hydroxides. The pure filtrate is then boiled with hydrochloric acid to destroy the excess of bromate and treated with ammonium chloride to precipitate platinum as ammonium hexachloroplatinate(IV); this is filtered off, washed, dried and finally heated very slowly up to 1000°C to give more than 99.9% pure platinum sponge.

1.3 PHYSICAL AND CHEMICAL PROPERTIES

Platinum is grey-white, lustrous metal which is sufficiently ductile and malleable to be drawn into wire, rolled into sheet or formed by spinning and stamping. It has high melting-points and considerable resistance to corrosion. Its main physical properties are summarised in Table 1 which gives the currently acceptable values, some of which are critically dependent on purity.

Platinum and palladium are noble metals owing to a combination of sublimation energy and high ionisation potential. Of the two metals, platinum is slightly the less reactive. It is not attacked by any single mineral acid but readily dissolves in aqua-regia, whereas palladium, even in the compact state, is attacked by hot concentrated nitric and sulphuric acids, particularly in the presence of oxygen and the oxides of nitrogen. In powder form palladium is slowly dissolved by hydrochloric acid in the presence of oxygen. Platinum is not oxidised when heated in air whereas palladium is oxidised to palladium(II) oxide in air at 700°C. Above 875°C the oxide dissociated to the free metal and oxygen⁽¹⁾. Palladium, but not platinum, is attacked by moist chlorine and bromine at room temperature.

1.3.1 USES

The properties of platinum make it of use for laboratory ware subject to high temperatures and certain corrosive

materials, and in industry for the lining of crucibles used in the melting of special glasses and of orifices through which glass fibre is extruded. The metal is employed as a surface catalyst in the oxidation of ammonia. Other uses are found in contact-breakers, electrical furnaces and as electrodes in laboratory apparatus and industrial plant.

The pure metal is relatively soft and for many purposes is alloyed with either gold or rhodium- with the latter for spinnerets in nylon fibre manufacture, since the alloy resists both acid and alkali attack. Platinum is employed in the jewellery trade.

Platinum and palladium⁽²⁾ are potentially important in electroplating, but no applications have been found for them which would justify their cost. This situation will change if platinum-plated titanium is adopted widely for the cathodic protection of ships and pipelines. Ruthenium, iridium and osmium may be ruled out as practical plating metal for the time being owing to a combination of scarcity, cost, lack of demand, technological difficulties and properties.

Since the platinum metals are noble, it might expect that it would be possible to electroplate them as easily as silver and gold. There are, however, as many problems as in the electrodeposition of the average base metal. These problems are due partly to the tendency of the platinum metals to form complex compounds, many of which are too stable for use as plating salts; for instance, platinum metals can not be electrodeposited from aqueous solutions

of their alkali metal cyanides. On the other hand, certain possible plating 'salts' from which the metal can be deposited, such as chloroplatinic acid, suffer from the disadvantage that they hydrolyse too readily, hence yielding satisfactory plates only from solutions which are too acid for plating base metal cathodes. Nevertheless, the difficulties have been overcome with varying degrees of success, and plating procedures are now available for the platinum metals except osmium.

In view of the high cost of platinum metals it is not surprising that at first attention was concentrated on the use of very thin, hard electroplates (only a few millionths of microns thick) of maximum brightness as finishing plates. The next stage came during World War II, when rhodium electroplates were used for surfacing electrical contacts in conditions requiring resistance to both wear and corrosion.

The use of a very thin plate of a noble metal, such as platinum or rhodium, for protecting metals against tarnishing is subject to the drawback that corrosion of the underlying base metal at the inevitable pinholes is usually accelerated by the galvanic couple effect. In order to lessen this effect it is customary to plate base metals with nickel or silver before applying a finishing plate of rhodium; the use of rhodium without an underplate has been limited almost entirely to the plating of white gold, platinum jewellery and silver. These underplates also afford some protection against the action of the more corrosive baths in the early stages of plating. The preservation of the importance when they are used as a finish

for costume jewellery, is helped by the use of modern clear synthetic lacquers which are hardened by special baking procedures.

The galvanic couple effect is not, however, detrimental in the case of a few base metals, such as titanium and tantalum, which develop a protective oxide film when made anodic. Somewhat similar considerations apply to the use of platinum-plated titanium anodes, which show promise for the cathodic protection of ships and pipelines. If a critical voltage is not exceeded, the titanium, being anodic, will not corrode when it becomes exposed at pinholes or scratches, with the result minor imperfections in the plating will not materially shorten the effective life of the anodes.

1.4 CHARACTERISTICS OF THE PLATINUM METALS⁽³⁾

The most distinctive characteristics of the platinum metals is their nobility, which can be defined by their position in the emf series, or by their tendency to remain unchanged in various environments which oxidize, corrode, or tarnish base metals. At elevated temperatures and under certain anodic electrochemical conditions, some of these metals do form oxides readily and there is a school of thought that attributes the superior corrosion resistance of these metals to the presence of a passive oxide film. If such a passive oxide film is responsible for the superior corrosion resistance of these metals, it is very thin and it does not thicken with time as such films usually do. For example, the potential required to

pass a given current from a platinum anode to an electrolyte does not significantly increase with time. It is precisely this lack of a significant insulating film coupled with a high resistance to corrosion that justifies many of the applications of the platinum metals. The very high corrosion resistance is most generally employed to avoid any overall corrosion or tarnish in a very mild atmospheric environment such as the air we breathe. Very thin coatings of the platinum metals frequently offer advantage in service of this kind. In a few applications, severe environments are involved. One such application which uses the film-developing metal, titanium, as a base is platinum-plated titanium used as an insoluble anode in electroplating. Here a thin porous platinum coating transmits the current to the electrolyte and prevents the underlying titanium from developing an insulating anodized film. At pores or cracks in the platinum, the insulating, anodized film which does not develop protects the underlying titanium by inhibiting the passage of current. For the protection of refractory metals and graphite from oxidation at high temperature, it is essential that platinum metal deposits be thick enough to isolate the substrate completely and allow for some diffusion at high service temperatures.

Melting points and electrical resistivities for the annealed wrought precious metals, including silver and gold, are presented graphically in figures(2-3). The melting points of the platinum metals are all substantially higher than those of the other precious metals, silver and gold. coatings having higher melting points are of advantage in

minimizing the welding or sticking of mating electrical contacts and in minimizing the diffusion of basis metal through the deposit. The electrical resistivities of silver and gold are substantially lower than those of the platinum metals. The values shown can be a guide to the electrical resistivity of electrodeposits which are sensitive to impurities and conditions of deposition. A low resistance is frequently desirable for signal transmission in electrical contact or connector service.

The hardness numbers plotted in figure.4 provide an indication of the strength and ductility of the wrought precious metals. For example, ruthenium and osmium are hard and strong but relatively brittle. On the other hand, silver, palladium, gold, and platinum are soft, of low strength, and very brittle. Figure.4 also shows the range of hardness values reported for electrodeposits of the precious metals. The hardness of an electrodeposit can be influenced to a significant degree by the specific bath employed, the operating conditions, and the impurities present. Reliable hardness values are very difficult to obtain on the usually very thin electrodeposits of the platinum metals, so thicker deposits frequently are especially prepared for this purpose. In general, the harder deposits are preferred for applications requiring superior resistance to wear. Thin, hard deposit should have a reasonably hard support for effective service. On soft metals, bright nickel plate provides a good support for thin, hard platinum metal finishes intended for wear-resisting applications.

One of the important advantages of plating over coating

processes is the higher hardness levels frequently produced. It is believed that the higher hardness values of electrodeposits develop as a result of a very fine grain size, formed at a much lower temperature than in cast and wrought metals, and the inclusion in the deposit of a hydrolytic precipitate, an incompletely reduced metal, or a bath constituent which becomes insoluble in the usually more alkaline cathode layer.

Figure.5 shows the reflectivities of the precious metals over a reasonable range of the spectrum. Gold has a high reflectivity in the infrared and is used for finishing reflectors operating in this range. Silver, a very 'white' metal, has a lower reflectivity than clean silver but it does not tarnish. It is this feature that justifies the use of rhodium as a finish on reflectors, mirrors, jewellery, and decorative items.

1.5 GENERAL CONSIDERATIONS (3)

In a number of important ways platinum metal plating baths differ from the usual base metal plating baths. Their position at the anode end of the emf series, their marked tendency to form complex ions, their resistance to corrosion, and their high cost are factors accounting for these differences.

High-metal-ion-concentration acid baths for some of the platinum metals have been developed for the production of heavy deposits or for electroforming.

These baths are of very limited use, since there is little demand for heavy deposits which are necessarily expensive.

These baths are not of interest for producing thin plates since all base metals must be well protected by a preliminary deposit of a noble metal to avoid displacement plating by immersion.

Fortunately, the platinum metals readily form complex compounds which when dissolved in an appropriate electrolyte yield a solution having a low platinum metal ion concentration and little tendency to deposit metal by replacement. As a result, baths containing complex compounds frequently can be used for direct plating on the less reactive base metals such as nickel and copper. However, in many cases a strike from a noncorrosive bath, such as gold cyanide, is desirable and in cases where the platinum metal is not well complexed, such a strike is essential. The more reactive base metals will in most cases require a preliminary plate of nickel in addition to a precious metal strike.

In most of the platinum metal plating baths, the platinum metal does not dissolve anodically, and insoluble anodes must be used. As a consequence, the metal plated out must be replaced by the addition of an appropriate salt to the bath. Palladium and platinum anodes dissolve anodically in the appropriate acid chloride bath, and for these baths are preferred over insoluble anodes such as graphite. Palladium anodes are also used to maintain the metal content of the tetranitrite-sodium chloride bath when the pH is in the 4.5 to 6.5 range.

The high cost of the platinum metals tends to limit the metal concentration in the plating bath in order to lower the capital investment. For example the Watts nickel bath

uses 50 to 60 g/l of nickel while 2 g/l of rhodium is a frequent concentration in rhodium plating. Higher metal content baths have become popular, particularly where requirements are technical rather than decorative. The higher metal content bath generally permits higher current density operation, shorter plating time, and frequently, a lower stress.

The high cost of the platinum metals also tends to limit the deposit thickness to the minimum required to accomplish the objective. Thicknesses range from a low of about 0.1 μ m to rarely higher than 5 μ m. However, it should perhaps be emphasized that even with these costly metals, thin deposits are not expensive on a cost per item basis. More importantly, even very thin coatings of the platinum metals are particularly effective in serving a need. For example, 0.1 to 0.2 μ m of rhodium serves to prevent sticking of silver-plated seals of Apollo rocket engines as well as to prevent tarnishing of costume jewelry, and 1.2 μ m of platinum makes titanium an effective insoluble anode.

Appearance (bright, graininess, and colour), adhesion, deposit thickness, porosity, and uniformity are plate characteristics examined in quality control. Where applicable, a bend or other deformation test provides a fairly reliable indicator of adhesion. The pressure-sensitive tape test is not quite so reliable but is more generally applicable.

Under appropriate conditions, deposit thickness can be calculated from ampere-hour data or from gain in weight. The time-honoured metallographic method of thickness

determination is neither easy to use nor accurate on the less than 5µm thickness range common for precious metal deposits. Instrumental methods based on X-ray and β-Ray penetration and reflection methods are nondestructive and generally applicable for production control.

Many tests have been proposed for determining porosity of electrodeposits, particularly precious metal electrodeposits. A number of these are basically exposure tests, the environments including prepared atmospheres, usually containing sulphur compounds or nitric acid vapour, natural, industrial, or marine atmospheres, and salt spray. The electrographic test is also quite commonly employed, particularly on high production items. A number of modifications have been proposed. Where the application involves exposure to heat, a direct test has been most valuable. The absence of blistering, flaking, or colour change after heating under controlled conditions can provide an assurance of overall plating quality.

Accelerated tests are most useful for process quality control and for guiding research, but extensive experience in many fields suggests that such tests frequently are inadequate indicators of service behaviour. For determination of overall electrical contact performance and particularly where corrosion and wear resistance are involved, life tests under service conditions provide a superior indication of performance.

(a)MOLTEN CYANIDE ELECTROLYTES⁽⁴⁾

Plating from molten cyanide electrolytes of the platinum

metals are superior to most of those from aqueous electrolytes with respect to thickness plateable, soundness, and freedom from stress. Operating restrictions imposed by the 600°C bath temperature and the need for an argon atmosphere have in the past severely limited interest in these baths. However, the commercial plating of tantalum, titanium, and tungsten from molten baths suggests a reevaluation of these restrictions. Certainly, these baths merit consideration for the plating of heavy deposits of the platinum metals, especially when readily oxidized refractory metals or graphite are used as substrates.

(b)ELECTROLESS PLATING

Electroless plating, in which the metal is deposited by the action of the reducing agent added to the bath, has been developed for both platinum and palladium. The elimination of the need for electrical connection to the part to be plated and the uniformity of deposit thickness are advantages of the electroless process. The deposited metal is pure except where hypophosphites are used as reducers, in which case phosphorus may be present. Many investigators have had difficulty with electroless plating due to general decomposition of the plating bath. In the main this difficulty is due to the use of a high plating temperature in order to increase the plating rate, the addition at one time of an excess of reducing agent, and dust or other contaminants in the bath.

1.6 ANODES AND PLATING SALTS

With one or two exceptions mentioned later, the platinum metals do not dissolve anodically in the solutions used for their electrodeposition. Therefore, most plating processes are operated with insoluble anodes, usually platinum, and salts have to be added from time to time to replace metal removed by electrodeposition and drag-out. One resulting problem has been the accumulation of residuals, which tends to limit the useful life of the solution. Since the periodical replacement of such contaminated solutions by new solutions adds to operating costs, processes have been developed which use replenishment salts (for example, dinitrodiammine platinum) which do not add any residual ions to the bath. Such processes are capable of operating indefinitely without changing the solution, provided no other contamination occurs.

1.7 PROTECTIVE COATINGS FOR GAS TURBINES⁽⁴⁾

1.7.1 SUMMARY

The development of high strength superalloys to cope with increased turbine entry temperatures and the associated severity of the mechanical and thermal operating environment within the engine has generally been achieved by decreasing the alloy chromium content and increasing the amount of gamma prime formers such as Al and Ti, the

overall result being a loss of environmental degradation resistance, thus necessitating the development of surface coatings to ensure that components meet their design lifetimes.

This section describes the variety of protection systems and deposition processes available for the production of coatings for aero gas turbines, with particular reference to blade and vane applications. The use of diffusion, overlay and thermal barrier coatings and their deposition processes such as pack and vapour metallizing, plasma spraying and PDV techniques are discussed.

1.7.2 INTRODUCTION

High pressure turbine aerofoils experience a wide variety of thermal and mechanical loading during service, depending upon a combination of cyclic thermal, centrifugal and gas-bearing loads. In addition, the components are exposed to a highly oxidizing atmosphere which may contain contaminants such as sulphates and chlorides and under certain conditions, erosive media.

The development of superalloys for higher creep strengths to permit increased turbine operating temperatures has generally been achieved at the expense of the alloy Cr content with an increase in the gamma-prime formers such as Al and Ti. In addition, the elements W and Mo have been added as solid solution strengtheners⁽⁵⁻⁶⁾. The development of superalloys with particular reference to gas turbine applications has been in detail elsewhere⁽⁶⁻⁷⁾. The improvement in mechanical properties due to the compo-

sitional changes has generally been accompanied by a marked decrease in the corrosion resistance of the alloys although their oxidation performance is relatively unaffected. The decreased corrosion resistance, with the consequence that component life may well be corrosion-limited, has necessitated the development of surface coatings to ensure that components achieve the desired performance and required service lifetimes.

1.7.3 ENVIRONMENTAL DEGRADATION OF HIGH TEMPERATURE ALLOYS

There are three basic forms of corrosion attack encountered by aerofoil components in gas turbines⁽⁸⁻⁹⁾:

- (i) low-temperature sulphidation, known as type II corrosion, associated with high SO_3 in the combustion product environment, which occurs over the range 500°C - 750°C
- (ii) high-temperature sulphidation, known as type I corrosion, which is primarily attributable to corrosion by molten sulphates and occurs over the range 750°C - 950°C
- (iii) high temperature oxidation, which occurs at around 950°C and above.

Since there is a temperature variation on a turbine aerofoil, perhaps ranging from 500°C - 1100°C , more than one form of attack may occur on a single component.

The exact temperature at which the transition from one form of attack to another occurs has been reported to be dependent upon the time at temperature⁽¹⁰⁾ and the composition, contaminant flux rate, time and engine operating conditions⁽¹¹⁻¹²⁾.

The detailed mechanisms via which low and high temperature

corrosion proceed have been excellently described by Giggins and Pettit⁽⁴⁾ whilst high temperature oxidation has been well reviewed by Wood⁽¹³⁾ and Whittle⁽¹⁴⁾.

1.7.4 SURFACE COATINGS

It is now generally accepted practice to coat high temperature components in gas turbine engines. A wide range of coatings and coating processes are available for protecting components in gas turbines operating in a variety of conditions. Coatings are used on turbine vane and blade components in civil and military aero engines, marine engines and industrial gas turbines.

The two principal reasons for the application of surface coatings are;

- (i) to maintain component shape
- (ii) to ensure that the component is capable of operating for the design lifetime.

1.7.5 PROPERTY REQUIREMENTS OF TURBINE AEROFOIL COATING SYSTEMS

The service conditions encountered by aero gas turbine aerofoils are severe, comprising complex mechanical, thermal and oxidizing/corrosive conditions. In turbine blades the primary failure modes involve creep, thermal fatigue and thermomechanical fatigue with typical component surface temperatures of 550°C-1100°C.

The current philosophy with reference to coated turbine aerofoils is that the base material is developed to pass

optimised mechanical properties whilst the surface coating is selected to achieve maximum protection from the environment during service.

The properties required by a coating system are listed in Table 2 (15-16). Examination of Table 2 shows that the selected coating system must satisfy a complex range of property requirements. In addition, it should also be noted that the desired properties must be maintained over the whole operating temperature range of the component during service. Clearly, the development of a coating system to satisfy the full range of property requirements would be extremely difficult and a more realistic approach involves the use of coatings offering a compromise between the properties.

1.7.6 CLASSIFICATION OF CURRENT COATING SYSTEMS

The coating systems currently in use in gas turbine vane and blade applications can be divided into three basic groups;-

(i) Diffusion coatings

These comprise intermetallic compounds, mainly aluminides. They are most often produced via CVD techniques, usually pack cementation. Their formation is generally controlled by diffusion mechanisms.

(ii) Overlay coatings

These comprise complex alloys based on the M-Cr-Al-X system (M= Ni, Co, Ni-Co, Co-Ni; X=Y, Si, Ta, Hf etc) whose exact compositions depend upon proposed applications. The deposition of these coatings is usually per-

formed by plasma spraying techniques or PVD processes.

(iii) Thermal Barrier coating systems

These comprise a ceramic over a M-Cr-Al-X (overlay) coated substrate. Deposition of the ceramic is currently achieved via plasma spraying or PVD techniques.

1.7.7 CONCLUDING REMARKS

(1) High temperature components require coatings in order to maintain design geometry and to achieve acceptable operational lifetimes.

(2) A variety of coating systems and processes are available for the coating of turbine aerofoils and selection of both the deposition technique and the coating type/composition will depend upon the envisaged use of the component and the type of engine.

(3) A knowledge of the thermal, mechanical and environmental 'history' to be encountered by a component will facilitate the development of a satisfactory coating system with optimised structure and composition.

(4) The complete alloy-coating system must be considered during the development of surface coatings since complex interdiffusional interactions occur in service which markedly influence coating and alloy behaviour.

(5) The concept of a coated blade or vane should be considered at an early stage in engine design.

(6) Further work is required to develop overlay and thermal barrier systems to function in the increasingly severe conditions encountered by components in and future engines.

1.8 COATINGS FOR CORROSION CONTROL

Coatings find widespread applications in the engineering field and the following applications cover the main areas.

1. Corrosion control.
2. Wear resistance.
3. Decorative metal finishing.
4. Electroforming.
5. Electronics.
6. Reclamation and repair.

Competition exists between coating types and between coating technologies, and involves metals and non-metals.

Methods of coating technology is shown in table 3.

Some characteristics of the various coatings techniques may be enumerated;

(a) Electrodeposition for metal deposits on conducting substrates.

Best for moderate thicknesses(1-50um) with good control of thickness possible. Dull and bright deposits produced.

(b) Electroless deposition uses chemicals rather than electrons as reducing agents thereby enabling deposition on non-metallic substrates, after suitable pretreatment, to be feasible. It is a relatively slow process, but does enable good coverage of recessed parts to be obtained.

(c) Electrophoresis enables charged suspended particles, in a covalent medium, to be electrostatically attracted and consolidated on a metal surface. Rapid deposition

possible with good throwing power.

(d) Hot dipping is limited to low melting point metals where the substrate is not seriously affected by any heat treatment incidentally achieved.

Relatively thick coatings possible. Same techniques used for paints, tars and lacquers.

(e) Spraying is possible for paints and metals where thinner coating than in hot dipping are required. Plasma technology enables refractory metals and ceramics to be sprayed.

(f) Cladding involves the laminating or compositing of coating and substrate often in a sandwich fabrication process. Thick coatings of good integrity possible and novel mechanical properties may result.

(g) Vacuum/vapour techniques are expensive and hazardous and so are used for high technology applications or special requirements, eg very thin films for electronic applications.

(h) Diffusion coatings offer least dimensional changes and mechanical inhomogeneity and thick layers suitable for mechanical uses, eg wear and hardness.

(i) Fusion coatings may be diffused but may otherwise offer superb coating adhesion through covalent bonding. Vitreous enamel is a widely used example.

(j) Roller coating offers even coatings of large areas on a continuous basis. Pattern printing possible for architectural applications.

(k) Conversion coatings are post-treatments of metal surfaces used to provide increased stability in mild environments. Modest improvements in properties cheaply

attained.. Widely practised especially for aluminium.

In the context of corrosion control other approaches altogether may become possible, desirable or even essential. For example, the non-coating methods include:

(a) Environmental control: eg use of inhibitors or deoxygenation of boiler waters.

(b) Cathodic protection: eg sacrificial anode and impressed current protection of pipeline, ships hulls etc.

(c) Anodic protection: eg stabilization of protective oxide films.

(d) Material selection: eg use an alloy steels in place of mild steel or coated steel.

(e) Design to minimize corrosion: eg eliminate box section door sills on cars.

In designing a corrosion control system it is common to employ a main protection method with a second back-up system. Thus cathodic protection of a steel structure is usually accompanied by a thick barrier-type coating which may be regarded initially as the main mode of protection.

CHAPTER 2

2.0 PRINCIPLES OF ELECTRODEPOSITION

2.1 BASIC ELECTROPLATING THEORY (17-19)

Electrodeposition is the process of depositing a metallic coating or other conductive layer on surfaces by means of electrolysis or electrochemical processes, ie passage of current from an anode of the metal which is to be deposited, to the cathode on the which the deposit is to be obtained by using Faraday's law.

The amount of metal theoretically deposited may be calculated as follows;

$$W = ItA/ZF \dots \dots \dots (1)$$

where; W = weight of metal deposited

A = atomic weight of metal deposited

Z = valency of deposited metal

F = Faraday's constant

t = Plating time in Seconds

I = Current density in AMPS (mA/cm²)

from (1) it follows that;

$$1 \text{ gramme chemical equivalent} = \frac{\text{Atomic weight of component}}{\text{Valency of above component}}$$

Faraday's law states two principles:

(a) For the current (It), the weight of metal deposited is

directly proportional to its chemical equivalent.

(b) The weight (W) of metal deposited is directly proportional to the quantity of electricity passed ie current (I)*Time(sec).

One Faraday (96,490 Amp.secs) of electricity yields one gramme chemical equivalent. THE CHEMICAL EQUIVALENT can be defined as the weight of the component which will replace or combine eight parts of oxygen by weight.

THE VALENCY can be defined as the number of atoms of hydrogen which replace or combine with one atom of element or substance.

Therefore, for platinum deposition from the chemical equivalent state, 96,500 coulombs (ampere seconds) deposit 97.54 grams of platinum.

1 coulomb therefore deposits $97.54/96,500$ grams of platinum.

One ampere hour is 1 ampere flowing for 3,600 seconds ie, 3,600 as coulomb.

Therefore 1 ampere hour deposits $(97.54*3,600)/96,500=3.64$ grams of platinum for 100% efficiency.

As a guide 1 ampere minute deposits 30.3 mg of platinum i.e. 0.303 ml of concentrate code 3747 plating addition.

2.2 MECHANISM OF GENERAL ELECTRODEPOSITION

Much effort has been given in recent years to studying the mechanism of electrodeposition. Most investigators⁽²⁰⁾ have assumed that electrodeposition should follow a mechanism akin to that for the deposition of a

crystalline coating by condensation of a vapour. The solvated metal ion approaches and adsorbs on the cathode, losing some of its solvation sheath as the cathode gains the requisite electrons. The ad-ion which is mobile, diffuses over the cathode surface until it reaches an atomic step. It adsorbs on the step, losing more water of solvation, and reducing its freedom to diffuse along the step. Further desolvation and co-ordination follows when it reaches a kink in the step, at which stage it is mobilised. When other ad-ions following this path eventually join and submerge the first, co-ordination occurs with metal ions in the metallic lattice. The view of Capuano et al⁽²⁰⁾ was that this mechanism of electrodeposition was plausible, compatible and consistent with later views on metallic crystals and their defects, and certain properties of electrodeposits.

The actual process of deposition is as follows (21-23)

Salts consist of ions that have negative or positive charges, and migration of these ions in the solution constitutes a flow of electricity. Salts are electrolytes; they conduct electricity, not only in solution, but also in molten state. Such electrolytes are decomposed in the process called electrolysis, in which electrical energy becomes chemical energy. But chemical energy can also be converted to electrical energy.

A simple cell shown in Fig 6 may be used to illustrate the mechanism involved. The potential difference across the cell due to the current source makes an excess of

electrons available at the cathode as it becomes more negative than the anode. This potential attracts positive ions in the solution to the cathode where they are neutralised either by free electrons in the lattice, or by ions accepting electrons and hence becoming incorporated into the lattice at the cathode surface. Whichever process by which the positive ions become neutralised at the cathode, electrons are required from the external circuit. Therefore, as positive ions are deposited at the cathode, then current must be supplied to the cell. Reduction of metal ions by addition of electrons at the cathode must be accompanied by an oxidation process, loss of electrons at the anode. The latter process generally involves the removal of electrons from the metal into the external circuit. This leads to the loosening of metal ions at the anode surface due to the reduced binding forces. These metal ions may then form a hydrated ion by combining with a water molecule in order to facilitate effective transport of metal ions through the solution. This hydrated ion in the solution is then attracted to the cathode and becomes incorporated in the cathode lattice as it separates from the water molecule which stays in the plating solution and can then contribute to further metal ion transport. The anodic and cathodic processes are necessarily self-regulating and occur on average at the same rate, simply because the cell potential governed by the external power supply is common to both electrodes. Any difference in reaction rates at either electrode leads to a change in the potential which slows down the reaction rate at whichever electrode is involved, speeding up the

reaction rate at the other in order to equalise the rates.

However, other investigators⁽²⁴⁻²⁵⁾ have a more detailed approach than that shown by the previous model. They indicate that under the influence of an imposed electrical field as well as by diffusion and convection, the hydrated metal ion present in the electrolyte arrives at the cathode. The hydrated metal ion enters the diffusion layer in which the migration velocity is determined by the concentration gradient. The field strength in the diffusion layer is not sufficient to liberate the metal ion from its hydrate envelope. At most, the loosely bound water molecules are aligned by the field. The metal ions then pass through the diffuse part of the double layer and enter the external layer of the fixed double layer. The field strength, (E) in the double layer is approximately 10^7 v/cm, and at this high field strength the metal ion is deprived of its hydrate envelope. As shown in fig 7 the repelled water dipoles become components of the double layer.

Brandes, Erdey-Gruz⁽²³⁻²⁴⁾ and others have proposed that the dehydrated metal ion migrates within the outer zone of the double layer to a point opposite an energetically favourable growth point on the cathode surface. From this point the metal ion passes through the double layer, is neutralised, and deposited on the cathode. According to Kohlschutter⁽²⁵⁾, the metal ion passes through the double layer at the point where contact first occurs. It is then neutralised and adsorbed for the time being at the cathode

surface as an ad-atom. This ad-atom now diffuses on the cathode to a growth point and is there incorporated into the crystal lattice of the cathode. Only when the first contact chances to be at the site of a growth point of a crystallite can it immediately be built into the crystal lattice.

2.3 ELECTRODE POTENTIALS

An aqueous electrolyte solution consists of a variety of charged and uncharged species as follows:

- (1) cations, which are positively charged ion and migrate to the cathode in a galvanic or voltaic cell,
- (2) anions, which are negatively charged ion; they migrate to the anode a galvanic or voltaic cell,
- (3) water dipoles,
- (4) organic molecules, trace impurities which under equilibrium conditions are randomly oriented so that within the solution there is no preferentially directed field. Under the influence of a potential difference, the charge will be transported through the solution by cations and anions that migrate to cathode and anode, respectively; this migration of charge is through an electrolyte for electrolytic conduction. At each electrode there will be a transfer of electrical charge and a consequent electrode reaction that results in a change in the concentration of the reacting species at the surface of the electrode. Under these circumstances the transport of species to and from the electrodes is by diffusion and convection as well

as migration; the term 'transport' is used to include diffusion, convection and migration. Fig 8 shows the potential differences and concentration gradients in the cell $\text{Cu}/\text{NiSO}_4/\text{Cu}$. Fig 8a. represents the electrodes being unpolarised; the potential difference is the equilibrium potential $E_{e.q}$ and there is no concentration gradient in the diffusion layer. Whereas, in fig 8b. the electrodes are polarised; E_p of the anode is now more positive than E_{eq} whilst E_p of the cathode is more negative and concentration gradients exist across the diffusion layer; C_e, C_b are the concentration at the electrode and in the bulk solution. Conversely, the solution deposits ions on the metal and are incorporated into the metal lattice. Because the ions are at the same time charge-carriers, this passage of ions creates "an electrical double" layer at the metal-solution interface.

An electrical double layer (E.D.L) and also known as the (Helmholtz double layer) is the combination of the positive "adsorbed fixed layer" outside and the negative ions diffuse from it to form a "diffuse mobile layer" shown in Fig 9. These layers are loosely held there by electrostatic attraction. The potential between the layers is a result of the equilibrium of the chemical and electrical forces. The potential difference which exists between metal and solution in the equilibrium state is known as the galvanic potential. This electrochemical equilibrium is dynamic, so that in the equilibrium state the interaction between metal and electrolyte does not cease although in a given interval of time the number of ions entering

the solution from the metal is equal to the number of ions deposited on the metal from the solution. Nernst termed the tendency of the metal to send ions into solution the electrolytic solution pressure and the tendency of the solution to be diluted by depositing ions on the metal, the "osmotic pressure" of the ions.

The galvanic potential existing at the metal-solution interface as a result of the various tendencies of the ions to pass into solution or, alternatively into the metallic state, is manifested at the phase boundary in the form of the electrical double layer. According to Nernst and Helmholtz, this E.D.L must be visualised as consisting of a small but still measurable number of excess positive cations confronting an equal number of negatively charged anions at the interface. When metal ions are transferred from solution into the metal lattice, the metal is at the positive side of the E.D.L, opposed to which is the negative side in the adjacent solution layer. When ions escape from the metal and enter the solution, the metal ion is at the negative side of the double layer and the adjacent solution layer at the positive side. The magnitude of the galvanic potential depends upon which of those processes predominates.

A simple mode of the E.D.L was suggested by Helmholtz in which the changes at the interface were regarded as the two plates constituting a parallel plate capacitor, eg, a plate of metal with excess electrons (the inner Helmholtz plane- I.H.P) and a plate of excess positively charged

ions (the outer Helmholtz plane-O.H.P) in the solution adjacent to the metal. The changes at the interface balance one another so that the E.D.L is neutral as a whole. Fig.9A shows the E.D.L to consist of a plane of excess negative charges on the surface of the metal.

2.4 ELECTROLYTIC CRYSTALLIZATION

The final step which takes place during the electrodeposition of a metal at the cathode is known as electro-crystallization ie, the transition of the discharged metal atoms into the crystalline state.

In electro-crystallization, which proceeds under the simultaneous influence of lattice forces and electrostatic forces, two types of crystal growth are possible. These types are firstly crystal growth starting at edges and corners, where the highest current densities are present and secondly, at the centres of the crystal planes. The type of growth which predominates depends on the minimum crystallization energy.

According to Kossel⁽²⁶⁾, the energy required for continuation of the growth of a given crystal lattice is least where the newly arrived atom can be built into an unfinished lattice plane. Owing to the minimal energy requirement for crystallization at these points, this partial step is repeated many times. Crystal growth thus proceeds by "repeatable" steps called "half-crystal" positions and

also called "active" and "growth areas" by Fischer and Lorenz⁽²⁷⁻²⁸⁾. The forces of attraction in the interior of a metal are compensated by the neighbouring atoms. However, at the surfaces, this is no longer true, and they thus exert growth in the vicinity of the surface. Therefore, these growths are strongest at corners and edges projecting from the surface⁽²⁹⁾. At the growth areas crystallization proceeds in such a manner that one ad-atom at a time is built into the crystal lattice in the immediate vicinity of an atom previously incorporated into the lattice.

In addition to the lattice forces, electrostatic forces also play a part in electro-crystallization. Furthermore, it is necessary to take into account the fact that the metal ions in electro-crystallization, in contrast to other crystallization processes, are always surrounded by foreign cations, anions, neutral molecules and other electrolyte components.

2.5 ELECTROLYTES FOR THE DEPOSITION OF PLATINUM⁽³⁰⁾

Electrolytes may be divided into two groups:

- (a) baths containing platinum in the divalent state and
- (b) those with it in the tetravalent state. Within both groups a further differentiation can be made based on the typical salts used, which may not always be identical with the metal supplying compounds. In Tables (4-5) a survey of electrolytes producing worthwhile deposits is given.

2.5.1 PLATINUM PLATING

The first important platinum plating solution was discovered by Roseleur and Lannaux in 1855. It was made by dissolving hexachloroplatinate(IV) acid in a boiling solution containing ammonium and sodium phosphates, and with minor modifications it has been the one chiefly used until comparatively recent times⁽³¹⁾. An historical review has been published⁽³²⁾.

Tetrammineplatinum(II) Nitrite bath, $\text{Pt}(\text{NH}_3)_4(\text{NO}_2)_2$. This bath, developed by Keitel and Zschiegner⁽³³⁾, has the following composition shown in Table 6.

The dinitrodiammine platinum is dissolved in hot 5% ammonia solution to form the readily soluble tetrammine salt before adding to the bath and also when replenishing. The bath, which is operated near the boiling point, should be kept ammoniacal by replacing at intervals the ammonia lost by evaporation. Flash deposits can be obtained in from 30-60 sec at about 1 A/dm^2 ; for heavier deposits a low current density of about 0.4 A/dm^2 is recommended by the sponsors, but Tripler et al⁽³⁴⁾ found it better to use periodic reverse current.

Theoretically there should not be any accumulation of objectionable salts in the bath because nitrite should be removed by the following reaction;



In practice, however, it is found necessary to boil the solution from time to time with the addition of ammonium nitrate to counteract a tendency for the current efficiency to fall to zero, which is thought to be due to excess

NO₂ in some form.

Disadvantages of the bath are

1. High temperature of operation.
 2. Cathode current efficiency, initially 10%, soon falls to 5% or lower and tends to be unpredictable.
 3. Corrosion of exposed metal parts by hot ammonia fumes.
- Tripler, Beach, and Faust⁽³⁴⁾ used this type of bath for electrocladding zirconium with platinum. In order to obtain smooth, dense coatings up to 15 mils thick, however, they found it necessary to use periodic reverse current. They reported that, although no metal was depleted during the reverse cycle, the depolarizing action was beneficial. Nickel test specimens coated with only 0.2 mil platinum showed no weight loss after 5 hours immersion in boiling 20% hydrochloric acid.

This bath is operated at a temperature of 95 to 100°C and current density of 30-100 mA/cm².

It is assumed that pore formation in platinum deposited with periodic reverse(PR) is prevented by depolarization of the cathode. It would be hard to imagine that the beneficial effect of PR current on the deposit structure is confined to platinum deposited from this one plating solution. If depolarization alone is involved in the possibility of producing denser platinum coatings from solutions which operate at low cathode current efficiencies, every other platinum plating bath should benefit in the same way. Indeed, it appears to have done so in the case of the Russian solution already mentioned.

2.5.2 POWELL AND SCOTT BATH

Nearly all the platinum plating baths used until recently have had a poor cathode efficiency. An exception is an alkaline bath which has been patented by Johnson Matthey & Co.Ltd⁽³⁵⁾. In this solution the platinum is used as sodium hexahydroxyplatinate $\text{Na}_2\text{Pt}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ dissolved in dilute sodium hydroxide. Wernick⁽³⁶⁾ gave the following composition shown in Table 7.

This bath is worked at temperatures between 65 and 85°C and a current density of 3-15 mA/cm². The cathode efficiency of this solution is reported to be almost 100%. Laister⁽³⁷⁾ has described this electrolyte in detail and believed that it was the best of those available provided certain precautions were taken. The bath is very sensitive to contamination by cyanides, which have the effect of reducing the cathode efficiency to appreciably lower values. The solution is also affected by the presence of silicates, although not quite to the same extent. While silicates do not decrease the cathode efficiency they have an adverse effect on the deposit by producing grey streaks. Although it is possible to operate this process in glass tanks for a considerable period of time without observing this discolouration of the coating, the use of nickel or nickel plated copper tanks is to be preferred. Experiments carried out at the Degussa Co, Germany, have shown that plastic linings which are resistant to alkaline solutions and high temperatures are also suitable for this purpose. Polyethylene is an example of such a plastic. In spite of these defects and the fact that the solution

must be analysed carefully to determine the alkalinity and the stabilizing salt content(which is present to prevent hydrolysis), this process has been referred to as the best of those available. Dense and very bright platinum deposits can be plated from a solution which contains as little as 3 g/l platinum and these coatings may be compared to rhodium deposits in quality and can only be distinguished from the latter by a trained eye. The slightly greyish shade cannot be entirely eliminated, as this is characteristic of the metal itself. On the other hand, it has been shown that the deposits are dense enough to protect silver from tarnishing in a sulphur containing atmosphere. For this purpose silver plated specimens were partly plated with platinum deposits 0.15 to 1.26 μm (6 to 50 microinches) thick and stored for 72 hours in freshly-prepared hard rubber fragments. No tarnishing could be observed on any of the specimens.

A more detailed investigation of this plating bath showed that the cathode efficiency is low at low operating temperatures. The cathode efficiency rises steeply as the temperature is increased above 30°C; above 70°C the cathode efficiency increases only slowly. Further 3 g/l platinum is the minimum concentration for this electrolyte. As the platinum concentration decreases below this value the cathode efficiency drops very rapidly. The same relationship has already been determined in the deposition of rhodium. The current density range is also restricted. In a 3 g/l platinum plating bath, the best results are obtained between 3-15 mA/cm^2 , while at 12 g/l platinum concentration the optimum current density is

between 3-25 mA/cm² at 70°C. At otherwise constant operating conditions, thicker platinum deposits can be plated. For this purpose it is important that the bath temperature should be controlled carefully and maintained at a constant value throughout the plating process since otherwise the coatings exfoliate in layers.

The Powell and Scott bath absorbs carbon dioxide from the atmosphere. Caustic soda must therefore be added from time to time with a consequent build-up of sodium carbonate in the bath.

2.5.3 PLATINUM PLATING FROM ALKALINE SOLUTIONS⁽³⁵⁾

Howell, in 1846, proposed to prepare a platinum plating bath by dissolving 1 part of the metal in aqua-regia, evaporating the solution to dryness, dissolving the residual chloroplatinic acid in water, adding 1 part of caustic potash and dissolving the resulting yellow precipitate by boiling the mixture with 2 parts of oxalic acid. This bath undoubtedly contained the platinum as a double oxalate and not as alkali platinate. Under the above conditions, the yellow precipitate formed by addition of potash is potassium chloroplatinate and this dissolves slowly in the oxalate solution to form a complex oxalate in which the metal is chiefly divalent.

In 1890, Wahl investigated true alkali platinate baths and was able to obtain bright plates from a solution of platinum hydroxide dissolved in caustic potash solution.

In 1930 when, owing to the slump, it became necessary to investigate further possible uses of platinum, attention

was turned in this country and America to the possibilities of using platinum plate as a decorative and protective coating for silver and base metals, and many efforts were made to produce a more satisfactory bath than the phosphate bath then in use. From a review of the literature it appeared that the alkali platinate solution afforded a promising field for investigation.

2.5.4 SULPHATO-DINITRITO-PLATINATE SOLUTION

The sulphato-dinitrito-platinite solution⁽³⁸⁾ is a stable bath capable of producing heavy and bright deposits on a wide range of base metals. Early in the investigations of Hopkins and Wilson⁽³⁸⁾ attempts were made to produce electrodeposits from a wide range of platinum compounds. The only promising results were obtained from solutions of complex nitritoplatinates, of general formula $K_2Pt(NO_2)_aX_{4-a}$ where X represents an anion, eg. chloride or sulphate.

Little was known of the preparation and properties of complex nitritoplatinates and an extensive study was begun of the chemistry of these compounds. A large number of compounds of this general type were prepared, including;

$K_2Pt(NO_2)_3Cl$ Potassium chloro-trinitrito-platinite.

$K_2Pt(NO_2)_2Cl_2$ Potassium dichloro-dinitrito-platinite.

$K_2Pt(NO_2)Cl_3$ Potassium trichloro-nitrito-platinite.

$K_2Pt(NO_2)_2SO_4$ Potassium sulphato-dinitrito-platinite.

The corresponding perchlorato-nitrito-platinates were also prepared, as were the sulphato-dinitritoplatinates of sodium, ammonium, lithium, magnesium, aluminium, nickel,

and zinc. Further compounds prepared and studied were the potassium dinitritoplatinite salts with acetate, borate, tartrate, citrate, fluoborate, phosphate, sulphate and sulphanilate radicals.

Practically all of these compounds in solution yielded electrodeposits of good quality on a laboratory scale, with cathode efficiencies of the order of 10 to 15 per cent. Plating tests were carried out on 1 inch square copper specimens, degreased in trichlorethylene and electrolytically cleaned in an alkali phosphate solution. Operating conditions were 0.5 A/dm^2 (5 mA/cm^2) and 40°C ; the platinum concentration was 10 g/l and platinum anodes were used. The pH of all solutions was adjusted to below 2 with sulphuric acid.

Extended plating tests were then carried out to establish the working life of the solutions, the platinum concentration being maintained by daily addition of a concentrated solution of the platinum compound. In a number of cases the solutions darkened rapidly during use, and after a time either cracked, or rough and powdery deposits were produced. In other cases, however, plating was continued until a turnover of more than 500 per cent of the initial content had been achieved.

Of all the compounds investigated they found that while sodium and potassium sulphato-dinitritoplatinites gave good results a solution containing sulphato-dinitritoplatinous acid, $\text{H}_2(\text{NO}_2)_2\text{SO}_4$, gave optimum results. A solution of this compound has now been prepared for commercial use under the name DNS platinum plating solution and patent applications covering baths of this type have been

used in a number of countries.

2.5.4.1 PLATING CONDITIONS

Good deposits are obtained from the new bath with a platinum concentration above 4g/l. Below this figure the plates are even and dark in appearance. The concentration recommended for general use is 5 g/l. Platinum anodes, which are completely insoluble, are used and the concentrated solution of DNS as necessary.

The pH of the solution has a marked effect on the plating properties. Above pH=2, black powdery deposits were obtained and there is heavy gassing at the cathode. Below this value satisfactory deposits are produced and variation of the pH below 2 leads to only slight changes in cathode efficiency.

Bright plates are produced with current densities up to 2.5 A/dm^2 (25mA/cm^2), but cracking occurs above 2 A/dm^2 . At 1.0 A/dm^2 (10 mA/cm^2) there was no evidence of cracking, but a current density of 5 mA/cm^2 is recommended for building up heavy deposits.

If the temperature of the bath is below 25°C the deposits may be rough and have a 'frosted' appearance, but in the range 30° to 70° the smooth bright character of the deposits remains unchanged. The deposition rate at 50°C is 0.1 mil in 2 hours at 0.5 A/dm^2 (5 mA/cm^2), which is ideal for general use, though for fast plating this time can be reduced to 30 minutes by using a 15 g/l bath at 2.0 A/dm^2 . Despite the low cathode efficiency of the bath no gassing occurs, making agitation unnecessary and removing the

danger of porosity due to gas pitting. There is a tendency for a slight precipitate to form in a new bath and after a few days operation the solution may need to be filtered. During use the bath gradually darkens to orange-red colour but this has no effect on plating.

Platinum from DNS solution can be deposited successfully on to copper, brass, silver, nickel, lead and titanium. Owing to the acidity of the bath it can not be used to plate directly on to iron, tin, zinc, or cadmium, and with these metals an undercoat of nickel or silver is needed.

The deposits from the new bath are exceptionally bright and lustrous at all thicknesses. Electrographic tests have shown that deposits up to 0.05 μm on polished copper are free from porosity, but that above 0.25 μm deposits are liable to show cracking. However, on etched copper surfaces, deposits in the range 0.001 to 0.002 μm can be prepared in which the cracking is much less severe than corresponding deposits on highly polished surfaces. Microhardness tests on deposits give values of 400 to 450 V.P.H.

Plates 0.001 and 0.003 μm in thickness, on polished copper, corrosion tested in 25% nitric acid, remain unattacked for four and sixteen hours respectively. Similar plates exposed over a 5% sodium sulphide solution for one week remain unattacked.

The advantage of the DNS bath may be summarized as follows;

1. The deposits are bright and smooth and no polishing is necessary.
2. Deposits may readily be obtained up to 1 mil in thick-

ness.

3. The bath is stable, gives consistent results, and does not deteriorate on standing.

4. The bath can be used for plating on some base metals.

2.5.5 PLATINUM 209*

Platinum 209⁽³⁹⁾ is represented by $\{(\text{Pt}^{\text{II}}(\text{NH}_3)_4(\text{NO}_2)_2)^{(69)}\}$.

This solution for the deposition of platinum metal has been formulated to give uniform adherent mat deposits of platinum. It uses proven chemistry resulting in reliability, reproducibility and easy maintenance. The operating conditions are given in Table 8.

2.5.5.1 BATH MAINTENANCE

2.5.5.1.1 PLATINUM METAL

Normally platinum metal ion is the only maintenance required.

All additions of the replenisher solution should be made on analysis. When working characteristics are established most additions can be based on ampere minutes.

The above recommendation does not take drag-out into account. This of course, will vary with the type of work being plated, and it was found by experience that these additions may have to be increased to compensate for it.

Overheating of the solution and the reduction in volume produced by evaporation can cause some precipitation of platinum compounds. Dilution of the solution to its original volume and heating to 80-90°C will normally dissolve most of any such precipitate.

* Trade name of Engelhard solution.

The pH of the solution was found to decrease slowly during use and should be checked periodically. To raise the pH additions of ammonium hydroxide should be made.

Loss of the conducting salt components were minimal and additions on a regular basis were not normally required. Unplasticised P.V.C. and polypropylene are the recommended materials for tank fabrication. P.T.F.E. sheathed immersion heaters should be used in conjunction with a suitable thermostat.

Continuous filtration is recommended. The rectifier employed should be equipped with an amp-meter, volt meter and infinitely variable current control. The inclusion of an amp hour minute meter in the circuit is advantageous. Engelhard recommends that the anode material used should be precious metal coated anodes to their specification.

2.5.6 PLATINUM SOLUTION 3745*

Platinum 3745⁽³⁹⁾ is represented by $\{\text{Na}_2\text{Pt}^{\text{iv}}(\text{OH})_6\}$

This solution for the deposition of platinum metal is based upon a solution of Hexahydroxy platinic acid and produces an adherent mat deposit of platinum.

Operating conditions are also shown in Table 8.

* Trade name of Engelhard solution.

2.5.6.1 BATH MAINTENANCE

2.5.6.1.1 PLATINUM METAL

Normally platinum metal ion is the only maintenance required.

As a guide 1 ampere minute deposits 30.3 mg of platinum i.e. 0.303 ml of concentrate code 3747 plating addition.

The above recommendation does not take drag-out into account. This of course, will vary the type of work being plated, and it was found by experience that these additions may have to be increased to compensate for it.

Overheating of the solution and the reduction in volume produced by evaporation can cause some precipitation of platinum compounds. Dilution of the solution to its original volume and heating to 80°C will normally dissolve most of any such precipitate. If this not effective, small additions of potassium hydroxide are beneficial. If, however, overheating has been excessive and particularly if the solution is contaminated, there may be some residue which will not redissolve. This material should be filtered off and retained for platinum recovery later.

Unplasticised P.V.C. polypropylene or stainless steel are recommended material for tank fabrication. Stainless steel or P.T.F.E sheathed immersion heaters should be used in conjunction with a suitable thermostat.

Filtration is not required. However, the rectifier employed should be equipped with an amp-meter, volt meter and infinitely variable current control. The inclusion of an amp hour minute meter in the circuit is advantageous.

The anodes should be high grade molybdenum stabilised

stainless steel.

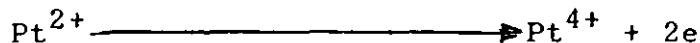
2.5.7 PROCESS SEQUENCE

1. Ultra-sonic vapour degrease. 30 seconds.
2. Cathodic clean. 1 min, 60°C, 40mA/cm².
3. Demineralised water rinse.
4. 50 v/v hydrochloric acid. 5mins., 50°C.
5. Demineralised water rinse.
6. Pt 209, 8 mins., 20mA/cm², 90°C, pH=8.0-9.0.
7. Demineralised water rinse.
8. Pt 3745, 110 mins, 7.5mA/cm², 80°C, pH≥12.0. 10um.
9. Demineralised water rinse. (Also used to top up No 8.)
10. Demineralised water spray rinse.
11. Dry.

2.6 LOSS OF STABILITY OF PLATINUM FROM BECOMING OXIDISED

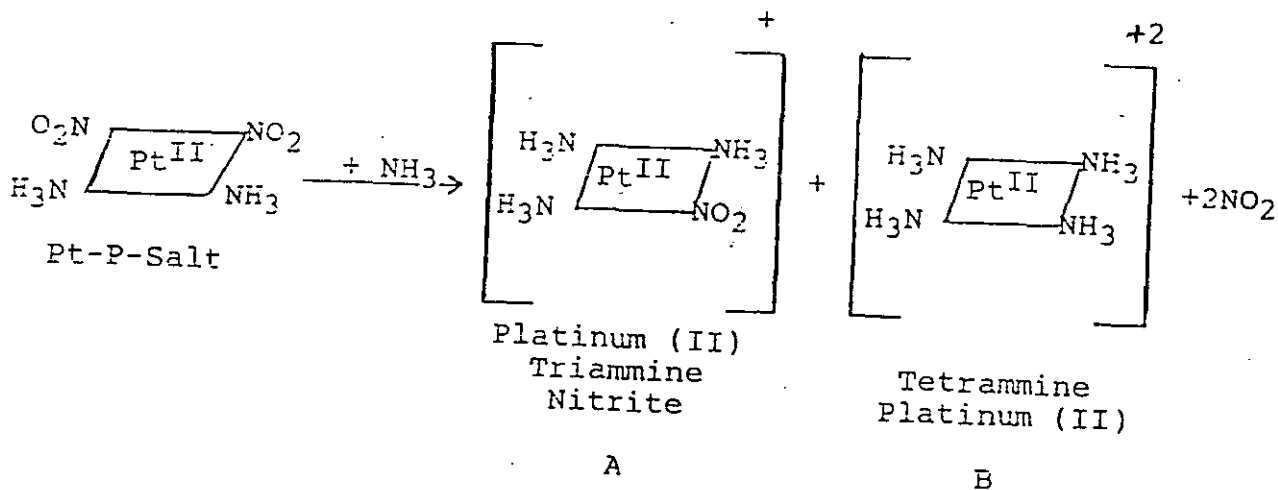
According to the method of manufacture of platinum solution(ENGELHARD)⁽³⁹⁾, plating efficiency of the 'p'salt solution tends to decrease with time and use. On initial make up the efficiency should approach 15% (ie, 1um deposited in 15 minutes), however, this will drop depending on the bath's workload and overall age.

The reason for the decline in efficiency was initially thought to be due to oxidation of the platinum; ie,

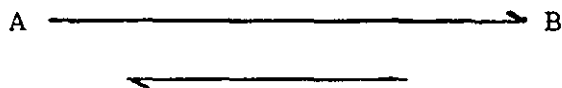


However, recent NMR(nuclear magnetic resonance) studies have shown that the formation of an electrochemically stable species may hold the key to a steady decline in plating efficiency.

i.e.:



During the dissolution of 'p'salt in aqueous ammonia, two distinct products are formed. In a newly prepared bath the following equilibrium is formed;



As the bath is worked, the equilibrium slowly drifts towards species B. This shift is speeded by high current density plating through preferential depletion of complex A.

To reduce this drift there are two important factors to consider. Firstly, a high excess of ammonia will tend to drive the equilibrium from left to right. Hence, the bath

should be operated at the low end of pH range. Secondly, the replenisher stocks should be kept to a minimum to prevent 'long storage' decomposition.

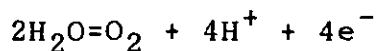
2.6.1 ELECTROCHEMICAL PROPERTIES OF THE PLATINUM METALS (40)

It is often possible to understand, and indeed to predict, experimental results or practical applications in the field of electrochemistry and corrosion, by bearing in mind the fundamental principle that any change is impossible unless it tends to the realisation of a state of thermodynamic equilibrium.

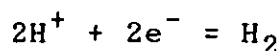
The conditions of thermodynamic equilibrium of all the reactions that can occur when a metal is in contact with an aqueous solution at a given temperature are expressed on potential-pH diagrams in which the equilibrium potential is plotted against pH for each reaction. As will be shown in future work, any solid, liquid, gaseous or dissolved substance having a definite chemical potential is thermodynamically stable in the presence of an aqueous solution only in conditions corresponding to certain definite domains in potential-pH diagram. The limits of these domains depend on the concentrations and presences of the substances present. These diagrams must be regarded only as rough approximations, and the conclusions to which they lead must be accepted with reserve, but they do nevertheless, provide an interpretation of observed facts sufficiently accurate for many purposes and they indicate

profitable lines for further experiment. They show the conditions in which the occurrence of a given oxidation and reduction reactions is possible from the thermodynamic standpoint, and enable one to predict and interpret many phenomena in the fields of electrochemistry, of corrosion, of electrodeposition, of cathodic protection and other branches of electrochemistry.

The form of potential-pH diagrams is best considered by reference to a simple example, that of water, which is shown in Fig 10. The dotted line x refers to the conditions of equilibrium of the reaction;



and the line y to;



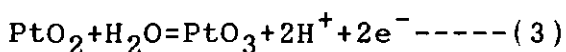
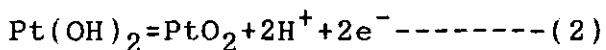
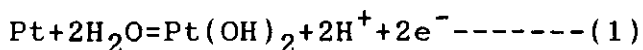
At equilibrium the pressure of oxygen and hydrogen in the respective reactions is equal to one atmosphere. The area shown in Fig 11, enclosed by the two lines x and y, represents the domain of thermodynamic stability of water at 25° C and one atmosphere; outside the two lines x and y is this pressure is greater than one atmosphere, hence oxygen and hydrogen tend to be evolved and the water is no longer stable.

2.6.2 APPLICATIONS IN ELECTROCHEMISTRY⁽⁴⁰⁾

PLATINUM

A potential-pH diagram Fig 14 for the platinum-water system at 25°C was obtained (Equation.2) by a consideration of the following six reactions;

Heterogeneous reactions involving two solid components-electrochemical reactions;



Substituting the relevant values of E in the expression in equation(4)

$$E = E^\circ - (0.0591 \ln pH) / n + (0.0591) / n \{ \log(B) - \log(A) \}$$

where E=equilibrium potential

and E° =standard equilibrium potential, a quantity which can be calculated from thermodynamic properties of the reaction components.

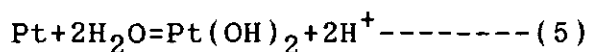
(A) and(B) represent the concentrations of the components A and B and remembering that since, in these cases, the components A and B are solids the equilibrium is not dependent on their concentration, the following values for equilibrium potential E are obtained;

For reaction(1); $E = 0.980 - 0.0591\text{pH}$

For reaction(2); $E = 1.045 - 0.0591\text{pH}$

For reaction(3); $E = 2.000 - 0.0591\text{pH}$

Heterogeneous reactions involving one solid component-
chemical reaction;



By substitution in equation(6)

$\text{alog}(\text{A}) - \text{blog}(\text{B}) = \text{logK} - m \text{pH} \text{-----} (6)$, non-oxidising reaction
involving hydrogen ions

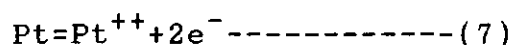
where;

K=equilibrium constant

m= coefficient of hydrogen ion

$$\text{log}(\text{Pt}^{++}) = -7.06 + 2\text{pH}$$

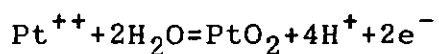
Electrochemical reactions



substituting in equation(8)

$\text{E} = \text{E}^\circ + 0.0591[\text{blog}(\text{B}) - \text{alog}(\text{A})] \text{---} (8)$, oxidising reactions
not involving hydrogen ions.

$$\text{E} = 1.188 - 0.0295 \text{log}(\text{Pt}^{++})$$



where

$$\text{E} = 0.837 - 0.1182\text{pH} - 0.0295 \text{log}(\text{Pt}^{++})$$

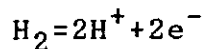
2.6.3 ELECTRODEPOSITION OF PLATINUM

Fig 12 (or Fig 14 drawn in bigger scale) indicates that metallic platinum is stable in aqueous solution at low potentials, hence it can be deduced that elemental platinum will be formed by the reduction of aqueous solutions of its salts. Such reduction may be achieved electrolytically and platinum is electrodeposited on a commercial scale from electrolytes comprising solutions of complex salts.

Fig 13, deduced from Fig 12, shows the theoretical conditions for the corrosion, immunity and passivation of platinum. Platinum is seen to be very noble metal since its domain of stability covers most of the domain of stability of water.

2.6.4 PLATINUM ELECTRODES FOR THE MEASUREMENT OF pH

Platinum is stable under the conditions of potential and pH corresponding to the equilibrium of the reaction;



indicated in fig 12 by line x. This reaction can be accomplished practically reversibly on the surface of platinum which has a great facility for absorbing hydrogen. Because of this, platinum can, as is well known, be used for the construction of hydrogen electrodes for the measurement of pH, particularly since it can be employed in a finely divided form previously saturated with hydrogen by cathod-

ic treatment. The potential of this electrode depends on pH and on hydrogen pressure according to the following equation, at 25°C;

$$E=0.000-0.0591\text{pH}-0.0295\log P_{\text{H}_2}$$

when the hydrogen pressure is one atmosphere this relation can be simplified to

$$\underline{E=-0.0591\text{pH}}$$

In the study of electrode processes with solid electrodes, it is essential to keep in mind the possibilities of the electrode surface. For example, films of oxide and adsorbed oxygen are formed by anodic polarization. Such films can be reduced by subsequent cathodic polarization, and this may interfere with the electrochemical reaction being studied. Likewise, the deposition of a metal on a platinum electrode may result in the formation of an alloy at the interface platinum deposited metal. When the platinum electrode is subsequently cleaned in acid, the alloy is generally attacked and the surface of the platinum electrode is altered. One should also remember that the effective area of a solid electrode is not the geometric area one measures without taking into account the 'roughness' of the electrode. The roughness factor, ie. the ratio of the actual area to the apparent geometric area, may be of the order of 2 or even larger according to the treatment of the metallic surface. Limiting currents are mainly determined by the apparent geometric area of the electrode rather than by the true area, because of the rapid depletion of the reacting species in the 'crevices' at the electrode surface. Conversely, currents resulting from the charging or discharging of the double layer are approxi-

mately determined by the true area of the electrode.

2.6.5 CURRENT EFFICIENCY OF ELECTRODE PROCESSES

2.6.5.1 CONDITIONS CONTROLLING THE EFFICIENCY OF ELECTRODE PROCESSES

The following conditions should be fulfilled to obtain 100 per cent current efficiency in electrode processes;

- (i) there should be no side reaction,
- (ii) there should be no leak in the electrical circuit.

The first condition requires a detailed discussion; the second one can be disposed of very simple by assuming that the equipment being used is in satisfactory condition.

Various side reactions can be distinguished according to the nature of the reacting substances, and the following types of substances will be considered;

- (1) the solvent
- (2) the electrode (oxidation of the electrode)
- (3) substances which are not consumed or liberated in the electrode process (supporting electrolyte, dissolved oxygen)
- (4) the products of electrolysis.

Type(1) has been investigated using the current-potential relationship.

2.6.6 CHARACTERISTIC OF PLATINUM COATED ANODES

Insoluble anodes have the ability to pass current to the plating solution in which they are immersed, but they do not dissolve in proportion to Faraday's law like sacrifi-

cial anodes. A.J.Haley⁽⁴¹⁾ has carried out some work on different materials and especially platinum valve metals. Valve metals have the ability to pass current to a plating solution when they are used as a cathode, but they will not pass current when they are used as an anode. When made anodic, a very tenacious oxide film is instantly formed on the surface, preventing the flow of current. Because of this unique ability, he used tantalum to rectify alternating current to direct current in some applications many years ago, but it never found widespread use. The tenacious oxide film not only prevents the flow of current but protects the underlying valve metal so it does not dissolve in most plating solutions and consequently does not introduce contamination. He also showed that tantalum has the highest anodic breakdown potential (anodic breakdown potential refers to the voltage required to initiate breakdown or disintegration of the tenacious oxide film on a valve metal) in the electrolytes and titanium the lowest, with niobium (columbium) falling in between. It is obvious that pure titanium is perfectly suitable for use as an anode material in most plating operations where the anode voltage does not exceed 12 volts. Typical of these operations in rack plating, in gold and other plating solutions.

2.6.7 ANODE WORKING AREA

With the understanding that the platinum coated area of an anode is the only area that functions in a plating bath, it is easy to measure the working area of a platinum

coated solid sheet anode. If the sheet is 30.5*30.5 cm and is completely coated on one side, the working area is $30.5*30.5=930 \text{ cm}^2$. If it is completely coated on both sides the working area is 1860 cm^2 .

Unfortunately, measuring the working area of an expanded mesh anode is not as simple. A diamond size area, defined as the major and minor axes of the diamond area, and strand size ie., the width and thickness of the metal strands surrounding the diamond shaped holes, are the principle factors that determine the area of the mesh. The specific area of a piece of mesh is the total area, including the inside, outside, front side and back side of the strands, as well as the area existing at the intersections of strands at the points of the diamond.

Measurements of specific area carried out by above investigator were made using voltage-amperage curves developed at values below the theoretical reversible potential and comparing unknown areas against accurately prepared standards made of thin solid sheet. Samples of some commonly used titanium meshes were selected for specific area measurement based on the fact that all samples had the same diamond size and only the strand size of each sample was different. He illustrated that when an anode to cathode ratio at least 1:1 is required for a particular plating operation, it is essential to have a reasonably accurate value for the working area of the mesh anode used in the process. The 25.4*25.4 cm anode does not have a working area of 645 cm^2 . as one might calculate by multiplying the length times the width but rather about one-half of that area if it is completely coated with platinum. It may

be necessary to select mesh anodes with larger strand dimensions in order to obtain a 1:1 anode to cathode ratio in this case. The specific area of an anode changes significantly with a change of only 0.02 cm on the width and thickness of the strands, so that a 0.76*0.76 cm strand mesh has a specific area almost 40% larger than the 0.5*0.5 cm mesh with the same size diamond area.

2.6.8 EFFECT OF CURRENT DENSITY

Haley⁽⁴¹⁾ showed that the life of platinum coating is depend upon the current density. As current density increased, the platinum wear rate increases and the anode life becomes shorter as an exponential function.

2.6.9 PREPARATION OF CLEAN ELECTRODE SURFACES

Two general methods of preparing a clean surface exist. The first involves preparing a fresh surface by evaporation of metal or by cleaving or abrasion of a solid sample. Such techniques must generally be applied in vacua and require ultra-high vacuums to prevent rapid contamination of the fresh surface. Such techniques have rarely been applied to the study of solid electrodes. The second method involves cleansing of a contaminated surface (any surface exposed to the atmosphere for even an instant must be assumed contaminated). Of course, any cleaning procedure can be held suspect of incorporating foreign atoms into the surface layer. Ultimately we may only judge the efficacy of a cleaning procedure from the properties of

the resulting surface. It has long been recognized that combined anodic and cathodic pulsing of platinum electrodes causes them to behave more 'actively' with respect to certain electrochemical processes, particularly hydrogen evolution. Some investigators feel that anodic activation operates, not simply through the cleansing of the platinum surface, but through such indirect mechanisms as absorption of oxygen, production of 'active oxides' and recrystallization of the surface. The fact that can be established is that the 'active' state may be produced through anodic (or anodic-cathodic) pretreatment and that this state may be retained for as long a period as is permitted by the level of solution purity. Stirring of the solution hastens decay of the 'active' state, and purification of the solution delays this decay. If highly developed surfaces are used, the active state may be retained for hours. This would be anticipated on the basis of decreased transport of contaminants per unit area of 'true' surface.

2.7 BRUSH PLATING⁽⁴²⁾

2.7.1 INTRODUCTION

Brush plating is an electroplating process that is performed with a hand-held or portable plating tool rather than a tank of solution. The brush plating process is also called contact plating, selective plating or swab plating.

In its simplest form, the brush plating process is similar to a painting operation. The operator soaks the plating

tool in the solution and then deposits the plating material by brushing the plating tool against the base material. Plating solution is delivered to the work area by a porous, absorbent cover wrapped over the anode of the plating tool.

A portable power pack provides a source of direct current for the process. The power pack has two leads. One is connected to the plating tool and the other is connect to the part being plated.

A direct current circuit is completed when the plating tool is placed on the part and electroplating occurs. The plating tool is always kept in motion whenever it touches the part to assure that a sound deposit is applied.

Operations which prepare the base material for plating are similar to the plating operation itself. Performed prior to plating, these operations ensure an adherent deposit.

2.7.2 SOLUTIONS

Brush plating solutions can be divided into three groups according to their use. (Tables 9-10 lists those commonly used.

The first group contains preparatory solutions. These are used to prepare various types of base material for plating. Preparatory solutions are used prior to plating. They condition the surface so that an atomic bond will develop between the plating material and the base material.

Preparation procedures have been developed for all the base materials commonly encountered. These include steel, cast iron, stainless steel aluminium, copper-base alloys

and nickel-base alloys. When the procedures are properly followed, the strength of the bond between the plating material and the base material is equivalent to the cohesive strength of the base material itself.

Preparation of a base material usually begins with pre-cleaning. This is followed by electrocleaning and then electroplating. Depending on base material, a desmut, active and/ or pre-plate step may be required.

The second group of solutions consists of the plating solutions. Solutions in this are used for depositing a wide variety of pure metals or metal alloys onto base material. Brush plating solutions are quite different from those used for tank plating. There are several reasons for the difference.

Compared with tank plating solutions, the solution used for brush plating have a higher metal content, are less likely to utilize a toxic material such as cyanide, are more likely to use metal-organic salts rather than metal-inorganic salts and are more likely to be complexed and/or buffered with special chemicals.

The solutions used for brush plating must produce a good quality deposit over a wider range of current densities and temperatures than plating solutions. They must plate rapidly, operate with insoluble anodes and produce a good yield, i.e, plate a good deposit under identical conditions for a prolonged period of time. In addition, the solutions should be as nontoxic as possible; and they should not require chemical control by the operator. Special formulations are required to achieve these objectives.

The third group contains special solutions. These are

solutions that have been developed to meet specific application requirements such as anodizing, specialized black optical coatings, electropolishing, etc.

2.7.3 ADVANTAGES AND DISADVANTAGES

Brush plating is used approximately 50% of the time because it is a better way to apply an electroplate, and 50% of the time because it is a better repair method for worn or mismachined parts.

Whether or not brush plating should be used instead of tank plating, welding or metal spraying, depends on the specific application. There are distinct advantages and disadvantages which should be considered. Some advantages of brush plating over other repair methods are;

(a) The equipment is compact and portable. It can be taken to the part without tearing down process assemblies and without moving large process components.

(b) No special surface preparation such as knurling, grit blasting or undercutting is required. The only requirement is that the surface be reasonably clean. Usually this can be accomplished by solvent cleaning, sanding, etc.

(c) The part being plated is not heated significantly. Only occasionally is the part heated to approximately 54°C, and never does the temperature of the part exceed 100°C. Hence, distortion of the part does not occur.

(d) The process can be used on most metals and alloys. Excellent adhesion is obtained on all of the commonly used metals including steel, cast iron, aluminium, copper, zinc and chromium. Adhesion is a limiting factor only on some

uncommon metals such as titanium and tantalum.

(e) Parts having a wide variety of size and shape can be brush plated.

Some disadvantages of brush plating are;

(a) The rate at which the deposit is applied is moderate. Even though deposits are applied at least 10 times faster than tank plating, this is still considerably slower than metal spraying or welding.

(b) The deposits are limited in hardness and are not used when extremely higher wear resistance is required.

2.8 BASIC ION CHROMATOGRAPHY

2.8.1 HISTORY

Since its introduction in mid-1970's, Ion Chromatography (IC) has become a widely used analytical technique for the determination of all types of ions.

Ion Chromatography is a liquid chromatographic technique using ion exchange mechanism and suppressed conductivity detection for the separation and determination of anions and cations. Other detection schemes can be employed with IC such as electrochemical, UV/VIS, and fluorescence detection.

Chromatography as a separations technique, was commenced and the word chromatography coined by Mikhail Tswett, a Russian botanist, in 1903. Tswett described his work on using a chalk column to separate the pigments of green leaves.

He described the coloured zones that moved down the column as "colour writing" hence, chromatography⁽⁴³⁾. Since then,

various people have slowly added to our knowledge of liquid chromatography as shown in Tables (11-12).

Ion exchange chromatography is probably the oldest separation and purification process reported in the literature, possibly dating back about 5,000 years to the times of Moses when he threw a decomposed log (which acts as an ion-exchange resin), into a pool of brackish water at Marah. Apparently, the exchange of ions made the water drinkable⁽⁴⁴⁾.

Chromatography basically involves separation due to difference in the equilibrium distribution of sample components between two different phases. One of these phases is a moving or mobile phase and the other is a stationary phase. The sample components migrate through the chromatographic system only when they are in the mobile phase. The velocity of migration of a component is a function of the equilibrium distribution. The components having distributions favouring the stationary phase migrate slower than those having distributions favouring the mobile phase. Separation then results from different velocities of migration as a consequence of difference in equilibrium distributions.

2.8.2 THE ION CHROMATOGRAPHY

The components of a typical Ion chromatography are schematically indicated in figure 15.

2.8.2.1 PUMPS

The mobile phase or eluent in Ion chromatography is, of

course, a liquid. Some means of propelling it constantly and precisely through the column is required. There are two major types of pumps used, constant pressure and constant displacement. The Dionex 2000i analytical pump is a constant pressure/constant flow pump.

2.8.2.2 INJECTORS

The sample should be introduced at the head of the column with minimum disturbance of the column packing. A loop valve injector is used in the Ion chromatography. This type of injector is commonly used for injecting volumes greater than 10 microliters. Shown schematically in figures (16-17), in the load and injection positions, the sample loop is filled at atmospheric pressure. When the valve is actuated, the sample in the loop is swept into the flowing eluent stream and onto the column.

2.8.2.3 COLUMNS

The analytical column is the heart of an Ion chromatography. The success or failure of an analysis depends on the choice of column and proper operating conditions. The analytical columns used in the Ion chromatography have typical inside diameter of the Dionex ion exclusion column (HPICE) is 9 mm. The length of the analytical column is dependent upon both the type of packing and type of application. The columns are typically made from either a fluoropolymer or epoxy. They are generally operated at ambient temperatures, however, elevated temperatures can

be used. The individual column packings are dependent upon the mode of separation, ie. HPIC, HPICE, or MMPIC.

2.8.2.4 DETECTORS

A detector is required to sense the presence and measure the amount of a sample component in the column effluent. Good IC detectors exhibit high sensitivity, low noise, a wide linear response range, and response to all types of ions. A low sensitivity to flow and temperature fluctuations is also desirable.

The workhorse detector of Ion Chromatography is the conductivity detector. Conductivity is a universal property of ionic species in solution and shows a simple dependence on species concentration. However, the conductivity from the sample ions may be "masked" by that from the much more abundant eluent ions. This detection problem is alleviated by using chemical suppression which reduces the background conductivity of the eluent to a low or negligible level. The chemical suppression is accomplished by using a suppressor device which is either an ion exchange resin or ion exchange membrane. The suppressor also converts the sample ions to a single highly conductive form. The conductivity detector provides high sensitivity and selectivity. IC is not limited to conductivity detection. Electrochemical, UV-VIS, and fluorescence detectors are also compatible with the Ion chromatography, thus increasing the problem solving capabilities of Ion chromatography.

2.8.2.5 DATA HANDLING

Electronic integration offers the ion chromatographer highly precise and automatic conversion of the chromatographic signal into numerical form. This technique eliminates errors from the recorder since the detector output is sent directly to the integrator. The electronic integrator is a device which automatically measures the peak area or height and retention times. More sophisticated versions correct for baseline drift. Integrators generally give better accuracy and precision for peak and area measurements compared to manual determinations.

The results of the chromatographic separation may be displayed on a strip chart recorder. From a chromatogram, the retention time or volume can be obtained. This may be used, if conditions are properly controlled, to qualitatively identify a component. The area under the peak and the peak height are proportional to concentration and can be used to obtain quantitative results.

2.8.3 THE USE OF ION CHROMATOGRAPHY IN THE ELECTROPLATING INDUSTRY⁽⁴⁵⁾

The rapidly growing area of circuit technology is placing higher demands on the analytical techniques required for maintenance and troubleshooting of plating baths, etchants, cleaning solutions and rinse waters. Analytical techniques offering speed, ease of operation and versatility are needed. The purpose of using IC is to demonstrate how ion chromatography has been and can be applied for the determination of major constituents as well as trace

contaminants in these types of solution.

Ion chromatography(IC) is a technique which can be used to rapidly detect, identify and quantify a wide variety of ionic species. Some species of special interest include metal complexes ($\text{Au}(\text{CN})_2^-$, $\text{Au}(\text{CN})_4^-$, $\text{Co}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{Ni}(\text{EDTA})^{2-}$, $\text{Cu}(\text{EDTA})^{2-}$); common anions (Cl^- , Br^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} , BF_4^-); cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}); organic acids (citric, formic, succinic) as well as carbonate and borate); transition metals (Fe^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+}); and surfactants such as sodium lauryl sulphate.

2.8.4 PRINCIPLES OF THE TECHNIQUE

Ion chromatography(IC) is modern analytical technique which specifically addresses the chromatography of ionic species. The system, which is schematically depicted in figure 15 , consists of an eluent delivery mode, a separation mode, and a detection mode. An eluent is pumped through the system and a liquid sample is introduced into the flowing eluent stream via an injection valve situated upstream of the separator column. The eluent flow carries the ionic species through an analytical column that contain a neutral, anionic or cationic resin. Since the respective ionic species present in the sample have different affinities for the resin, they are separated into discrete bands before entering the detector. Identification and quantification are determined by comparing the retention times and peak heights with those of known standard solutions. Data reduction is accomplished manual-

ly or by use of electronic integration.

2.8.5 MODES OF SEPARATION

The separation mode employed depends upon the ionic nature of the sample ions of interest. Three distinct separation modes can be employed and are summarised in Table 13.

(i) High performance Ion chromatography(HPIC) is the mode of choice for common inorganic ions such as F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Fe^3 and Zn^{2+} . The separation, based on ion exchange, is accomplished on a low capacity ion exchange resin. The theory of HPIC has been discussed by Small, et al⁽⁴⁶⁾.

(ii) Mobile phase Ion chromatography(MPIC) is the optimal separation mode for hydrophobic ions such as alkyl and aryl sulphonates and sulphates, metal cyanide complexes, SCN^- , BF_4^- , and quaternary and alkyl amines. The mechanism of separation is ionpairing and adsorption which occurs on a neutral resin. This separation theory has been discussed in depth by Iskandarani⁽⁴⁷⁾ and Bidlingmeyer⁽⁴⁸⁾.

(iii) High performance Ion chromatography Exclusion(HPICE) is commonly used for the separation of weak organic acids such as formic, succinic and citric. The mechanism is predominantly dependent on pKa values and ion exclusion; however, adsorption also plays a role. The column packing material utilised in all of the separation modes, regardless of the resin functionality, is based on a polystyrene-divinylbenzene (PS/DVB) support. Unlike silica based packing these resins are stable from pH (1-13). The excel-

lent durability of the column packing material allows easy column clean-up with either strong acid or strong base. Detection of the ions of interest can be accomplished in a variety of ways, depending upon the chemical and optical properties of the sample ions. Four distinct detection modes are employed and these are summarised in Table 17. Suppressed conductivity is the most common detection mode used for ions with pH values < 7 . Highly conductive eluents are required to elute the sample ions from the separator column. If a conductivity detector cell was placed immediately after the separator column, the sample ions would be detected as small conductivity changes in a large background signals. Insertion of a suppressed, a second ion exchange device connected in series after the separator column, chemically converts the eluent to a less conductive form. The sample ions are thus detected as large changes in a low background conductivity. This increases sensitivity, extends the linear range and promotes selectivity in detection. The actual suppression mechanism differ, depending on the chemical content of the eluent. Small et al⁽⁴⁶⁾ should be consulted regarding the actual mechanisms.

2.8.6 METHODS DEVELOPMENT

To solve an ion analysis problem, the analyst needs to select the best separation and detection modes for that sample(analyte and matrix). Factors that must be considered are;

(a) complexity of the sample

- (b) sensitivity required
- (c) speed
- (d) reproducibility

Optimizing a method may require a certain amount of compromise. With the availability of packing materials of varying capacity and selectivity as well as a wide range of detectors, the analyst has a variety of tools that can be used to optimize a method to his specific requirements.

2.9 PULSE PLATING

2.9.1 INTRODUCTION

Pulse plating has gained acceptance in some sectors of the metal finishing industry, especially electronics, gold plating and finally decorative applications. The pulsed current has beneficial effects on deposit properties, for example, many investigators⁽⁴⁹⁻⁵⁰⁾ have reported that coatings with fine grain structure, high purity and low electrical resistance can be obtained for copper, silver, gold and palladium.

Pulse plating can be defined as a method of electroplating by means of an 'on-off' direct current or potential in place of the continuous direct current used in conventional plating. Electrodeposition of metals using pulsed-current electrolysis has been extensively studied in recent years⁽⁴⁹⁻⁵²⁾. Metal deposits produced by pulsed-current electrolysis have many properties distinguishing them from those obtained by direct current electrolysis.

N.Kubota⁽⁵³⁾ has investigated the effects of using pulse plating upon the platinum('p'salt)complex solution and has shown that in the electrolysis of platinum, increasing the pulsed-current density (i_p)while decreasing the on-time and off-time periods has reduced the hydrogen co-deposited hydrogen, and subsequently improved current efficiency. The increase of i_p has shifted the cathode potential to the more negative value.

using the normal plating , the higher the current density being used the less time the 'adion' have to find the most suitable discharge sites which could lead to greater distortion in the growing lattice. In practice this distortion would show up as 'stress' in the deposits. It is an ideal to measure the internal stresses within the deposit while the electroplating process is taking place. Therefore, a stressmeter should be used during plating.

2.9.2 THE TERMINOLOGY OF PULSE PLATING

Pulse plating can be defined as current-interrupted electroplating. Figure 18 shows the typical square-wave form. Figure 19 is a typical oscilloscope trace of a square wave attainable with existing pulse equipment. However, the figure does not show a pure square wave because there is a gradual curvature to both the ascending and descending current flows. The curvature on the rising flow is intentionally induced electronically to avoid an instantaneous rise and current overshoot.

This type of pulse process is suggested as a means of

obtaining smooth and bright deposits. If, for example, dc flows for five sec and is interrupted for one sec between periods of flow, there is greater opportunity for replenishment of the cathode film through diffusion and convection. Cathode polarization is decreased, and cathode efficiency may be increased. Consequently, a higher current density can be used and a desired thickness can be deposited in less time, even though the current is not flowing continuously. In pulse electrolysis, selection of the electrolyte, peak current density, on-time, and off-time determine the physical characteristics of the electrodeposits.

The process of pulse plating is that during the period when the current is on, the metal ions next to the cathode are depleted as in the normal way, but during the time that the current is off, the processes of mass transport via diffusion, ionic migration and convection, (both natural, and forced by agitation), have time to replenish the concentration of metal ions within the diffusion layer at the cathode, and do the same for negative ions in the analogous layer at the anode. When the current is then switched back on again, the cell can operate with better than average efficiency, reduced stress, and possibly higher than normal plating rates can be achieved even after the current 'off'-time has been accounted for.

The application of a pulsed current(P.C) has shown that due to the surplus of electrical measures/parameters present, the mechanical properties of some materials could be particularly influenced. This particularly important

parameter is known as the 'off' or 'dead'time and when the current is off, desorption phenomena will take place. Desorption is defined as ions may break away from the metal surface and move off into the solution and new atoms may then ionise to replace the desorbed ions. Due to the desorption of decomposition products of salts, the metal density, the ductility, in certain cases even hardness increases and the tendency to produce porosity is reduced.

In pulse plating it is possible to control four parameters which will depend on the equipment used. Figures 18-19 illustrate these parameters and are followed as;⁽⁵⁴⁻⁵⁵⁾

- (1) width,(on-time), the length of individual pulses.
- (2) delay,(off-time), the length of time between individual pulses.
- (3) frequency, the number of pulses of electricity and it can be expressed as;

$$F(\text{frequency})=1/(\text{on time} + \text{off time})$$

- (4) current density, the amount of current per square centimetre supplied to the cell during each pulse.

Other advantages include wider current density range for alloy plating. Faster coverage on molybdenum or tungsten surfaces and fifty microinches of pulse plated Gold seems to have the same corrosion resistance as 100 microinches of D.C plated Gold deposits.

The use of pulsed current is quite well known as a re-

search tool for studying the electrodeposition mechanism of metals. With increasing emphasis on the properties of the deposits, it is therefore realised that this method of deposition could well provide a means of improving their properties. However, the good metal deposits are⁽⁵⁶⁾ produced by pulse plating in the frequency range of 10-500 Hz.

Ibl et al⁽⁵⁷⁾ have shown that, with using short pulses of large current amplitude followed by a relaxation time adequately long to allow complete relaxation of the diffusion layer, good quality deposits can be obtained. Also Gurovich and Krivtsov⁽⁶⁸⁾ have shown that increasing pause - to pulse ratio will result in a decrease in the surface roughness of metal deposits.

According to Viswan and Raub⁽⁵⁹⁾, with short current pulses and longer 'off' times, no significant diffusion polarisation occurs during plating.

Licarnini and Ibl⁽⁶⁰⁾ has reported that with pH=9 and high current density, it is possible to produce palladium coatings of 5 um thickness without cracks and porosity. As the current density (c.d) increases, the hardness and number of cracks decreases.

Hayashi, Kitanishi and Fwkumoto⁽⁶¹⁾ have shown the effect of 'off-time' [T] increases, with the duty cycle in the following order of 1/25 to 1/250, formation was favoured of granular growth to the block type deposits with the constant current ($50\text{A}/\text{dm}^2$) and T(0.5 or 1ms). Using X-ray diffraction analysis, it was found that with lower current density range ($0.5\text{-}1\text{A}/\text{dm}^2$), the domain size is greater

than 5000\AA and there is rather high stress in the deposits in the case of silver-ammonia bath. However, with silver deposits in cyanide bath, small domain size of about 3000\AA and low internal stress in deposits will result.

Popov, Maksinovic and Stevanovic⁽⁶²⁾ have reported that with increasing pause - to pulse ratio in pulsating current deposition leads to a decrease in the size and increase in the number of growing grains.

Raub and Knodler⁽⁶³⁾ have reported that with polymer formation in deposits of hard gold, the nickel and cobalt content are increased and at the same time reduces the oxygen, carbon and nitrogen/hydrogen contents. High bright deposits can result from high nickel but low polymer concentration.

CHAPTER 3

3.0 EXPERIMENTAL METHODS EMPLOYED

3.1 GENERAL DESCRIPTION OF THE EQUIPMENTS

Table 15 shows the list of main items used for pulse and conventional-plating.

3.1.1 POWER MOSFETS

The function of Power Mosfets is to offer the superior characteristics of field effect transistors at true high power levels. Power Mosfets simplify circuitry because they are voltage - controlled devices and require only very small instantaneous current from the signal source.

The advantages of Power Mosfets are;

1. They achieve switching times of less than 100 nanoseconds at high current levels.
2. They have great ruggedness because of the absence of the second break down failure mechanism of bipolar transistors.
3. In parallel operation they inherently 'current share' rather than 'current hog'. The stability of the gain and response time characteristics over a wide temperature range is outstanding.

Power Mosfets are majority carrier semi-conductor devices, and their construction and principles of operation are fundamentally different from those of traditional bipolar transistors, which are minority carrier semi-conductors as

shown in Fig 20.

The terminology used is referred to drain, gate and source, rather than to collector, base and emitter respectively for a Mosfet and this terminology is compared and shown in Fig 20a. Fig 20b shows the voltage must be applied between the gate and source terminals to produce a flow of current in the drain.

The gate is isolated electrically from the source by a layer of silicon oxide. Theoretically no current flows into the gate when a direct current (D.C) voltage is applied to it - though in practice there will be an extremely small leakage current, in order of nanoamperes.

The extremely low drive current requirement, ie, (input is low but output is high) of the power Mosfet, and the associated extremely high gain are a major advantage over the conventional bipolar transistor. The much lower drive requirement of the Mosfet will usually mean that the vastly superior switching speed will offer the possibility for lower losses current efficiency, or higher operating pulse frequency.

3.1.2 OSCILLOSCOPE

The oscilloscope used was a Philips type and the function of the oscilloscope is to show the variations in potential on the screen of a cathode ray tube, by means of deflection of a beam of electrons, (ie, variations of current as a wavy line).

3.1.3 POWER SUPPLY

A D.C power supply was used to produce a current up to 10 A. The current stability was determined by means of measuring output variations and this was shown to be effective by following causes;

- (a) current instability
- (b) mains supply change
- (c) temperature change in the equipment.

3.1.4 PULSE GENERATOR

The function of pulse generator is to provide a wide range of facilities and operating modes. ie, producing a train of square pulses.

Period is adjustable in seven decade ranges from 100ns(10MHz) to 10(1Hz) and a fine control is provided to give continuous adjustment between ranges.

The output is similarly adjustable from 30mV to 10V into 50 .

The instrument is normally supplied set for operation from an AC mains supply of 198 to 260 volts but can be supplied or adjusted for operation from 95 to 130 volts.

3.1.5 ATOMIC ABSORPTION SPECTROSCOPY

For the analysis of the alloy composition Pt or Pt alloy deposits electroplated on mild-steel/nimonic alloys was determined by atomic absorption spectroscopy(Varian 775

with Graphite Furnace).

3.1.6 ION CHROMATOGRAPHY

For the analysis of all anions such as Nitrates, Nitrites, Phosphates, Sulphates, Chlorides, Fluorides and etc, ion chromatography(Dionex 2000I/SP)with a computing integrator was used.

3.1.7 SCANNING ELECTRON MICROSCOPY (S.E.M)

Scanning electron microscopy studies of electro-deposited were carried out on plated samples from most platinum solutions. Energy dispersive X-ray analysis (EDX) was used to determine the percentage of Pt,Al and Ni present in the alloys to be analysed. Samples were mounted in conductive bakelite, polished to one micron surface finish. Percentage of iron and nickel as well as platinum in the alloys can effectively be analysed with the EDX system.

3.1.8 ADHESION DETERMINATION

The method of (tape test) ie adhesion test was carried out with mild steel specimens resulting from the nineteen solutions. These tests were carried out on specimens such as; 2-40 mA/cm² current densities using pulse plating and conventional plating in platinum solution. The method of 'tape test' according to British standard BS 5411 was followed that an adhesive cellulose tape with an adhesion value of approximately 8 N per 25 mm

width, whose adhesive side is applied to the coating under test, using a fixed - weight roller. Care was taken to exclude all air bubbles and after an interval of 10 seconds, the tape was removed by applying a steady pulling force to the tape, perpendicular to the surface of the coating. The adhesion of the coating was such that there was no evidence of detachment of the coating.

3.1.9 CURRENT EFFICIENCY DETERMINATION

Equation below gives the theoretical maximum mass of substance which can be discharged by a given current in a given time. Current efficiency refers to the cathode product which in practice is less than theoretically predicated. This parameter is defined as;

$$\text{CURRENT EFFICIENCY} = \frac{\text{ACTUAL MASS DISCHARGED}}{\text{THEORETICAL MASS DISCHARGED}} * 100\%$$

A plating unit was designed and constructed and electrodeposits was formed using a D.C power supply having a variable current output to 10 Amp and Amp-hour meter to determine the cell-efficiency of plating electrolytes.

3.2 EXPERIMENTAL PROCEDURES

3.2.1 INTRODUCTION

The main emphasis of the experimental work carried out was the collection and analysis of polarization and cell efficiency data for platinum plating from different solutions . Only cathodic potentiodynamic polarisation curves were plotted and, using this data as an indication of film forming ability, coatings were produced on the substrates previously listed. Owing to the price of platinum content it was used with care and precautions in order not to waste any amount of platinum.

The assessment of coatings produced was divided into two stages. Visual and electron microscopical techniques employed to assess the characteristic of the coatings and their microstructure and composition. Secondly, adhesive tests were performed to study the adhesiveness and reliability of the coatings.

Electroplating platinum from various electrolytes were studied with different concentration of platinum from 2.0 to 30 g/l Pt on to the metallic substrates such as mild steel and nimonic alloys.

3.2.2 CURRENT-POTENTIAL CURVES

Since currents and electrode potentials are measurable quantities, it is useful to represent graphically the relationship between these quantities.

Potentials were measured, and are quoted, with respect to a reference electrode in the same solution. Potential

control was achieved with the aid of a Laboratory potentiostat(Wenking. Model LB B1 M shown in figure 21).

3.2.3 MEASUREMENT OF THE REST POTENTIAL

Operating Selector on ' $-E_R$ ', 'Meter Indication' on potential with this setting the potentiostat acts as a high-impedence potential meter with potential conversion to the low-impedence recorder output. It is important to make the cell connections before switching to ' $-E_R$ ', otherwise the high-impedence input could capture wild fluctuations which drive the meter to full output (but do not cause any damage). The display shows the potential difference of the reference electrode against the working electrode. The polarity indication is therefore opposite to the normal electrochemical convention, as shown by the negative sign before position E_R (Fig 22).

3.2.4 POTENTIAL CONTROL OF THE ELECTROCHEMICAL CELL

Operating Selector in position 'I', 'Meter Indication' generally on 'current'. Initial potential selected on the 'control' dial.

When the operating switch is moved from $-E_R$ to I the cell electrodes are connected to the potentiostat control circuit. The potential between the working and reference electrodes is controlled at the start potential, provided no additional external control signals are applied at the inputs. This start potential can be recorded at the potential output. If the start potential differs from the rest

potential, the corresponding cell current required to control the cell is shown on the meter.

Current density/potential curves can be recorded either on an xy recorder or an oscilloscope.

3.2.5 CURRENT CONTROL OF THE ELECTROCHEMICAL CELL

Like all other potentiostats, the Laboratory potentiostat used can also be operated as a galvanostat (see Fig 22). In this application it controls the voltage drop E_S at an external resistor R_X instead of the potential of the working electrode against the reference electrode. The value of this resistor R_X which is inserted into the current line of the working electrode, and the voltage drop controlled by the potentiostat determine the cell current;

$$I_C = E_S / R_X$$

Where,

RE= reference electrode

CE= counter electrode

WE= working electrode

IC= cell current

E_S = control voltage

E_p = polarisation

C_i = control input

In the potential setting the digital meter shows the voltage drop across the external resistor R_X , and in the current setting the actual cell current under galvanostatic control.(see fig 22)

3.2.6 CHART RECORDER

A Servoscribe RE 511-20 potentiometric chart recorder was employed for the most experimental investigations. The unit input range selection of between 2 mV and 20 V and a chart drive with speed options of 30, 120, 600 mm/hr and 30, 120, 600 mm/min.

3.2.7 VOLTMETER AND AMMETER

RS model M2008 Analogue/Digital multimeters were used for potential and current monitoring.

3.2.8 REFERENCE ELECTRODE

A saturated calomel electrode(SCE) was employed as the reference electrode in all potential measurements. It was positioned remotely (which lessens any detrimental effects from high temperatures experienced in the cell) using a salt (saturated potassium chloride) bridge connected to a probe, which could be positioned close to the working electrode.

3.2.9 COUNTER (AUXILIARY) ELECTRODES

A mesh titanium substrate plated with platinum acted as a counter electrode was used for the polarisation trials. Platinum has the advantage of being relatively chemically inert and unlikely to be affected by the cell solution during inactive periods. Also during cathodic polarisa-

tion, when the platinum is acting as the anode, there will be little or no metallic dissolution which could affect the solution and hence the polarisation characteristics of the working electrode.

3.2.9.1 PROCESS CELL FOR POLARISATION MEASUREMENTS

The polarisation cell consisted of a 2.0 litre beaker with a separate lid (see Fig 23-24), which had five openings facilitating the insertion and removal of various electrodes, thermometer and gas bubbler. The lid of the beaker was sealed in the position with a gasket and clip.

3.3 SOLUTIONS FOR POLARISATION MEASUREMENTS

Anodic and cathodic polarisation tests were carried out in various group platinum with solutions and these followed as;

- (a) Fresh 'P'salt with phosphate buffers
- (b) Phosphate base solution(i.e, plating bath composition but without platinum).
- (c) Different ratio of platinum solutions
- (d) Plating solutions directly from plating tanks No.A,B,C,D and E.
- (e) 'Q' salt from Johnson Matthey
- (f) Fresh 'P'salt with sodium buffers were also tested.

3.3.1 PREPARATION OF SUBSTRATES

Table 16 indicates the steps which were used in preparing the samples before and after plating. The size of cathode and anodes are followed as;

Solid mild steel/nimonic 75 alloys cylinders with diameter of 1.3 cm and 8.9-9.0 cm long, surrounded by same shape mesh anode shown in fig 25 of diameter 5.0 cm and 10.1-10.5 cm long.

3.3.2 PREPARATION OF PLATINUM SOLUTIONS

The platinum solutions were made up from either individual chemical and brighteners or direct from manufacturer such as; Johnson Matthey or Engelhard.

Table 17 shows the standard solution make-up for platinum plating with phosphate buffers. Tables (18-24) show bath composition and operating conditions for nearly twenty different platinum solutions.

3.4 MISCELLANEOUS EXPERIMENTAL METHODS

3.4.1 CHEMICAL REAGENTS

All chemicals used in these investigations were either from manufacturer or SLR (Standard Laboratory Reagent) grade or higher. With the exception of strong acids and alkalis, used for pickling and pH adjustment, 'P'salt or 'Q' salts (containing platinum) or other salts were the most seriously toxic substance used. The harmful effect of

these salts are mainly due to their allergy to people and give rise to the evolution of ammonia gas.

3.4.2 WEIGHINGS

All weight measurements of reagents were carried out on Philips balance, to the nearest thousandth of a gramme.

3.4.3 ATTAINMENT

Solution pH adjustments were achieved with concentrated additions of sodium hydroxide/ammonia or phosphoric acid. The actual concentration was varied, for example when small adjustments were required the additions were diluted considerably. All pH measurements were made with a WPA model CD62 digital pH meter, the readings were measured to their nearest tenth of a pH unit(± 0.1 pH).

3.4.4 ACCURACY IN EXPERIMENTAL PROCEDURES

The reproducibility of a given polarisation test depends to a large extent on the effectiveness of a preparation of the standard platinum solution process to be capable of repeatedly producing metal specimen surfaces in a similar "clean" state. Other parameters such as solution composition, pH, temperature etc can be controlled more easily. Therefore, before the onset of extensive polarisation trials much thought was given to the question of standardisation of platinum solution (see literature survey), and

it is considered that the solutions and methods used are appropriate to the metals undergoing polarisation trials. When such a large number of polarisation tests were carried out it was found to be possible to repeat them all. these are shown in the results section.

3.5 EXPERIMENTAL PROCEDURE FOR PULSE PLATING

Deposits were produced on solid cylinders of mild steel with diameter of 1.25 cm and 8.75 cm. Platinum deposition was carried out using two litre electrolyte from a fresh platinum solution in a beaker as a cell connected to power supply and pulse equipments shown in the figures (26-27) and efficiency tests were carried out.

3.6 EXPERIMENTAL PROCEDURE FOR NITRATES

On plating, the nitrite NO_2 is released as a free -ve ion. In theory this ion is soon oxidised to NO_3 nitrate.

Dionex analysis of the old plating solution show high concentration of nitrate, up to 40g/l. Similar analysis of new solution gave low levels eg, below 1.0g/l.

It is possible that the continual usage can build up excesses amounts of nitrate in the plating solution, this can have an adverse effect on the plating efficiency of that solution.

In addition to the balance the nitrate ion, Na^+ from the phosphate is taken up, this requires additional NH_4^+ to be added to balance the phosphates which at temperature boil off giving wide variation in pH.

Plating shop trials have demonstrated that with the low efficiency tank, which was used to plate for 4 hours for turbine blades, now instead of adding ammonia (NH_4), NaOH was substituted and it has been shown that the duration of plating has dropped from 4 hours to 2.5 hours which indicates the improvement in efficiency of that tank.

3.6.1 TRIALS ON NITRATES

1- To establish critical nitrate concentration

3.6.2 METHOD

(i) New solution test for nitrate and nitrite by Dionex
(ii) plate and establish efficiency check for nitrate and nitrite.

(iii) Add nitrate in form of KNO_3 and repeat trials at different concentration; 10, 20 and 30g/l.

Alternatively, add old solution to obtain decrease levels of nitrate and adjust pH and carry out the plating trial.

2-investigation of possible recovery of baths by addition of NaOH (Sodium Hydroxide)

Aim to adjust phosphate balance of bath and reduce NH_3 (ammonia) content.

METHOD

- (i) To establish efficiency of used old solution,
- (ii) Add NaOH and control pH to around 8.0,
- (iii) Test for new efficiency

These tests were carried out and the results were summa-

rised in Table 32 and it was found that the amount of nitrates has been effective in generating the low cathode efficiencies.

3.7 EXPERIMENTAL PROCEDURE FOR PHOSPHATES

Deposits were produced on a solid cylinder mild steel electrode with a diameter of 1.25 cm and 8.75 cm long, surrounded by the same shape mesh anode of diameter 4.5 cm and 10 cm long. Platinum deposition was carried out using a 400ml electrolyte from tank No.C in a beaker as a cell connected to Amp-hour meter and power supply.

Efficiency tests were carried out as follows;

(1) Efficiency tests were carried out on plating tank in No.C at current status with pH=7.1

(2) Made up trial sample of proposed recovery solution for tank C;

130ml solution from tank No.C, plus 19ml fresh 'p'salt to make up to 400 ml solution with distilled water

(3) Made up trial sample of proposed recovery solution tank C;

130 ml solution from tank No.C, plus 19ml fresh 'p'salt and 16.56g disodium orthophosphate and 3.86g diammonium orthophosphate, make up to 400 ml with distilled water.

(4) Made up trial sample of 200 ml solution tank C, plus 12.3g disodium orthophosphate and diammonium orthophosphate, make up the above solution to 400 ml with distilled water.

(5) Finally efficiency testing was carried out on tank No.C at pH higher than the test(1).ie, pH=7.79. Results are given in section 4.0 and Tables(33-34).

3.7.1 PHOSPHATES; RECOVERY PROCEDURES(STAGE.2)

(i)Sample from tank No.C was tested with efficiency method and pH and temperature parameters were recorded and follows as;

pH=6.7 , temperature=85°C and 30mA/cm²(3A/dm²) was applied.

Although the amount of phosphates was within the limit of 70-90g/l, but the efficiency was around 1.0% and final pH was 6.6.

(ii)With above sample , the pH was adjusted with sodium hydroxide to 7.0 and 15mA/cm²(1.5 A/dm²) was applied. But this time the efficiency found to be 7.43% and increased weight gain compared with previous one and it was almost 12%(Not gain efficiency).

(iii) Addition of 10g/2l of disodium orthophosphates was added to above solution and using the above pH and current , the efficiency test was maintained and recorded as 7.0% and the weight gained was 11% higher, compared with test(i).

3.8 SUMMARY FOR THROWING POWER PROCEDURE

A series of different designed experiments were used to evaluate the high aspect of throwing power capabilities and opportunities for extending that capability to replace the Brush plating. Brush plating is currently used for those blades which required the platinum plating for example; RB211 Blades at concave aerofoil sections at (Rolls Royce Manufacturing Division situated at Derby in U.K). The investigation employed different sizes and shapes of anodes/cathodes to explore the effects of various factors in the Ni-plating and then as this technique was established using nickel instead of noble metals it could be used to implement this feature in platinum and rhodium plating.

A variety of different shaped and size of nickel anodes under a variety of operating conditions have been used to study throwing power of nickel deposition. In all cases stainless steel cathodes with dimensions of 3 cm * 2 cm, and the plating solutions (i) Ni-Sulphamate, (ii) Ni-Strike were used. The composition and operating conditions of above solutions are shown in Table 25. Figure 28 indicated the schematic representation of plating cell for nickel plating but for throwing power, anode bags were not used.

3.9 CALCULATION FOR THROWING POWER

Current efficiency refers to the cathode product which in practice is less than that theoretically predicted. This parameter is defined as:

$$\text{CURRENT EFFICIENCY} = (\text{ACTUAL MASS DISCHARGED} / \text{THEORETICAL MASS}) * 100\%$$

The amount of metal theoretically deposited may be calculated as follows;

$$W = ItA / ZF$$

where; W = Theoretical weight of metal deposited
A = atomic weight of metal deposited (58.7 for Ni)
Z = valency of deposited metal (2 for Ni)
t = plating time in seconds
I = current in Amps
F = Faraday constant (96500)

Volume measurements for spherical, circular and cone shape anodes were carried out by using the below equation;

$$V = 2/3(\pi r^2 h) \text{----- for spherical deposit}$$

h = thickness of deposit

r = radius of deposit

Whereas, the volume measurements for rectangular and ellipse shape anodes were used by considering the different equation;

$$V = 2/3(\pi abc) \text{----- for elliptical deposit}$$

where, a = half length of deposit

b = half width of deposit

c = thickness of deposit

CHAPTER 4

4.0 EXPERIMENTAL RESULTS

The electrodeposition of platinum involves difficulties caused mainly by its strong tendency to bring about displacement reactions, complex formation, high catalytic activity, variable oxidation states, low efficiencies and fluctuating operating conditions. These parameters are discussed below;

4.1 EFFECT OF CURRENT DENSITY

(a) SURFACE CHARACTERISTICS

Electro-plating was carried out at current densities varying from 15 to 40 mA/cm² (1.5-4.0 A/dm²) for nimonic alloy/mild steel substrates.

The deposition characteristics for platinum bath numbers 1-19 are shown in Tables(26-29). A comparison of the above nineteen baths was made in terms of their deposition characteristics.

Tables(26-29), indicate the use of the above substrates under optimum conditions given in the literature, with effects of lower current density, better surface finishing and adhesive deposits are produced compared with high current density.

(b)CELL EFFICIENCY

The effects of current density on the cathode current efficiency of the above deposits are shown in Tables 26-29.

The platinum deposits were well-adhered, have bright texture, uniform thickness and fined-grained at low current density with the exception of deposits from bath numbers 11,12 and 15. With high current density dull, dark, burnt and porous deposits were produced.

4.1.2 EFFECT OF ANODE TO CATHODE ELECTRODE RATIOS

This method carried out using 4:1 anode to cathode area ratio and the results are shown in figures 29-47. It can be seen that as the ratio of anode to cathode increased, the cell efficiency as well as surface appearance and thickness of deposit was enhanced considerably.

So far, the effect of various current densities on the cell-efficiency of Pt and Pt alloy deposits obtained from platinum solution currently used in commercial plating tanks(C.U.K Ltd) are shown such that with the lower current densities between 8-16 mA/cm² (0.8-1.6 A/dm²) have a significant increase in cell-efficiency, compared with high current densities. This effect is further shown in Figures(48-49). Comparison can be made when different electrolytes with different concentration of Pt on various current densities are used. This parameter will be examined on all electrolytes concerned.

'Q'salt from Johnson Matthey solution shows higher cathode efficiency with lower current density. The effects of

various current densities on 'Q'salt has been shown in tables(30-31) and figs(50-53). A new method was carried out for this electrolyte which resulted in obtaining the maximum cathode current efficiency. This method was carried out by applying low current density for one third of plating time and the remaining time with the usual current. For example; the overall current of 4.0 mA/cm^2 (0.4 A/dm^2) was decided upon. This was done by using a constant current of 2.0 mA/cm^2 (0.2 A/dm^2) for 3 minutes, followed by 4.0 mA/cm^2 (0.4 A/dm^2) for 7.0 minutes and the result was compared with the constant current of 4.0 mA/cm^2 (0.4 A/dm^2). This effect was significant and is shown in the above Tables(30-31) and Figs(50-53). The comparison between low current and high current at the beginning of deposition was also compared and this difference is almost 50% , resulting in the higher efficiency for lower current density.

The stability of 'Q' salt was also investigated and Figs(54-55) represent the effects of various current densities upon 'Q' salt. As current increases the stability of the solution deteriorates. The solution was seen to be stable up to 8.0 mA/cm^2 (0.8 A/dm^2) but as the current increased, the solution became black and platinum debris was found on the bottom of the beaker(ie, somehow, adhesion was not maintained). In general anodes were much darker(brownish-colour) than anodes resulting from 'P'salt usage.

4.1.3 EFFECT OF CONCENTRATION OF ELECTROLYTE

Laboratory work, as well as plating shop trials, demonstrated that the higher concentration of Platinum can be effective in generating higher cathode efficiency. This is shown in Fig 57.

Figure 57 shows the effects of various current densities and different concentrations of Pt on cathode efficiency. (i) With the 'p'salt Pt only $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$, (ii). With the fresh solution made on basis of 'p'salt and diammonium disodium orthophosphates which are given in Table 17 to make up a new solution for a tank in the plating shop. This parameter was also investigated with different electrolytes.

The effects of various current densities on fresh platinum solution('P'salt) with different concentration of platinum are shown in Figs 48-49. Figure 49 shows that with current 12-16 mA/cm^2 , the maximum current efficiency was obtained with all concentrations of platinum and this was not due to different concentration but merely due to the optimum current. Nevertheless, a slightly better result was obtained with higher concentration of platinum. ie, Pt=5.0 g/l.

Figure 48 represents the different concentrations of platinum with effects of various current densities. The weight gain from higher concentration is highest with the maximum current.

4.1.4 EFFECT OF pH WITH TYPES OF PLATING AND SUBSTRATES

The bath pH was found to be rather critical in all the platinum plating electrolytes. Tables(26-29) show the bath compositions and characteristics of all baths used for platinum plating. Bath(1) yielded deposits with poor efficiency below pH=6.0. Grey, dark and slightly peeled off deposits were obtained. Very low pH values were found to result in non-adherent deposits at higher thicknesses, probably due to the substrate attack in the initial stage. However, despite the fact that bath(6) was very acidic and pH was within range of 0.5-1.3, the deposits were bright, adherent as well as semi-reflective and also the solution was stable and did not deteriorate on standing but on the other hand, the efficiency was very low and effectively no oxidation has taken place on anode surfaces and the surface finish of the cathodes was clean and smooth.

Bath(1) also operated with nearly constant efficiency in a pH range of 7.0-7.5 but control of the bath especially at the higher operating temperature became difficult due presumably to escape of ammonia.

Bath(11) was operated with pH=13-14 and somehow, during the plating the solution has become blackened very rapidly and the question arose whether the reason for change of the solution colour was due;

- (i) higher current density
- (ii) higher temperature
- (iii) evolution of hydrogen

Therefore, bath Nos (8-10) were prepared by lowering the

amount of potassium hydroxide(KOH) and as well as lowering the temperature of the solution.

This parameter should also be investigated thoroughly.

4.1.5 EFFECT OF PLATING TEMPERATURE

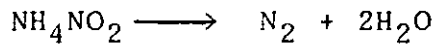
In general, a higher operating temperature for the plating bath permits higher plating rates because of improved mass transport, but it also increases the thermal decomposition of the plating bath, resulting in precipitation of the dissolved platinum-group metal(s).

Figure 56 shows the comparison between a temperature above normal plating temperature 94-96°C and the normal temperature 84-86°C. The cathode efficiency has improved slightly compared with the lower temperature. It also can be seen from Tables(26-29) that bath(1) functioned with a higher efficiency with an increase in its temperature from 87-97°C. However, the corresponding loss of ammonia leads to a progressive decrease in the pH value and the deposition ceases to continue. On the other hand this experimental test was carried out by covering the beaker top and there was not any need to add ammonia to the solution. Figures(29-47) show schematics of the parameters of all baths with high and low temperatures.

4.1.6 EFFECT OF NITRATE CONCENTRATION IN Pt SOLUTION

The concentration of nitrite/nitrate ions tends to rise during solution usage, suppressing the dissociation of the platinum complex and causing a decrease in current efficiency. Theoretically there should

not be any accumulation of objectionable salts in the bath because nitrite should be removed by the following reaction:



In practice, however, it is found necessary to boil the solution from time to time with the addition of ammonium nitrate to counteract a tendency for the current efficiency to fall to zero, which is thought to be due to excess NO_2 in some form.

To determine the amount of nitrates in each plating tank containing 170 litre platinum solution, assuming that 1 litre of 'p'salt' is 28.47g/l Pt concentration or $28.47/195.08=0.146$ moles of Pt.

Molar ratio of Pt to $\text{NO}_2(\text{NO}_3)=1:2$

hence, 0.292 Moles of Pt will result in 18.10g NO_3 and in 170 litres solution(tank)= $18.1/170=0.1064\text{g/l NO}_3^-$.

Therefore, for every 1.0 litre of 'p'salt' solution(at above concentration), there is an addition of 0.1064g/l NO_3 . Thus the total nitrate in tanks of volume 170 litre is 18.08g

For a freshly made solution corresponding to Table 33, there is hardly any amount of nitrate initially in plating tanks; this was revealed by ion chromatography(Dionex 2000i/sp). But as plating continued for some time the amount of nitrates gradually built up and is one of the reasons for platinum solutions to become 'sour', ie, very low in efficiency(usually for a RB211 blade needs to be plated around 1.5 hour, but with this effect the plating time would be prolonged and it needs twice as much time in

order to achieve the required plating thickness which is 10um). After this effect the solution will be collected and will be sent to the manufacture and Pt can be re-claimed back. The last time the concentration of nitrate was measured by Dionex in one of the plating tank it was 40g/l nitrates.

In order to prevent 'souring' of the solution, a few tests were carried out to bring the solution back 'alive' and in good working condition as follows;

4.1.7 EFFECT OF SODIUM NITRITE(NaNO_2) UPON CELL-EFFICIENCY

20g/1.5 litre of sodium nitrite was added to a freshly made solution('p'salt) and ion chromatography was used to assess the amount of nitrates, phosphate and nitrites before and after plating. Table 32 shows that after plating, the amount of nitrite has diminished and the cell-efficiency was lower compared with standard fresh solution which is around (7.0-9.0)%. As mentioned before, nitrite and nitrate have an adverse effect on plating efficiency of the solution.

4.1.8 HIGHEST CURRENT EFFICIENCY RESULTING FROM 'P'SALT

The highest current efficiency was obtained from the electrolyte in which phosphate salts were replaced by sodium acetate and sodium carbonates. Sodium citrate, sodium sulphate and sodium chloride can also be used in which case stability of the electrolytes was improved. Deposits from these baths were smooth, bright and free of

pores and cracks at thickness up to 10um. Tables(23-24) show the bath composition of four baths with different compositions, but constant platinum concentration.

The use of sodium acetate instead of the phosphate salts improved the efficiency and avoided the formation of a layer on the anode. Table 29 represents the characteristics, current efficiency, surface appearance, average thickness and finally the plating temperature.

4.1.9 INVESTIGATION OF PHOSPHATES IN PLATING TANKS

4.1.9.1 EFFECT OF PHOSPHATES CONCENTRATION IN PLATINUM SOLUTION

Table 33 shows the level of phosphates in tank Nos.(B,C and D) present in plating shop containing platinum solution . According to Table 17 the amount of phosphates in each tank should be (70-90)g/l and comparison can be made between the original make up and each solution at the end of a month; it was found that the loss of phosphates was due to drag out, because of removal from the plating tank the articles are swilled in warm water.

4.1.9.2 INVESTIGATION OF LOW CATHODE EFFICIENCY FROM TANK NUMBER C DUE TO PHOSPHATES; RECOVERY PROCEDURES(STAGE.1)

Current efficiency test methods have been employed on samples originating from tank No C. The effect of varying pH, addition of fresh 'p'salt solution and of mixed phosphate additives have been studied.

These results are shown in Table 34.

Table 34 indicates the variation of cathode current efficiency for each test mentioned as above and the results have shown that the highest efficiency was achieved with trial(3) with values of 5.0%, 4.0% with trial(5), 3.75% with trial(4) and finally 3.75% with trial(2).

These results have also shown that as plating times were prolonged, the addition of fresh 'P'salt to the plating tanks in the plating shop has somehow increased the efficiency of plating and this effect is more pronounced with the addition of fresh 'p'salt as well as phosphates in the plating trials solutions.

The result from trial(5) illustrates that with higher pH, ie, pH=7.79, the efficiency of plating can be increased slightly.

4.2 INVESTIGATION OF DIFFERENT CONCENTRATION OF PLATINUM FROM 'P'SALT

Two different batches of 'p'salt from ENGELHARD were investigated using the efficiency method. Figs(57-58) show the effects of various current densities on two different 'P'salts. The efficiency resulting from 'P'salt containing 28.27g/l was three times higher than the 'P'salt with 26.02g/l. This effect was also pronounced with weight gain measurements which shows in Fig 58.

4.2.1 INVESTIGATION OF ADDITION OF PHOSPHITES AND HYPOPHOSPHITES UPON FRESHLY MADE SOLUTION('P'SALT) CONTAINING PLATINUM CONTENT AND ALSO UPON TANK NUMBER D('P'salt)

Figure 59 shows the effects of disodium hypophosphite and phosphite upon fresh solution and tank D containing 'p'salt. As the amounts increased, the efficiency of the cell decreased to virtually 1.0%.

4.3 CATHODIC AND ANODIC POLARIZATIONS

Cathodic polarization curves for the electrodeposition of platinum are shown in following Figure 60 and Tables(35-36) list the data.

Figure 60 represents polarization curves for the phosphate base solution without addition of 'P-Salt'. Maximum and minimum current densities(mA/cm^2) were achieved within -1.1 and -0.7 Volts.

Figure 60 also illustrates polarization curves for tank A with the same pH value which was used in phosphate base solution. Current inflexion was more pronounced in the region of $15 \text{ mA}/\text{cm}^2$ to $5 \text{ mA}/\text{cm}^2$ and this was accounted by the hydrogen evolution. This effect was recorded within a range of $-(0.65-0.7)$ Volts. Table 35 shows cathodic polarization curves of phosphate base solution and tank A and comparison can be made in that a current drop was observed at -0.6 Volts due to the effect of hydrogen evolution for tank A.

Figure 60 also shows polarization curves for tank A with and without addition of sodium hydroxide(NaOH). Table

35 gives data for the platinum solution without addition of NaOH and hydrogen evolution was observed at -0.65 Volts; also Table 36 and Fig 60 represents platinum solution with an addition of 130ml of NaOH for a 2 litres solution and a hydrogen evolution effect coincided with Fig(i) but the polarization curve for this case was shifted towards more negative value and finally Fig (iii) represents platinum solution with a high addition of 20g NaOH for a 2 litres solution and hydrogen evolution was noted at -0.7 Volts which the polarization curve was shifted towards more negative value.

Fig 61 represents tank D(J.M). Polarization curves for tank D may be compared with tank A, freshly made solution (Pt,'p'salt) and phosphate only and although the pH and temperature values are different, allowance can be made by subtraction of $2*(59)\text{mV}$ for pH values for comparison between tank A & D. Nevertheless, the hydrogen evolution occurred at -1.0 Volts and the degree of current inflexion was low from $18\text{-}12\text{ mA/cm}^2$ compared with tank A.

Laboratory and experimental tests resulting from tank D have shown that the rate of plating, current efficiency, plating time have shown better improvement and these results indicate that when the polarization shifted towards more negative values are the operating difficulties encountered in the use of all baths .

Three electrolytes with different phosphate ratios, having constant platinum content of 3.0g/l were prepared. The bath composition and operating conditions are given in Table 37 and the effect of various potentials upon these electrolytes is shown in Tables(38-39). The phosphate

ratios of 7:1, 4:1 and 1:1 were prepared with a high degree of accuracy and cathode efficiency measurements were made and are given in Table 40.

Cathodic polarization were measured with the potentiostat and results are shown in Tables(38-39) and Figs (62-63). From the above results it can be concluded that the electrolyte with the high ratio ,ie, (7:1), has the highest cathode efficiency and hydrogen evolution did not take place until the maximum current density was achieved; this corresponds with cathodic polarization having a more negative value. This is probably due to the amount of disodium orthophosphate in solution.

Further tests were carried out with and without phosphates in platinum solutions and this method was repeated by using phosphates in platinum solution. (see Figs 64 & 65). Solution from tank No.A was used and results are shown in Fig 66. It appears from Fig 66, that higher temperatures could raise the current density and lower hydrogen evolution or vice versa. These tests were also carried out by using fresh platinum solutions shown in Fig 67.

Effects of high and low pH as well as temperature were investigated upon cathodic polarisation and this is shown in figs(68-69). Figures(70-71) represent the cathodic polarisation for platinum baths with high pH and platinum content compared with low pH and low platinum content.

Platinum plating bath No.16 was investigated for cathodic polarisation with and without platinum content as well as the effect of high and low temperatures and these are shown in figs (72-73).

4.4 INVESTIGATION OF THROWING POWER (LOCALISED PLATING) TO FIND THE OPTIMUM OPERATING CONDITIONS FOR THE DEPOSITION OF NICKEL

4.4.1 OBSERVATIONS

(a) NI-STRIKE

The effects of parameters such as applied current, interelectrode separation and plating duration upon the characteristic and shape deposits are shown in Tables (41-42). The Triangle, spherical, ellipse and rectangular anodes produced the acceptable deposit thicknesses, but due to the shape of the anodes, the deposits were always either circular or elliptical respectively. These results are shown in Tables (41-42).

(b) NI-SULPHAMATE

Tables (43-47) show the characteristics of deposit shapes with effects of parameters mentioned as above.

The same deposit shapes were resulted with various anodes. An exception with Ni-strike solution was that weight gain could not be measured due to acidic behaviour of Ni-strike solution. Therefore, the efficiency measurements could not be carried out.

Results representing the deposit thicknesses for Ni-sulphamate are shown in Figs(74-77). The results representing the deposit thickness for Ni-strike are shown in Figs(78-81). Figures(82-83) show the effect of throwing power with different shape of anodes, current densities

and finally interelectrode separations.

4.5 EXPERIMENTAL RESULTS FOR PULSE PLATING

Parameters involved in pulse plating and conventional plating can be classified as either variables or constants. The former consists of cathode current density, concentration of electrolytes, plating time, off-time and coating thickness, whereas; the latter consists of on-time, frequency and temperature. The aim was to keep these parameters within an optimum range suggested in the literature.

The numerical values for above parameters are as follows: 10msec 'ON'-TIME, 100-200msec 'OFF-TIME' with the range of frequency from 4.76-9.1(HZ).

The effects of the experimental parameters are described in the following sections.

4.5.1 EFFECT OF CURRENT DENSITY ON PULSE AND CONVENTIONAL PLATING

Electroplating tests were carried out at current density of 15-40 mA/cm² (1.5-4.0 A/dm²) for a mild steel substrate. In general, pulse plated samples gave darker deposits than those produced by conventional-plating, as shown in Fig 84.

4.5.2 INFLUENCE OF DURATION OF ELECTROLYSIS ON TYPES OF PLATING

Electroplating of platinum on to mild steel substrate has been performed with durations from 5 min for conventional and 55-105 min for pulse plating.

As a result of pulse plating, deposits from the platinum bath obtained during 55-105 minutes were dark deposits.

As the duration of electrolysis increased, the cell efficiency improved. This was more pronounced in the case of pulse plating. Figures(85-105) represent the comparison between conventional and pulse plating with the effect of current density upon cell efficiency of different platinum solutions.

4.6 PREVENTION OF THE DEPOSITION OF PLATINUM ON THE RUBBER BOOTS USED TO SHIELD THE FIR-TREE ROOTS OF BLADES DURING PLATING

For some time C.U.K Ltd have tried to substitute an improved material instead of H.V.R(high vulcanised rubber) to protect the fir-tree roots of blades during plating shown in Fig 107. Although, the above rubber boots initially managed to carry out the task, after 3/4 runs of plating platinum somehow managed to deposit in these rubber boots and they had to be cleaned with razor blades with a degree of accuracy and certain amount of lost time. Figure 106 shows the P.T.F.E material which was used before and after plating. Eventually, after long investigation, two methods were recommended for use in prolonged deposition using these materials;

- 1-Catering cling film
- 2- Natural rubber

4.6.1 Catering cling film has been used with some success as a means of preventing the deposition of platinum on the rubber boots used to shield the fir-tree roots of blades during plating. Figure 107 illustrates this success which managed to protect the rubber root from depositing platinum.

Cling film normally contains 2-4% low molecular weight polyisobutylene which could be leached out by an aqueous medium such as the plating solution. In a laboratory-scale plating experiment a single component with root and rubber boot wrapped in cling film was immersed in the standard plating solution for 2 hours. A 100ml sample, representing one quarter of the plating solution, was shaken with 100 ml of dichloromethane and the organic layer evaporated to dryness(In a separate experiment), it was shown that dichloromethane extracts 42% by weight of material from the film, thus, one can be confident that this solvent will extract any polyisobutylene present). The residue contained phosphates from the small amount of the aqueous fraction miscible with the organic solvent so this residue was extracted a second time to determine the weight of dichloromethane- soluble material.

4.7 RESULTS OF CLING FILM USAGE:

Weight of dichloromethane-soluble material extracted= 0.0343g. Therefore, total weight present in solution(400ml)= 0.1372g.

4.8 ERRORS IN PLATINGS & SUBSEQUENT EFFICIENCY AND THICKNESS DETERMINATIONS

The difficulty of reproducibility of data can be illustrated by direct reference to three sources of error.

(i) Random variation in plating conditions due to the small volume of solution used.

As already seen, there appear to be some anomalous results which are probably due to the fact that total control of all plating variables, particularly local pH, temperature & solution concentration is very difficult in the small 2.0 litre bath used in the experiments. Vigorous agitation using a magnetic stirrer and regular checking and adjustment of pH were carried out in an attempt to minimise these effects .

(ii) Errors incurred during the plating process.

The major error is the calculated efficiency of the cell made in every case. This arises from a number of interrelated factors including the actual area plated, the applied current, the time of plating and the measurement of the weight of deposit.

Although, the feeler gauges were used to measure the distance between anode and cathode electrodes(interelectrode separation), errors were made during actual plating.

Owing to agitation and slight movements of electrodes when the electrodes were immersed into the bath, it was found that due to various small interelectrode separation it was very difficult to accurately measure and reproduce the interelectrode separation required.

(iii) Errors incurred during pulse-plating.

As well as the errors mentioned in (ii) above, there is an added uncertainty here due to the non-square waveform of the pulsed cell current. Figure 19 shows the actual waveform achieved by the circuit shown in figure 27. This was taken from the output of the oscilloscope which was used to monitor the output voltage drop across a standard resistor which could then be converted to a current reading. To find the total current passed per unit time, it was necessary to integrate the area under one cycle of figure 19. This was done by plotting it onto graph paper and then simply counting 1 mm squares to work out the area under the waveform. This gives an error in current, (combined with the inherent error of the power supply/oscilloscope combination), of approximately ± 5 mA, leading to an error in current density of around ± 1.25 mAcm⁻².

All other errors were as in (ii), leading to an error in the deposit thickness of approximately ± 1.7 nm (± 1.7 μ m). Again, this is not sufficient to cause any major changes in efficiency values obtained and since it is a random error anyway will not affect the trends due to other factors.

CHAPTER 5

DISCUSSION

The Discussion section of this thesis can be broadly divided into three separate sections. The first surveys the data relating to the experimental investigations and electrochemical results, the second attempts to interrelate the findings as well as process implications, and the third section examines the industrial practice for gas turbine engines.

Discussion of the electrode behaviour should be related to the potential- pH diagram (Fig.14), whose characteristics were described in earlier sections.

5.0 DISCUSSION:ELECTROCHEMICAL RESULTS

5.1 CATHODIC AND ANODIC POLARIZATIONS

The cathodic polarization curves plotted for platinum are, in general, of a typical cathodic shape, culminating in the approach to a limiting current indicating mass transport limiting deposition.

The current density-potential curves of these electrolytes show very characteristic behaviour in the alkaline pH range, in so far as the current density increases up to a maximum limiting current, it drops to a low value of current before increasing again with potential due to hydrogen production. How far this kind of 'cathodic passi-

vation' is connected with the hydrogen co-discharge, and the adsorption of hydrogen, is not as yet clear; another explanation might be a sudden change in pH value in the cathodic layer caused by hydrogen evolution possibly yielding incipient precipitate films not obviously identified.

The critical current density can be increased by an increase in the concentration of the Pt'P'salt or 'Q'salt. Temperature has a very decisive influence on the critical current density, while potentials remain nearly constant. Passivation is no longer observed at pH values below 7.0, since hydrogen evolution starts before platinum discharge begins and presumably films are unable to be nucleated.

Initial investigations of 'P'salt solutions and 'Q'salt consisted of electroplating of the most promising solutions from the tanks A and D.

Cathodic polarization curves for the electrodeposition of platinum are shown in following Figs (60-73) and Tables(35-40) list the data in numerical form.

Figure 60 represents polarization curves for the phosphate base solution without addition of 'P'salt. Maximum and minimum current densities(mA/cm^2) were achieved within -1.1 and -0.7 Volts.

Figure 60 also illustrates polarization curves for tank A with the same pH value which was used in phosphate base solution. A Current inflexion was more pronounced in the region of $15 \text{ mA}/\text{cm}^2$ to $5 \text{ mA}/\text{cm}^2$ and this was accounted for by the hydrogen evolution. This effect was recorded within a range of $-(0.65-0.7)$ Volts. Table 35 shows cathodic polarization curves of phosphate base solution in tank A

and comparison can be made in that a current drop was observed at $-(0.65-0.70)$ Volts due to the effect of hydrogen evolution for tank A.

Figure 60 also shows polarization curves for tank A with and without addition of sodium hydroxide (NaOH) to the solution. It is interesting to note that inflections were observed on cathodic polarisation curves carried out in phosphate and plating tank A, with and without addition of sodium hydroxide. Table 35 gives data for the platinum solution without addition of NaOH and hydrogen evolution was observed at -0.65 Volts. Further, Table 36 and Fig 60 represent platinum solution with an addition of 130ml of NaOH for a 2 litres solution and a hydrogen evolution effect coincided with Fig 60(i) but the polarization curve for this case was shifted towards more negative value and finally fig 60 (iii) represents platinum solution with a high addition of 20g NaOH for a 2 litres solution and hydrogen evolution was noted at -0.7 Volts which the polarization curve was shifted towards more negative value. Sodium hydroxide had the effect of increasing the cathodic current and shifting the overpotential towards more negative values.

Examination of the early polarisation trials indicated that the concentration of sodium hydroxide had little effect on the passivation characteristic during anodic polarisation. Effects on cathodic currents were a general increase of current with increasing Pt concentration.

Fig 61 represents data for tank D (Johnson.Matthey). Polarization curves for tank D may be compared with tank A, freshly made solution (Pt, 'P'salt) and phosphate only and

although the pH and temperature values are different, allowance can be made by subtraction of $2 \times (59) \text{mV}$ for pH values for comparison between tank A & D. Nevertheless, the hydrogen evolution occurred at -1.0 Volts and the degree of current inflexion was low from $18-12 \text{ mA/cm}^2$ compared with tank A.

Laboratory and experimental tests resulting from tank D have shown that the rate of plating, current efficiency and plating time have shown better improvement and these results indicate that when the polarization shifted towards more negative values are the operating difficulties encountered in the use of all baths. The pH of tank D, ('Q'salt) has been kept constant at values 9-10 whereas, pH range values for tank A, ('P' salt) was 7.0-7.5 ; this effect generally agrees with the work of Dahms and Croll⁽⁶⁴⁾. Dahms and Croll⁽⁶⁴⁾ showed that a local pH rise near the electrode surface is favoured when H_2 evolution proceeds simultaneously with deposition and it seems that sodium hydroxide can be formed or even precipitated in the vicinity of the electrode surface; this adsorbed sodium hydroxide permits a high discharge rate of Pt^{+2} according to their postulation. Under these circumstances, according to results shown in Figs (60-73), the hydrogen evolution was delayed or shifted towards more negative value with a local pH rise .

The main influence on the passivation characteristics of a platinum solution, except for 'P'salt and 'Q'salt solutions, was the pH. In essence a very low pH value resulted in a high value for i_{crit} and consequently, a high dissolution rate for anodically formed films or coatings in

this type of solution.

All two groups showed remarkably dissimilar responses at the different pHs tested. pH 7.0 'P' salt solution curve exhibited high current densities for low overpotentials, and generally did exhibit a large number of inflections. pH 9.0 solution of 'Q'salt exhibited smaller current values for given potentials and also the appearance of less marked inflection phenomena. For all pH (9.0-10.0) 'Q'salt solutions currents at given potentials were generally smaller up to -1.0 volt. But it gradually increased to 34mA/cm^2 at high overpotentials -1.7 volts.

Surface characteristics after cathodic polarisation were recorded and 'P'salt solutions were formed to yield dark, dull finishes, with silver mat to grey shades being prominent. 'Q'salt samples were generally reflective, bright and less heavily coloured.

Although these superficial investigations for 'P'salt and 'Q'salt solutions have proved somewhat disappointing, it does appear that interest in the 'P'salt plating is growing in the commercial/ industrial sector. In general the 'P'salt solutions produced far more inflections than the corresponding 'Q'salt or other platinum solutions. The majority of these from 'P'salt solutions were also much more strongly defined than those from the other solutions. Broadly categorising the inflections is difficult because of the scatter of values from individual solutions. However, there does appear to be some evidence of a trend whereby all hydrogen-evolution analogues seem to produce inflection type features at the range of values around -700 mV vs SCE for 'P'salt and one also around -1000 mV vs

SCE for 'Q'salt. However, it must be reiterated that these values should be regarded as very approximate.

As a guide to corrosion resistance the diffusion coating test was found to be useful. The results indicate that 'P'salt coatings consistently produced the best performance. 'Q'salt coatings showed large variations between the duplicate samples tested for each processing condition. This suggests either the diffusion coating process was producing uneven coating or that the specimens coated at a particular condition were truly variable. 'P'salt coatings were clearly inferior to 'Q'salt, producing consistently high levels of uniform coating and surface platinum corrosion product.

Due to the difficulty in observing the actual commencement of hydrogen evolution in a large tank operation, it is assumed that the actual onset occurred before these experimental potentials. This suggests the second inflection(usually strong) on the 'P'salt curve appears to be around -800 mV vs SCE.

SEM investigations were carried out on 'P'salt and 'Q'salt coatings which were subjected to diffusion treatment. However, this type of processing produced a non-adherent coating from 'Q'salt solution. On examination the surface of the specimen from 'P'salt solutions generally appeared to consist of spherical crystals. The 'Q'salt coated surface was made of irregular spherical crystals (some of which exhibited internal cracks) which could possibly be as a result of post-treatment which resulted in the cracking of the initially-formed film.

Referring to three electrolytes with different phosphate

ratios having a constant platinum content of 3.0g/l Pt, the bath composition and operating conditions being given in Table 37 and the effect of various potentials upon these electrolytes shown in Tables(38-39). Although careful attempts were made to maintain constant experimental conditions, the weight gains obtained during a series of similar plating were subject to considerable variation. Thus large variations in the rate of cathode current efficiency obtained. The phosphate ratios of 7:1, 4:1 and 1:1 were prepared with a high degree of accuracy and cathode efficiency measurements were made and are given in Table 40.

From the above results it may be concluded that the electrolyte with the high ratio ,ie, (7:1), has the highest cathode efficiency and hydrogen evolution did not take place until the maximum current density was achieved; this corresponds with cathodic polarization having a more negative value. This is probably due to the amount of disodium orthophosphate in solution.

Further tests were carried out with and without phosphates in platinum solutions and this method was repeated by using phosphates in platinum solution. (see Figs 64 & 65). Solution from tank A was used and results are shown in Fig 66. It appears from Fig 66, that higher temperatures could raise the current density and lower hydrogen evolution or vice versa. These tests were also carried out by using fresh platinum solutions shown in Fig 67.

Effects of high and low pH as well as temperature were investigated upon cathodic polarisation and this is shown in figs(68-69). Figures(70-71) represent the cathodic

polarisation for platinum baths with high pH and platinum content compared with low pH and low platinum content.

Platinum plating bath No.16 was investigated for cathodic polarisation with and without platinum content as well as the effect of high and low temperatures and these are shown in Figs (72-73).

J.M.West⁽⁶⁵⁾ has explained that, where the deposition potential lies below the reversible hydrogen ion potential, there will generally be some concomitant hydrogen evolution and possibly also reduction of other foreign ions from solution. All these other processes consume non-useful current from the electroplater's point of view. When the cathodic overpotential for metal deposition is high there is a correspondingly increased opportunity for hydrogen gas evolution (particularly as the hydrogen reaction proceeds readily on the 'inert' or catalyst metals). Therefore, the current efficiency always tends to be low. This statement should be related to polarization curves of Fig 61 representing tank D (Johnson Matthey) processing. Polarization curves for tank D may also be compared with tank A, freshly made solution (Pt, 'p'salt) and phosphate only solution and, although the pH and temperature values are different, allowance can be made by subtraction of $2 \times (59)$ mV for pH values for comparison between tank A & D. Nevertheless, the hydrogen evolution occurred at -1.0 Volts and the degree of current drop was low from 18 to 12 mA/cm² compared with tank A.

Laboratory and experimental tests resulting from tank D have shown that the rate of plating, current efficiency and plating time have shown improvement and these results

indicate that with polarization shifted towards more negative values such operating difficulties must be encountered in the use of all these baths .

5.2 HYDROUS OXIDE FORMATION ON PLATINUM- A USEFUL ROUTE TO CONTROLLED PLATINIZATION

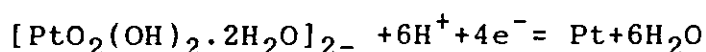
The formation of thick hydrous oxide film on platinum under potential cycling conditions has been investigated by R.J.Morrissey and L.D.Burke⁽⁶⁶⁻⁶⁷⁾ as a function of sweep limits, and solution pH. Hydrous oxide growth was observed in both acid and basic solution but not at intermediate pH values(4-10). One immediate practical implication of the work was for the activation (or reactivation) of platinum surfaces. An interesting fundamental point also emerging from the work was that from a thermodynamic viewpoint platinum may be surprisingly susceptible to oxidation to form an insoluble, highly hydrated species at quite low potentials(less than 0.0V vs RHE) in basic solutions. The reason why such species are not normally observed under positive, single-sweep conditions is probably due to the inability of the ligands involved(O^{2-} , OH^- and OH_2 species) to coordinate in a symmetrical manner about a platinum atom that is partially embedded in a metal lattice.

An extensive survey of the platinum electrode system was carried out just over a decade ago by Feltham and Spiro⁽⁶⁸⁾. This topic is still of considerable interest in the fuel cell field, in the context of platinized or

finely divided surface platinum. The use of the latter of course is not without its problems; apart from the question of expense, service lifetime is usually limited by poisoning, spalling and sintering phenomena during usage. R.J.Morrissey and L.D.Burke⁽⁶⁶⁻⁶⁷⁾ investigated the increase in electrocatalytic activity due to the formation of a finely divided platinum layer at the electrode surface on reduction of the hydrous oxide and it was found that it was first necessary to measure the surface area values.

Although the formation of hydrous oxide on platinum under anodic condition was very sluggish reaction, the reduction of this material appeared to occur with little inhibition. This is not only clear from the present work where a linear relationship between peak current density and sweep-rate is outlined for the reaction but also from the experiments reported by Shibata⁽⁷²⁾ where potential fluctuations during reduction of the hydrous film with periodically interrupted current were small especially compared with those recorded during reduction of the mono-type film in the same experiment. On the basis of the temperature dependence of the cathodic peaks, James⁽⁷⁰⁾ also concluded that the hydrous oxide reaction occurred without much inhibition. An interesting question in this area(which also applies to the work of Gold⁽⁷³⁾) is why, if the hydrous oxide reduction reaction is so facile, is its formation so strongly inhibited? Since the hydrous film is thermodynamically more stable than the anhydrous layer, it should be formed prior to the usual oxide monolayer. The reduction of the hydrous material has been represented

previously⁽⁶⁹⁾ by the equation:



Evidently the reverse reaction is inhibited by the existence of one of the reactants, not in the form of free isolated atoms, but as part of a metal lattice structure where access of ligands is strongly retarded. Before the overpotential for hydrous film formation reaches such a value, the activation barrier for this process must be overcome and monolayer oxide formation then commences. Since this probably may further stabilise the platinum species at the metal surface, it serves to increase the inhibition involved in forming hydrous Pt(IV) species at the electrode surface. The ability to produce hydrous material in a regular manner using the potential cycling technique seemed to depend largely on the metal atom displacement effect arising from the repetitive formation and reduction of this thin compact layer. Access of ligands to the central metal ion was apparently facilitated by the less compact nature of the oxide formed from such dispersed species. It is not clear in what part of the film reduction commences, eg. at the metal/oxide or oxide/solution interface. Reduction in any event entails electron insertion from the metal and proton insertion from solution and inhibition of either would lead to a rise in resistive (iR potential drop) effects, i.e. the decrease in peak potential with increasing sweep-rate (and increasing reduction peak current) may simply be due to an increasing iR component in the recorded peak potential

values. An odd feature, commented on previously also by Shibata⁽⁷²⁾, was the asymmetry of the hydrous oxide reduction peak. The unusually sharp drop at the more negative potential may be due to the fact that when most of the oxide is reduced, charge transfer inhibition, and similarly the iR component, virtually vanishes.

Under strongly anodic conditions some oxygen was assumed to penetrate, by means of place-exchange-type reactions, into the outer regions of the metal lattice. There is some controversy here⁽⁷¹⁾ as to whether these oxygen-rich layers should be regarded as adsorbed oxygen films, regular (PtO_2) or even $Pt(OH)_2$ or non-stoichiometric phase oxides. The important point, from the hydrous oxide growth and surface activation viewpoint, is that oxygen penetration results in the displacement of platinum atoms from regular metal lattice sites and weakening of metal-metal bonds in the outer layer.

5.2.1 EFFECT OF SOLUTION pH ON THE HYDROUS OXIDE GROWTH REACTION

The effect of solution pH on the hydrous oxide process was specifically studied and illustrates that the efficiency of the reaction decreased dramatically with increasing pH over the range 0 to 4 (not shown). Virtually no hydrous oxide formation was observed on cycling within the pH range 4 to 9. A major increase in the rate of oxide growth with increasing pH was observed within the range 9 to 14.

A somewhat similar pH dependence has been described previ-

osuly⁽⁷⁴⁾ for thermally prepared RuO₂ electrodes where the voltammetric charge associated mainly with surface pseudo-capacitance reactions showed a U-shaped variation with solution pH. In recent years, work on hydrous oxide growth on iridium under potential cycling conditions⁽⁷⁵⁾, also showed the same type of pH dependence at low pH as for platinum, interaction of the hydrous film with protons from solution at low pH (and, in the present case, hydroxide ions at high pH) was assumed to enhance oxide growth by catalysing the rearrangement of the initially amorphous surface oxide layer.

Apart from being of intrinsic interest, the production of hydrous oxide films on platinum in both acid and base solutions was of considerable practical importance as it provided a simple route to controlled platinization. Thus, along with the possibility of reactivating a platinum impregnated electrode system, the present work demonstrates that the cycling procedure is a useful technique for the pretreatment of platinum surfaces prior to fundamental investigations in electrochemistry and related areas.

The hydrous oxide produced on platinum is not unlike that formed on gold in that it reduces to the metal at more negative potentials (even in terms of a hydrogen reference electrode in the same solution) as the pH of the solution is increased. (The present results for platinum in this respect are in agreement with earlier observations by Shibata⁽⁷⁷⁾ who found it difficult to reduce dc grown thick oxide films on this metal in base). As outlined

previously⁽⁷³⁾ this is apparently due to the fact that the hydrous oxide is present in an anionic form: although direct experimental confirmation is lacking at the present time⁽⁷⁸⁻⁷⁹⁾, the oxyplatinum compound present is assumed to be a Pt(IV) species. One of the most interesting aspects of the present work from a fundamental viewpoint is that, of the various possible oxides in this system, the hydrous platinum oxide is the most stable. This is the reason why no electrochromic transition is observed. The higher oxidation state, probably Pt(IV), is more stable in the hydrous state than Pt(III), Pt(II) or Pt(I), i.e, when reduction eventually occurs it proceeds right through to the metal in one four-electron reduction step. From a thermodynamic viewpoint platinum seems to be susceptible to oxidation at surprisingly low potentials, certainly less than 0 V (RHE) in basic solutions. The barrier or inhibition associated with hydrous oxide formation is normally so high that the possible presence of this material is widely ignored. However, traces of this oxide, produced perhaps in surface pretreatment steps, especially in the case of work in basic solution where removal by reduction is quite difficult, may affect the kinetics of interfacial reactions in this system.

The Nernst equation for a reduction reaction



is:

$$E = E^\ominus - (RT/nF) \ln (a_M/a_M^{n+}) \text{-----(1)}$$

or at 298K and one atmosphere pressure and unit activity of solid metal deposit

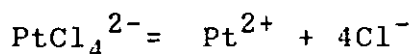
$$E = E^\ominus + (0.059/n) \log_{10} (a_M^{n+}) \text{----(2)}$$

Note that the potential shift due to non-standard conditions is approximately

$$\Delta E = (E - E_\ominus) \text{-----(3)}$$

This can be regarded as an overpotential.

The equilibrium constant for a complex is typically



ie, $[\text{PtCl}_4^{2-}] / [\text{Pt}^{2+}] \times [\text{Cl}]^4 = 10^{-16} \text{---(4)}$

From which $[\text{Pt}^{2+}]$ is approximately $10^{-16/5} \text{---(5)}$

because $[\text{PtCl}_4^{2-}]$ is approximately 1 for a strong complex and $1 \times \text{Pt}^{2+} + 4\text{Cl}^- = 5$ ions

each of activity approximately $10^{-16/5}$

Substituting values of E into equations (2) and (3) and

For -500 mV overpotential

$$-0.5 = (0.059/2) \log_{10} a_M^{n+}$$

$$-0.5 = 0.0295 \log_{10} a_M^{n+}$$

$$\log_{10} a_M^{n+} = -0.5/0.0295$$

$$\log_{10} a_M^{n+} = -16.95$$

$$a_M^{n+} = 10^{-16.95}$$

For -600 mV overpotential

$$-0.6 = (0.059/2) \log_{10} a_M^{n+}$$

$$-0.6 = 0.0295 \log_{10} a_M^{n+}$$

$$\log_{10} a_M^{n+} = -0.6/0.0295$$

$$\log_{10} a_M^{n+} = -20.34$$

$$a_M^{n+} = 10^{-20.34}$$

Similarly for -650 mV overpotential

$$a_M^{n+} = 10^{-22}$$

For -700 mV overpotential

$$a_M^{n+} = 10^{-23}$$

and for -750 mV overpotential

$$a_M^{n+} = 10^{-25.4}$$

From the above calculations it can be concluded that as excess Cl^- is high, the activity of Pt^{2+} is less and hence,

Pt^{2+} will be less than is being estimated so that the calculation is justified.

Comparison can now be made between the calculated values of Pt^{2+} activity for a given presumed potential shift and those potential shift values observed. Of all the combinations considered, the most credible is

$$a_{Pt^{2+}} = 10^{-16}, \quad \Delta E = 500 \text{ mV}$$

Consequently it is reasonable to attribute the potential shift primarily due to the chloride complexing effect for Pt^{2+} .

5.3 INVESTIGATION OF PHOSPHATES IN PLATING TANKS

5.3.1 EFFECT OF PHOSPHATES CONCENTRATION IN PLATINUM SOLUTION

The drag-out tank should preferably be lined with plastic and kept covered when not in use. Under these circumstances drag-out solution may be returned to the main tank but if there is any possibility of contamination, this should not be done. Somehow the drag-out solution has not been returned to the actual platinum plating tanks and as a result of this effect, the amount of phosphates in each tank was dropped at the end of each month. This is clearly an important matter if standard practice is to be introduced.

Considering, the maximum and minimum amounts of phosphates of each tank, the average loss of phosphates in each tank would be 15.3g/l. But the volume of each tank is 170

litres so;

$170 \times 15.3 = 2600\text{g}$ for 170 litres for two months or 1300g/month.

Assuming that, if 500 items or blades would be electroplated per week, during a month this would be 4000 items or blades so $1300/4000 = 0.325\text{g}$ phosphate. This reduction in phosphates could ultimately have significant effect on platinum losses and therefore losses in a company's financial profits due to the high price of platinum (approx. £11.0 per gram in 1991).

As the concentration of platinum in each tank is 3.0-4.0g/l Pt, for 170 litres the total is 510-680g Pt. Consequently, for 4000 items or blades $510-680 \times 0.325$ (loss in phosphates)/total phosphates in one tank, can result in 43 to 58g Pt loss over 4000 items. This means a loss of £(473-638) in financial terms.

5.4 RECOMMENDATIONS FOR THROWING POWER

The results related to the use of anode electrodes, given in the results section with the effect of Ni and Ni strike solutions and parameters, require one or two preliminary comments. Firstly, an increase in applied current resulted in producing a larger deposited or covered area; secondly, having used low current, the deposit thickness variations are more uniform and deposited in mid-section of deposit, compared with higher current.

According to Figure 80 the spherical anodes produced deposits of the required thickness within the deposit diameter. Nevertheless, these deposits tended to indicate

that with higher current (see Fig 80) the deposit size scattered within the longer range and the actual shape of deposit was not maintained. By contrast, with lower current the exact shape was reproduced, despite not producing the desired thickness. Now having used longer plating times (range between 5-10 minutes) with 5mm interelectrode separations , the desired thickness was attained successfully.

The interelectrode separation range of 3-5mm was used with the above solutions. However, using a Ni-strike with an operating current of 530-650mA, interelectrode separation of 3-5mm and a constant plating time of 5 min proved to be insufficient in maintaining the required thickness of 5.0 μm (not shown). Moreover, after thickness measurement, it was found that the maximum thickness was only 1.2 μm . A second attempt was made with higher current ranges of 1.0-1.4 and 1.5-1.6 Amp , plating time of 5 minutes with an interelectrode separation of 5mm. This time, the required thickness was achieved.

5.5 PULSE PLATING

The results presented in previous sections have shown how the use of pulse plating may be utilised to produce good, dark deposits of Pt when the following influences are established.

- (1) Effect of current densities upon deposit. .
- (2) Effect of on-time to off-time ratio.

5.5.1 EFFECTS OF CURRENT DENSITIES UPON DEPOSITS

As can be seen from the pulse-plating results, increasing the current densities used has achieved a number of advantages in electrodeposition. In particular, a higher cathode efficiency than in conventional plating has been obtained from all platinum solutions investigated.

An extensive study by Ibl⁽⁴⁹⁾ showed that a wide variety of current distribution effects could be found in every day plating practice. Increase in the current density results in an increased rate of formation of nuclei, which give a fine-grained and adherent deposit. But increase in current density using conventional-plating causes local impoverishment of metal ions round the cathode electrolysis with increased hydrogen evolution and, consequently, the deposits became either dark or unadherent. Premature hydrogen evolution leads to lower efficiencies of course.

Figure 7 shows a schematic representation of the mechanism of cathodic deposition. It would be appear that, by interrupting the plating process during the time that the current is off (100 or 200 msec), the solution concentration within the so-called diffusion layer, has time to become replenished and platinum atoms (Pt^{2+}) or 'adatoms' at the cathode surface shown in same figure have time to migrate to equilibrium sites of lattice. Before reaching the cathode surface the platinum atoms combine with water molecules: this process is an important part of the overall transfer process.

Using normal plating, the higher the current density being used the less time the 'adions' have to find the most

suitable discharge sites which could lead to greater distortion in the growing lattice. In practice this distortion would show up as stress in the deposits. The use of pulse plating associated with higher current densities have shown that a less distorted lattice can be formed and a softer more ductile deposit may be produced.

Figures(85-105) show a comparison between pulse and conventional plating used, for various current density. The results appear to indicate that pulse plating deposition for all solutions produced dark deposits and high cathode efficiency values compared with direct current.

5.5.2 EFFECT OF ON-TIME TO OFF-TIME

Pulsed-current electrolysis with ratio of on-time to off-time of 10/100 and 10/200 msec have been applied to the deposition from platinum solution. In pulse plating, the off duty factor, the pulse duration and the current density are all related to the obtaining of a high quality plating rate at least comparable to normal plating. The surface morphology of platinum deposits, plated with pulsed current of periods in the 10 msec on and 100 msec off range with fixed average plating current density, are affected significantly. This significant factor was observed during the pulse plating process and this is shown in Figures (84-105) . The most plausible explanation is that adsorption of an inhibiting species, which block the growth centres of the cathode during the off-time, yield finer grained deposit.

N.Ibl⁽⁴⁹⁾ has explained such features in terms of the

availability of high current density in pulse-plating which generates free additional energy, and because the free energy for the electrode reaction is much higher than that for direct current. Therefore, this can strongly influence the crystallization features. As the nucleation rate is enhanced in the initial crystallization, the final grain size become smaller. A summary of pulse plating's practical features are shown in Figure 108 for the specific equipment used. The use of pulse generator, oscilloscope, power mosfets distinguishes the pulse plating procedure from conventional plating arrangements, and obviously has implications for equipment usage and overall economics.

CHAPTER 6

6.0 DISCUSSION: PROCESS IMPLICATIONS

A study has been under-taken to define the processing parameters which influence the electrodeposition behaviour. The control of electrodeposition by means of pulse plating has been investigated and the following conclusions drawn;

- (i) Higher cathode current efficiencies have been achieved with higher current densities using pulse plating.
- (ii) Higher weight gains and darker deposits were resulted using pulse plating.

6.1 CLING FILM

The weight of low molecular weight polymeric contaminant entering the plating solution during a typical plating run with 30 components in the bath would be about 4.0g. Some or all of this could be removed by adsorption on the carbon filter in the recirculatory system of the bath. It is unlikely that small levels of contaminant would influence the efficiency of the plating process.

6.2 NATURAL RUBBER

After long research and communicating with other firms dealing with polymers and rubber, it was decided that natural rubber was the final choice; it was utilized for

over 10 hours and it was found that this material could withstand the electrodeposition of platinum without platinum depositing on it. Consequently, C.U.K Ltd decided to go ahead with ordering the actual mould for rubber boots.

6.3 COMPARISON OF SOLUTIONS

6.3.1 CHARACTERISTICS OF BATH COMPOSITION

Bath Nos 16-19 have given the highest cathode current efficiencies compared with bath Nos 1-15. The common additive factor is a 'P' Salt which all baths 1-19 contained. From Tables 24 and 29 it can be seen that phosphate salts were replaced by sodium acetate and sodium carbonates. It appeared that sodium citrate, sodium sulphate and sodium chloride could improve the stability of these baths.

M.Pushpavanam and et al⁽⁸¹⁾ have claimed that with baths No.s(16-19), the current efficiency starting from 4 g/l is about 5%, rising to 30% with 10g/l platinum content. It can be seen from the above tables that current efficiencies started from 18% and rose to a maximum 52% with constant usage of 5g/l platinum content. The only difference was higher pH value 11.5 that was used in above experiments compared with M.Pushpavanam and et al⁽⁸¹⁾ who used values of 8.0-9.5.

Bath No.6 from Table 27 has proved to have the lowest current efficiency due to the nature of solution (Platinum present as dinitritosulphato- platinum complex). OMI International⁽⁸²⁾ has shown that with above bath they found a very good performance in the current density range

of 5 to 10 mA/cm², ranging from 12% to 28% current efficiency with 4-10 g/l platinum content. Table 27 and Fig 90 show that the current efficiency was relatively high(4.9%) with lower current density and diminished to 0.3% with high current density.

The deposits obtained from these baths had a yellowish-white appearance.

'Q'Salt from Johnson Matthey has proved to produce the higher cathode efficiency with lower current density.

6.3.2 LOW AND HIGH CURRENT DENSITY CHARACTERISTICS OF PLATING BATHS

A new method of plating was described in section 4.1.2 which was shown to produce higher current efficiency. This method as described before and shown in Fig 50, uses a low current density for few minutes followed by higher current density for longer period. This method only applied with 'Q' Salt, and with 'P'Salt was ineffective.

6.3.3 METAL ION CHARACTERISTIC OF PLATING BATHS

One of the inherent disadvantages of platinum is their relatively purchase cost. It was this problem which led to the appraisal of much lower platinum concentration solutions for use in the electroplating and cathodic polarisation trials.

M.Pushpavanam et al⁽⁸¹⁾ have claimed that with use of 'P'Salt (Bath.I) exhibits an almost steady cathode current efficiency, whereas with combination of 'P'Salt and

other additives(Bath.II) such as sodium nitrite ,sodium sulphate and sodium chloride and finally bath containing 'Q'Salt (Bath.III)differences are observed beyond 6 g/l. The efficiency is higher for 'Q'Salt bath than for Bath.I and Bath.II. Bath.III is so influenced by the metal concentration, there is a drastic loss of efficiency which goes down to 5% for 3 g/l metal content in solution and the deposits obtained are grey in colour. Bath.II gives very poor efficiency for 5 g/l or less platinum in solution.

Bath.I, in which the optimum metal ion concentration is only 5 g/l , yields good deposits and there was sufficient platinum present to eliminate the need for constant replenishment. Bath.I, yields even with 3 g/l platinum in solution, but below this concentration black streaky deposits, which become powdery with an increase in thickness, are obtained.

It can be seen from the practical results given in Figs 48-49 that the range of platinum content is between 2.0-5.0 g/l and was found to give high current efficiency and good performance in the current density of range 8-16 mA/cm² . Whereas, with (81) results in the range of 5 to 10 mA/cm². Figs 54-58 that 'P'Salt and 'Q'salt baths have similar results compared with above results.

Consider the virtue of increasing the platinum concentration in solution to increase current density, using equation below;

$$i_L = \eta FCD / \delta \text{ in which } i_L \propto C$$

The limiting current is equal to the product of limiting

current density and electrode area:

$$i_L = j_L A \text{ -----(1)}$$

Where; $j_L = nFD_O C_O / \delta_N$ (Fick's First Law)---(2)

and equation (1) may be written:

$$i_L = A n F D_O C_O / \delta_N \text{ -----(3)}$$

Where;

D_O = Diffusion coefficient of oxidation ($m^2 S^{-1}$)

C_O = Concentration of oxidation ($mol m^{-3}$)

F = Faraday Constant ($96485 C mol^{-1}$)

A = Electrode area (m^2)

δ_N = Nernst diffusion layer thickness (m)

For a given electrode reaction and electrolyte, the limiting current may therefore be increased by adopting the following strategies:

(1) Increasing the active electrode area, A .

(2) Increasing the diffusion coefficient, D_O by, for example, elevating the temperature.

(3) Increasing the reactant concentration, C_O .

(4) Decreasing the Nernst Diffusion layer thickness, δ_N , by enhancing relative electrode/ electrolyte movement.

The concept of a diffusion layer is widely used but it is not usually possible to directly measure δ_N experimentally. Electrochemical Engineers therefore prefer to write equation (3) as:

$$I_L = A n F K_m C_O \text{ -----(4)}$$

Where K_m is a rate constant for mass transport and is known as the mass transport coefficient (unit: ms^{-1}). It is defined by the equation:

$$K_m = j_L / n F C_o \text{ -----(5)}$$

and is measurable by experiment.

A comparison of equations (3) and (4) shows that the mass transport coefficient is directly related to the Nernst diffusion layer thickness as follows:

$$K_m = D_o / s_N \text{ -----(6)}$$

It is important to relate K_m to the electrolyte flow conditions. It is generally found, for a given electrode geometry and electrolyte flow condition, that:

$$K_m \propto V^a \text{ -----(7)}$$

Where V is a characteristic velocity (e.g. the linear velocity of an electrolyte or the rotation speed of a rotating electrode). The velocity exponent ($0.3 < a < 1$) depends upon the electrode geometry and the flow regime (e.g. laminar or turbulent flow).

Considering expressions (4) and (7), we may write an expression for the limiting current:

$$I_L = K A C_o V^a \text{ -----(8)}$$

Where K is a constant which depends upon the electrode geometry and the flow conditions^(83,85).

For a rotating disc electrode (RDE) in laminar flow, the constants 'K' and 'a' are very well established and expression (8) becomes:

$$I_L = 0.62 n F D_o^{2/3} v^{-1/6} A C_o w^{1/2} \text{ --- (9)}$$

Where v is the Kinematic viscosity of the electrolyte and w is the rotation speed of the RDE⁽⁸³⁻⁸⁷⁾.

6.4 CURRENT VERSUS ELECTRODE POTENTIAL RELATIONSHIPS UNDER PURE MASS TRANSPORT CONTROL

At equilibrium, the electrode potential may be described by the Nernst equation :

$$E_e = E_e^\ominus + (RT/nF)\ln C_o \text{ ----- (7)}$$

Where E_e^\ominus , is the formal potential i.e, the equilibrium potential when $C_o = 1 \text{ mol dm}^{-3}$. If the electrode is reversibly taken away from equilibrium to a more negative value its new potential will be

$$E_e = E_e^\ominus + (RT/nF)\ln C_o, \text{ ----- (8)}$$

Where C_o , is the new metal ion concentration, which must be less than the original value due to metal deposition ($C_o < C_o$). The overpotential, η , is defined as the difference between the actual potential and its equilibrium value:

$$\eta = E - E_e \text{ ----- (9)}$$

and the concentration overpotential, which exists due to mass transport control, is obtained by subtracting equa-

tion (7) from (8) as:

$$\eta_{\text{conc}} = (RT/nF)(\ln C_o', -\ln C_o) \text{ ---(10)}$$

or

$$\eta_{\text{conc}} = (RT/nF)\ln(C_o' / C_o) \text{ ---(11)}$$

C_o may be identified as the bulk concentration of reactant and C_o' , as the surface concentration under limiting current conditions such that:

$$\eta_{\text{conc}} = (RT/nF)[\ln(C_o')_{x=0} / C_o] \text{ ---(12)}$$

The concentration terms may also be related to Fick's First Law which may be written as :

$$j/nF = -K_m [C_o' - C_o]_{x=0} \text{ ---(13)}$$

or

$$(C_o' - C_o)_{x=0} = -j/nFK_m \text{ ---(14)}$$

Division of equation (14) by C_o gives:

$$(C_o' / C_o - C_o)_{x=0} / C_o = -j/nFK_m C_o \text{ ---(15)}$$

$$C_o'_{x=0} / C_o = 1 - j/nFK_m C_o \text{ ---(16)}$$

Substituting the left hand side of equation(16) into equation (9) gives:

$$\eta_{\text{conc}} = (RT/nF)\ln(1 - j/nFK_m C_o) \text{ ---(17)}$$

Recalling equation (4) allows equation (17) to be written

as:

$$\eta_{\text{conc}} = (RT/nF) \ln(1 - I/I_L) \text{ --- (18)}$$

Which describes the overpotential in terms of the current for a reaction which is under pure mass transport control. Such reaction conditions are usually termed 'reversible' or 'fast. Equation (18) may also be written as an expression for the current:

$$I = I_L (1 - \exp nF \eta_{\text{conc}} / RT) \text{ ---- (19)}$$

This relationship describes the idealised shape of the current versus overpotential. At more negative overpotentials, the current becomes more negative (corresponding to an increasing rate for a cathodic process) until the limiting current is reached. At $I = I_L$, the concentration overpotential becomes infinite ($\eta_{\text{conc}} \rightarrow \infty$) and the limiting current plateau represent a current which is independent of potential. In practice, the continuation of the plateau is restricted by the onset of a secondary reaction (such as deposition of a less noble metal or the evolution of hydrogen) when the overpotential becomes sufficiently negative.

Such theoretical concepts may sometimes neglect important practical factors which have a bearing on commercial decisions. For example, increased platinum concentrations in solutions raises the inventory charge for the process; enhanced agitation requires substantial energy use. Such aspects are not being considered in the context of this thesis but should be noted at this point.

6.4.1 THE INTERPLAY BETWEEN ELECTRON TRANSFER AND MASS TRANSPORT CONTROL

So far pure mass transport mass has been considered, i.e. the rate of transport of a species to (or from) the electrode surface is the slowest (and therefore the rate determining) step in the overall reaction. F.C.Walsh⁽⁸⁸⁾ has considered another extreme case in which electron transfer was the slow step. In practice, it is common to experience a large region of overpotential where the reaction rate is controlled partly by electron transfer. Such reaction conditions are said to be under 'mixed control'. In certain cases, it is possible to experience three distinct potential regions;

- 1- Pure electron transfer control
- 2- Mixed control
- 3- Pure mass transport control

6.5 EFFECT OF TEMPERATURE CHARACTERISTICS OF PLATING BATHS

M.Pushpavanam and et al⁽⁶⁹⁾ have claimed that with 'P'Salt(Bath.I)a solution could be operated at ambient temperature (32°C), but for obtaining thin coatings (< 0.8mm)at a slightly higher rate of deposition, higher temperatures of the order of 45°C to 50°C can be utilised. Higher temperature operation is, however, not advisable for prolonged production of thicker coatings since only flaky deposits are obtained. Even a nickel undercoat does help in obtaining thick coatings at higher temperatures. Bath.II functions at a higher efficiency with increase in

its temperature; however, the corresponding loss of ammonia leads to a progressive decrease in the pH value and the deposition eventually ceases. A bath temperature of 65 to 70°C is suitable for obtaining quality deposits with a reasonable current efficiency. Below 65°C, however, no deposition was found to take place.

Bath.III also exhibits a similar behaviour at temperatures below 50°C. The bath has a high efficiency and produces dull deposits at temperatures of 55 to 65°C. At still higher temperatures the bath decomposes.

In fact higher temperatures were investigated and these results are given in Fig 56. With a temperature of 96°C the steady increase of cathode efficiency can be seen compared with lower temperature 86°C. In general, a higher operating temperature for the plating bath permits higher plating rates because of improved mass transport, but it also increases the thermal decomposition tendency of the plating bath, resulting in precipitation of the dissolved platinum group metal(s).

It is a common misapprehension that reaction rates increase with temperature only because molecules collide more frequently. Clearly there is another factor to consider apart from collision frequency. This factor is the proportion of collisions which actually lead to a reaction ('fruitful' collisions). The proportion of 'fruitful' collisions rises steeply with temperature for many reactions. On the basis of activation energy and potential energy, it is clear that for many reactions only a small proportion of molecules have sufficient kinetic energy for 'fruitful' collision. As temperature increases,

the average kinetic energy increases and the proportion of molecules with kinetic energy greater than or equal to E_A also increases. This is demonstrated by Maxwell-Boltzman distributions at two temperatures. He showed the number of molecules of different kinetic energies plotted against the average kinetic energy. The numbers of molecules having kinetic energy greater than or equal to E_a areas were obviously greater at the higher temperature. The proportion of molecules having kinetic energy greater than or equal to e_A is given by

$$e^{-E/RT}$$

Considering the temperature effect as a means of increasing rates. The Arrhenius law describes classical behaviour under thermal activation;

$$\text{Rate} = K_0 \exp (-Q/RT)$$

Where Q is the activation energy.

6.5.1 LOW TEMPERATURE

Since the very existence of a metal is determined by the skin of oxide on its surface, and since the reaction of a metal in gaseous media at all temperatures determines the possible uses of that metal, it is clearly important that the mechanism of oxide growth should be understood.

Oxidation rates are usually described with reference to the mathematical relationship found between the oxide

thickness, y , which is assumed to be uniform, and time, t . At low temperatures and for thin films the relationships are of the form $y = K_1 \log t$, logarithmic, $1/y = K_2 - K_3 \log t$, inverse logarithmic, and $y = K_4 [1 - \exp(-K_5 t)]$, asymptotic, where $K_1 - K_5$ are constants.

Across very thin layers of oxide a very strong electric field is created. Under this field oxide growth can be expected. Metal ions are pulled through the film. As the film thickens, the effect of the field diminishes rapidly and is no longer sufficient for further growth. Unless there is sufficient thermal energy present to cause continued growth by ionic diffusion under a concentration gradient in the film, the rate of oxidation will fall off rapidly.

It is important to observe at this point that logarithmic growth is found in films that are very much thicker than it is possible to form under a high electric field. Explanations are usually based upon physical changes that occur within the oxide. One common example arises where vacancies in a film condense to form cavities. Assuming that there is no transport of matter across the cavities, the oxidation paths will be constricted as the film thickens. Usually the growth-rate of this type of film becomes logarithmic only gradually and the initial growth-rate is much faster, being associated with relatively high temperatures. Other explanations are based upon 'ageing' of films, producing changes that are not well understood, but which produce logarithmic growth-rates. Logarithmic growth is usually associated with thin films at low temperatures.

6.5.2 HIGH TEMPERATURE

At higher temperature ranges the rate of oxidation ceases to obey a logarithmic type law. Growth now becomes more rapid and above some temperature follows a parabolic law, generally described as $y^2 = Kt$, where K is the parabolic rate constant and different from any previously mentioned constants.

In parabolic oxidation the driving force for the reaction is twofold. Firstly, there is a concentration gradient across the film and secondly, there is an electric potential gradient. These are responsible for diffusion and migration, respectively, across the film. Since the rate for both is inversely proportional to the thickness, the thickening rate of the oxide,

$$dy/dt = K_{\text{diffusion}}/y + K_{\text{migration}}/y$$

and $K_{\text{diff}} + K_{\text{mig}} = K$, the observed parabolic rate constant. Under the conditions that (a) boundary reactions can be ignored, and (b) the field does not act on the moving particles asymmetrically, the energy dissipated is the same in both cases so that it is legitimate to consider parabolic oxidation from a diffusion or an electrical migration aspect.

The concentration gradient in the film produces a difference in chemical potential across the film which in turn results in the necessary free energy change for diffusion to occur.

From the simple version of Fick's diffusion law:

$$dm/dt = D A (dc/dx) \text{ -----(1)}$$

Where dm = mass of matter diffusing across a distance dx in time dt , D = constant, A = area, and dc = concentration difference across the distance dx .

Integrating,

$$m = D A (dc/dt) t + \text{constant} \text{ -----(2)}$$

If m = mass of diffusing species in an oxide, ρ = oxide density, W = molecular weight of the oxide, M = atomic weight of the diffusing species in the oxide and n = number of atoms of that species in a molecule of oxide, then:

$$m = y A \rho * n M / W \text{ -----(3)}$$

Substituting for m in equation (3) from equation (2) and for dx which is equal to y :

$$y A (M n/W) \rho = D A (dc/y) t$$

Therefore,

$$y^2 = K t.$$

The parabolic growth of oxides is commonly found in nearly all metals over some temperature range. It is a thermally activated diffusion process and the rate constant,

$$K = K_0 \exp - (Q/RT),$$

Where,

Q= activation energy for the diffusion process, involved,

R= gas constant,

T= absolute temperature

K_0 = is a constant

If only one ion is diffusing through the oxide during its growth, then the value of q for the oxidation process will be the activation energy for the diffusion of that ion. This value can sometimes be compared with independently determined values of activation energy for ion diffusion in oxides and thereby provide an important experimental verification for the rate-determining process.

In general, an increase in the temperature of deposition causes an increase in the crystalite size. This increase in crystal size corresponds to a decrease in polarisation at the higher temperature.

That fine-grained, smooth deposits are often produced in intentionally heated solutions is caused by the fact that, at higher temperatures, higher current densities are possible and customary. The higher current density counteracts the effect of the higher temperature. The influence of temperature is caused by a greater solubility and dissociation of the metal salt, which, in turn, leads to a higher conductivity of the solution. A high temperature increases the mobility of the metal ions and decreases the viscosity of the solution, so that the cathode film is more rapidly replenished. This reduces the tendency toward treeing and also increases the current density obtained with a given voltage. Another advantage of high tempera-

ture is that there is usually less absorption of hydrogen in the deposits and less stress and tendency toward cracking, this is especially true of iron, nickel, or cobalt.

6.5.3 BATH COMPOSITION-METAL CONCENTRATION

Because metal can be deposited only from solutions that contain some dissolved compound of that metal, it might appear advisable to have the highest possible concentration of that salt, e.g., a saturated solution.

Among the advantages of using a strong solutions are;

- (1) a higher conductivity,
- (2) a higher permissible current density,
- (3) a higher cathode efficiency.

Its disadvantages include;

- (1) its increased cost, both for initial preparation and to replace the drag out(which is relatively greater in stronger and more viscous solutions),
- (2) the tendency to salts crystallize out if evaporation occurs or the temperature is lowered,
- (3) a probable decrease in anode efficiency.

In practice, intermediate concentrations are used, but the present tendency is to employ as strong a solution as feasible. An increase in metal concentration under given conditions decreases the cathode polarization and , as predicted, increases the crystal size. Just as with an increase in temperature, the higher current density that can be used with more concentrated solutions may effectively counteract the effect of concentration on the crystal size.

6.5.4 METAL-ION CONCENTRATION

Because metal deposition is the result of discharge of the metal ions, the concentration of the latter is more important than that of the metal compounds from which they are derived. In general, a decrease in metal-ion concentration increases the cathode polarization, decrease the crystal size, and improve the throwing power. If the desired low metal-ion concentration were obtained by merely using a dilute solution of a simple metal salt, the supply of metal at the cathode would be very quickly exhausted and the limiting current density would be so low as to be impractical. This difficulty can be overcome by using solutions that have a high concentration of metal compounds but a low metal-ion concentration. The metal compound then serves as a reservoir that replenishes the supply of ions as they are discharged.

6.6 OPTIMUM SOLUTION COMPOSITION

Optimum solution compositions have been established for a number of solutions. Preferred solutions are bath Nos 16-19 have given the highest cathode current efficiencies compared with bath Nos 1-15. The common additive compound is a 'P' Salt which all baths 1-19 contained. From Tables 24 and 29 it can be seen that phosphate salts were replaced by sodium acetate and sodium carbonate. It appeared that sodium citrate, sodium sulphate and sodium chloride could improve the stability of these baths.

CHAPTER 7

7.0 DISCUSSION: INDUSTRIAL PRACTICE FOR GAS TURBINE ENGINES

In this chapter three case studies are provided of how, in very practical terms, turbine blade components have been coated with platinum. These demonstrate how the scientific ideas discussed earlier have been transferred to the factory shop and produced successful products.

7.1 CONSEQUENCES FOR PLATING TURBINE BLADES; ROLLS-ROYCE RESULTS

INTRODUCTION

12 off TG20 1st buckets and 12 off TG20 2nd stage buckets were supplied to CUK Ltd by Fiat Avio for RT22 platinum aluminium process validation.

This section outlines the processing of these parts, the final visual and metallurgical inspection findings and the results of the required mechanical testing.

INITIAL VISUAL INSPECTION

Initial inspection of the 1st stage buckets revealed 3 off to have cooling holes blocked by glass contamination,

these components were rejected, to be returned to Fiat. The remaining 9 off components found to be in a satisfactory condition for processing. Initial inspection of the 2nd stage buckets showed them all to be in a satisfactory condition for processing.

PROCESSING REPORT

Both 1st and 2nd buckets were platinum aluminised by the procedure outlined in CUK's route card 08-2038. On post diffusion inspection 1 off 1st stage bucket, was rejected due to blistering of the plated layer on the convex platform aerofoil radius. This component was reworked by over plating to restore the lost Pt layer and rediffusion. Inspection following rework showed it to be in a satisfactory condition for coating.

FINAL INSPECTION REPORT

TG20 1st stage and 2nd stage buckets in tables 48-49.

METALLURGICAL ASSESSMENT OF APPLIED RT22 COATING

2 off buckets of each type, designated by Fiat, were sectioned, shown in figure 109. The 3 off aerofoil sections and 1 off root section obtained from each blade mounted and prepared for metallurgical examination to assess the achieved coating structure, thickness and chemistry.

Figures 109-112 illustrate the coating parameters observed on each of the 4 off buckets respectively. Fig 113 illus-

trates the coating observed on the test tabs.

Examination of each of the aerofoil sections revealed a uniform coating of typical RT22 structure with a thickness in the range 0.0032-0.0042 inch(5-6um), some slight build up being noted around the leading and trailing edges.

The final coating structure consists of an outer Pt rich layer, a mid nickel aluminide layer and an inner layer containing precipitated carbides. The Pt content of the outer layer was found to contain 41.0 to 59.7 wt% of Pt and the nickel aluminide to contain a maximum of 20.1 to 21.4 wt% of Al.

The Pt content is considered satisfactory and within the required specification, the Al content is just below the required specification, this is considered due to the high temperature of the final solution heat treatment and is as expected.

Void type defects were observed within the coating particularly around the leading edges and convex aerofoil faces. These voids occur between the outer Pt rich layer and mid nickel aluminide. Investigation of the nature of these voids suggested that formation occurs during aluminising and is an alloy related phenomena.

Photomicrographs 1 and 2 illustrate a typical defect.

Further investigation and development is required to understand the cause of voiding and to develop a viable production route to prevent the defect. CUK will present their proposal for this development work under separate cover.

Examination of the root sections taken revealed no evidence of any bleed or Pt plate overspill onto the machined

serrations. Examination of the platform side faces showed effective stopping off of the aluminising confining the coating to the gas washed surface. However, some Pt over-
spill onto the side and root shank was noted.

Examination of the U500 test tabs confirmed the coating thickness and chemical composition observed on the component.

DYE PENETRANT INSPECTION

The 9 off 1st stage buckets and 12 off 2nd stage buckets were processed through CUK F2 group class B post emulsified dye penetrant. No evidence of any linear defects was observed on any component.

NON-DESTRUCTIVE HARDNESS TESTING

Both the 9 off 1st stage buckets and 12 off stage buckets were hardness tested and the results are illustrated in table 50.

STRESS RUPTURE TESTING

Stress rupture test bars were machined from 1 off 1st stage bucket, and 1 off 2nd stage bucket, in accordance with Fiat spec 601-092 and PDS83275, in addition test bars were also machined from the U500 blank processed in each coating retort, 2 off total.

The stress rupture testing was carried out by ERA Technology in accordance with the conditions laid out in PDS83275.

The results of the stress rupture testing are detailed in

Table 51 and shows 3 off bars to have failed the test, of the remainder 3 off stripped the threads from the loading bars and 2 off are on hold subject to review of the testing parameter.

Joint assessment of the testing parameter and results obtained is required to resolve the poor performance of these test pieces.

CONCLUSION

Process validation of RT22 platinum Aluminising on Westinghouse TG20 1st and 2nd stage buckets has demonstrated the ability of CUK to apply a uniform coating of the correct thickness on both stages of buckets.

Detailed inspection and metallurgical examination has highlighted several problem areas which need joint discussion to resolve.

1) Visual inspection of both stages revealed a generally acceptable coating. However, on a large number of component overspill of stop off onto the aerofoil surface caused unacceptable defects.

CUK believe this problem can be solved by further operator training and by the introduction of a 100% overcheck of all stopped off blades prior to aluminising. This overcheck to be carried out by an inspector.

2) Metallographic examination revealed the presence of void defect within the coating, generally associated with the leading edge and convex aerofoil faces.

Agreement is required for a further programme of work to investigate and eliminate the cause of this problem.

3) Chemical analysis of the coating revealed an aluminium

content below the required specification range. CUK believe that within the confines of the required coating thickness and final heat treatment specification increased aluminium content will be difficult to achieve.

4) All stress rupture test to date have proved unacceptable. Joint assessment of the performance to date is required.

7.2 WESTINGHOUSE TG20 1ST AND 2ND STAGE VANES

7.2.1 RHODIUM MODIFIED PLATINUM ALUMINISING TO RT22LT

7.2.1.1 PROCESS VALIDATION REPORT

INTRODUCTION

Fiat Avio supplied CUK Ltd with 12 off TG 20 1st stage vanes and 12 off TG20 2nd stage vanes for RT44 Rhodium modified platinum Aluminising.

This section outlines the processing of these parts, the final visual and metallurgical inspection findings and the results of the required mechanical testing.

INITIAL VISUAL INSPECTION

Initial inspection of the 1st stage vanes revealed 1 off to be partially coated, this component was rejected to be returned to the customer.

The remaining 11 off components were all accepted for processing. Initial inspection of the 2nd stage vanes accepted all the parts for processing.

PROCESSING REPORT

1st and 2nd stage vanes were both RT44 coated to the procedure outlined in CUK's route card 08-2040. A copy of the 08 and its associated data cards is appended to this report together with all relevant furnace charts.

Application of Pt plating proved satisfactory. However, some difficulties were experienced in the Pt plating of

both 1st and 2nd stage vanes, relating to the localised stressing of plate particularly on gas washed platform and radii.

This level of stressing caused some lack of adhesion of the plate during vacuum diffusion resulting in local spalling of the plate.

Non destructive assessment of these defects indicated that only the platinum had failed to adhere, the rhodium diffusing satisfactorily.

To recover these components the parts were over plated with platinum and rediffused. Inspection following rework confirmed the part to now be satisfactorily plated although evidence of this rework was visible as a step 0.0005~(approx) between the reworked and unreworked areas. 10 off of the 1st stage vanes and all 12 off of the 2nd stage vanes were reworked. (Vane IH 1798 not require rework).

FINAL INSPECTION REPORT

TG20 1st stage vane are shown in Table 52.

TG20 2nd stage vane are shown in Table 53.

METALLURGICAL ASSESSMENT OF APPLIED RT44 COATING

Two off vanes, of each type, designated by Fiat, were sectioned in accordance with PDS 83262 AE.

Each section obtained, 3 off aerofoil and inner and outer platform section from each 1st vane and 6 off aerofoil and inner and outer platform sections from each 2nd vane, were mounted and prepared for metallurgical examination to

assess the achieved coating structure, thickness and chemically.

Sections were also taken from the X45 test tabs processed with the components to confirm compatibility in the coating achieved.

Figures 114 and 115 illustrate the coating parameters observed on the 2 off 1st stage vanes and figures achieved on the 2nd stage vane. Figures 116-117 illustrates the coating parameter of the X45 test tabs.

Examination of each aerofoil section revealed a uniform coating with an average mid chord coating thickness 0.0034~ range of thicknesses observed 0.0029 up to 0.0038~. Coating build of up to 0.0042~ was observed around the trailing edges.

In general the observed RT44 coating structure was found to be uniform around the complete aerofoil.

The chemical composition of the coating was found to be typically Pt 50wt%, Al 27wt% and Rh 3wt%. The Pt and Al contents of the coating are considered to be satisfactory. However, the Rh content is noted to be under spec. CUK require to do further work to establish an effective control procedure to measure the thickness of Rh deposited during plating.

No significant evidence of any widespread cratering, blistering or loss of outer precious metal rich coating was observed.

Examination of the root sections revealed similar coating thickness and structure on the gas washed surfaces to that seen on the aerofoil.

Examination of the non gas washed surfaces showed evidence

of effective stopping off of these surfaces.

Examination of X45 test tabs the coating thickness and chemical composition observed on the sectioned components.

DYE PENETRANT INSPECTION

The 11 off 1st stage vanes and 12 off 2nd stage vanes were processed through CUK's F2 group class B post emulsified dye penetrant system.

No evidence of any linear defects were observed on any components.

STRESS RUPTURE TESTING

Stress rupture test bars were machined from each sectioned component in accordance with Fiat spec 601-091. In addition stress rupture test bars were also machined from X45 blanks processed in each aluminising retort (Fig 118).

The stress rupture testing was carried out by ERA Technology in accordance with the condition laid out in PDS 83262E.

The reported results are listed in Table 54.

CONCLUSION

Process validation of RT44 Rhodium Modified Platinum Aluminising on Westinghouse TG20 1st and 2nd stage vanes has demonstrated CUK ability to apply a uniform coating with the required thickness specification on both vane stages. Effective stopping off of non gas washed surfaces was also demonstrated.

Processing and subsequent inspection and metallurgical examination has identified several areas which require

detailed assessment and action.

1) EDX analysis of the final coating produced satisfactory results for platinum and Aluminium contents. However, Rh content found to be under specification, average was observed to be 3 wt%.

Detailed work is required to develop an effective control technique to ensure correct thickness of Rh is deposited.

2) Processing highlighted difficulties in the application of Pt plate on such large components, problems occurring on platforms and radii.

Modification of the plating fixture used, especially use of a conforming anode, greatly improved the situation; further refining of the fixtures is expected to produce acceptable results.

3) Stress rupture testing of bars machined from the 2nd stage vanes and X45 blanks processed with the parts proved satisfactory. However, testing of bars machined from the 1st stage vanes proved unsatisfactory, the bars rupturing before the required 15 hour life.

Joint discussion is required to resolve the problem.

7.3 TM319 HP NOZZLE PLATINUM ALUMINISED TO RT22 LT

Report on processing and cut up of a part section of nozzle used for RT22 LT application development work.

7.3.1 PLATINUM ALUMINISING RT22 LT PROCESS ROUTE

- (i) prepare for plate
- (ii) platinum plate
- (iii) vacuum diffusion 1000°C 1 hour
- (iv) stop off
- (v) coating 900°C 20 hours
- (vi) post coat clean
- (vii) inspection

VISUAL INSPECTION

The whole of the component showed evidence of being aluminised, apart from the area around the aerofoil core exits which were stopped off during coating.

The non Pt plated areas showed no evidence of any defects or shadowing. All cooling holes were found clear.

The Pt plated aerofoil platforms exhibit a uniform silver grey colouration. Present on the aerofoil and platform, some yellow particles were observed, these being indicative of the outer Pt rich layer of the coating blistering and cratering.

In general the surface finish of the nozzle was found to be poor due mainly to the poor as stripped finish found prior to processing. It is considered that this pitted finish led to some of the cratering problem encountered.

METALLOGRAPHIC EXAMINATION

The observed platinum Aluminide thickness, range of 40 to 53 um is (Fig 119) is below the desired 50 to 75 um range. This short fall in coating thickness is felt to be due to a powder problem and that moving to more high controlled specialist powder will overcome this problem.

COATING STRUCTURE AND COMPOSITION

Examination of the platinum Aluminide coating around the aerofoil revealed a uniform two layered structure typical of RT22 LT coatings, consisting of an outer Pt rich layer(light etching) and an inner Nickel aluminide layer(dark etching).

The Pt rich layer was generally found to be 75% of the total coating. Photomicrographs 1 to 4 illustrate of Fig 120 the coating observed around the aerofoil and are shown in conjunction with the respective chemical analysis.

Consideration of the analysis figure show a uniformity around the aerofoil with only the trailing figure deviating due to aluminide coating build up.

CONCLUSION

The results of the metallographic examinations Fig 119 show that it is possible to produce an even coating with the correct structure and chemistry around the complex nozzle configuration.

CUK believe that a thin coating can be resolved by adjustment in the powder used and in thermal cycle, these adjustment being considered, 'fine tuning'.

The blistering problem is considered to be associated with the poor quality of the trial piece. However, for future nozzles CUK will carry out careful inspection and rectification to prevent recurrence.

CHAPTER 8

8.0 GENERAL CONCLUSIONS

Electrochemical characteristics of Pt plating solutions have been studied and a number of characteristics have been identified and their effects analysed with a view to improving process performance.

1. Improved deposition can be achieved by control of current density, temperature, pH values, concentration of electrolytes, additives, substrate, ratio of anode to cathode area.

2. Optimum plating conditions have been established for a number of solutions. Preferred solutions are bath Nos 16-19; they have given the highest cathode current efficiencies compared with bath Nos 1-15. Table 55 shows the main bath composition ranges, current density, temperature, pH and cathode current efficiencies. The common additive factor is a 'P' Salt which all baths 1-19 contained. It can be seen that phosphate salts were replaced by sodium acetate and sodium carbonates. It appeared that sodium citrate, sodium sulphate and sodium chloride could improve the stability of these baths.

3. Modified Pt plating procedures have been employed for a number of important aerospace products, ie, Westinghouse TG20 1st and 2nd stage Buckets (Platinum Aluminising to RT22LT), Westinghouse TG20 1st and 2nd stage Vanes (Rhodium modified platinum aluminising to RT22LT) and finally, TM

333 HP nozzle(Platinum aluminising to RT22LT).

Three case histories have been presented describing particular examples of process exploitation.

4. Higher cathode current efficiencies have been achieved with lower current densities using pulse plating.

5. Cathode efficiency data showed a distinct difference between DC and pulsing due to processing technique. The pulse plated alloys were consistently darker in surface finish than direct plated alloys, and had the highest cathode efficiency values. Table 56 shows the effects of conventional, pulse and pulse with longer off-period.

6. A series of different designed experiments were used to evaluate the high aspect of throwing power(localised plating) capabilities and opportunities for extending that capability to replace the Brush plating. Firstly, an increase in applied current resulted in producing a larger deposited area; secondly, having used low current, the deposit thickness variations are more uniform in mid-section of deposit, compared with higher current.

According to Figure 80 the spherical anodes produced deposits of the required thickness within the deposit diameter . Nevertheless, these deposits tended to indicate that with higher current (see Fig.80) the deposit size scattered within the longer range and the actual shape of deposit was not maintained. By contrast, with lower current the exact shape was reproduced, despite not producing the desired thickness. Now having used longer plating time range between 5-10 minutes with 5mm interelectrode separations , the desired thickness was attained.

The interelectrode separations range of 3-5mm were used

with the above solutions. However, using a Ni-strike with an operating current of 530-650mA, interelectrode separation of 3-5mm and a constant plating time of 5 min proved to be insufficient in maintaining the required thickness of 5.0 μm (not shown).

7. Electroless techniques have been developed in an attempt to successfully apply platinum deposit on commonly used substrate using 'Q' Salt manufactured by Johnson Matthey.

The control of electrodeposition by means of adjusting other parameters has been investigated and the following conclusions drawn.

8. Lower current densities have a significant increase on cell-efficiency.

9. Higher concentration of platinum can be effective in generating higher cell-efficiency.

10. Low pH values were found to result in nonadherent deposits at higher thicknesses, probably due to the substrate attack in the initial stage. However, the solutions with high acidic conditions were stable and did not deteriorate on standing.

11. High temperatures were found to be effective in increasing the cell-efficiency.

12. It is possible that the continual usage, ie, electroplating for over a long period can build up excessive amounts of nitrates in the plating solution. This can have an adverse effect on the plating efficiency of that solution.

13. The results have shown that as plating time is pro-

longed for each tank, ie, over a period of several months, it is advisable to replace some of phosphates from plating tanks with fresh phosphates plus 'P'salt platinum.

14. Laboratory and experimental tests resulting from tanks A, D, freshly made solution and phosphate base only have shown that the rate of plating, current efficiency plating time can be improved and these results indicate that with cathodic polarization shifted towards more negative values, better result can be obtained.

CHAPTER 9

9.0 SUGGESTIONS FOR FUTURE WORK

(i) The results of a continuing development programme demonstrate that many of the difficulties associated with existing platinum electroplating systems, including low efficiencies, oxidation states and fluctuating operating conditions, can be eliminated, or substantially reduced, by a few generation of electroplating baths. Therefore, the various platinum electrolytes should be fully compared.

(ii) For industrial applications such as gas turbines, the properties expected of platinum electrodeposits may include, good adhesion to the substrate and good electrical conductivity. These in turn depend upon other factors such as the uniformity of thickness of the deposit and the effectiveness of the pretreatment. Thus, from a practical point of view it is intended to establish the parameters controlling the formation of high efficiencies, conductivities and coherent alloy coatings of predetermined and homogeneous composition. A substantial laboratory work programme should be carried out in relation to the thermodynamic equilibrium of all reactions that can occur (ie, cathodic and anodic polarizations). Elucidation of the deposition mechanism may enable further improvements to be made.

(iii) Further work should be carried out to investigate

the efficiency of other electrolytes. It has been concluded that the current density, concentration of platinum, temperature of plating, pH range, phosphates and finally nitrates have the most important effect in controlling the efficiency of the platinum solution.

(iv) Some experimental considerations should be explored in terms of a thermodynamic point of view relating to;

(a) Hydrogen adsorption on platinum electrodes and it can be divided into;

(i) effect of temperature on hydrogen adsorption

(ii) effect of anions on the adsorption of hydrogen

(b) Oxygen film on platinum and it can be divided into;

(i) oxygen coverage under conditions of varying potential

(ii) oxygen coverage under conditions of constant potential,

(iii) charge balance in oxidation and reduction of platinum surface.

(v) One of the disadvantages of the long established process based upon platinum 'p'salt, which may cease to deposit platinum due to the formation of non-active plating species. A measure of the long-term performance of a platinum bath can be gained from turnover trials; one turnover being taken to mean that the weight of platinum originally present in the bath has been removed by deposition and the bath replenished by the addition of concentrated platinum solution. So other salts should be considered to substitute or replace the 'P'salt.

(vi) It has been shown by other investigators that periodic reverse currents could result in smoother and sounder

deposits, hence, periodic reverse current techniques should be carried out to confirm the above statement. On the other hand pulse plating was beneficial in obtaining high cell-efficiency, smooth, adherent deposits. Consequently, those two methods should be carried out and investigated.

CHAPTER 10

10.0 REFERENCES

1. F.R.Hartley; The chemistry of Platinum and Palladium, Applied Science,1971,P 1-21.
2. R.H.Atkinson, Platinum Metals,P310-319,1974.
3. R.F.Vines, R.H.Atkinson, Platinum Metals, P342-349,1972.
4. C S Giggins and F S Pettit; in ' Unified Theory of Hot Corrosion', 1979, USAF office of Science Research, Report FR-11545.
5. D L Driver, D W Hall and G W Meetham; in 'The development of Gas Turbine Materials', ppl-30, 1981, Applied Science Publishers.
6. C T Sims; in 'High Temperature Alloys for Gas Turbines', pp13-68, 2978, Applied Science publishers.
7. F L Versnyder; in 'High Temperature Alloys for Gas Turbines', pp1-52, 1982, D Reidel publishing company.
8. C Duret, A Davin, G Marijnissen and R Pichoir; in 'High Temperature Alloys for Gas Turbines', pp53-76, 1982, D Reidel publishing company.
9. J Stringer; in 'Materials Science and Technology', vol 3, No 7, pp482-493, 1987.
10. S D R Saunders, M K Hossain and J M Ferguson; in 'High Temperature Alloys for Gas Turbines', pp177-206, 1982, D Reidel publishing company.
11. P Hancock; in 'Corrosion Science', vol 1, No, pp51-65,

1982.

12. T N Rhys-Jones, J R Nicholls and P Hancock;
in 'Proc of International Conference on the prediction of
Materials performance in plants operating with Corrosive
Environment', 1986, Cranfield, Beds, UK- in press.
13. G C Wood; 'Oxidation of Metals', vol 2, pp11, 1970.
14. D P Whittle; in 'High Temperature Alloys for Gas Tur-
bines', pp109-123, 1978, Applied Science publishers.
15. P Hancock and J R Nicholls;
in 'Advanced Workshop on Coatings for Heat Engines',
(April) 1983, Maratea, Italy.
16. T N Rhys-Jones and D F Bettridge; to be published.
17. "Nickel Plating: Technique and Applications". Interna-
tional Nickel, (rajthby, Lawrence and Company Limited).
18. F.A. Lowenheim, "Guide to the Selection and use of
Electroplated and Related Finishes".ASTM(1982).
19. L.F. Spencer "Modern Electroforming". Metal Finishing,
64(February and April 1973).
20. G.A. Capuano, and W.G. Davenport, Plating, 60, 251
(1973).
21. M. Balkanski ; Zum Mechanismus der elektrolytischen
Metallabscheidung, insbesondere Zur Abscheidung des
Zinks.Z.Electrochem. 61,141 (1957).
22. B.E. Conway, and J.O'M. Bockris: An introduction to
fundamental research of the mechanism of the electrodepo-
sition of metals. Plating 47, 169 (1960).
23. H. Brandes, : Zur Theorie des Kristallwachstums. Z.
physik. Chem. 126. 196 (1927).
24. T. Erdey-Gruz, and M . Volmer: Electrolytisches Kris-
tallwachstum . Z. physik. Chem . A 157, 165 (1931).

25. V. Kohlschutter, and E.A. Vulleumier, Cathodic Processes during Metal Deposition, Z, Electrochem, 24, 309(1918).
26. W. Kossel, : Die molekularen Vorgange beim Kristallwachstum. Leipziger Vortrage 1928. Quantentheorie und Chemel.
27. H.Fischer, : Electrolytes deposition and electrocrystallization of metals. Z. Electrochem 59, 612 (1955).
28. W. Lorenz, : Zur Theories of Electrocrystallizations, phy. Chem. 202, 275 (1953).
29. L. Cambi, and R. Piontelli, "Sulphamate Solutions for the electrodeposition of metals" Rend. Inst. Lombardo Soi. 72, 128-138 (1938-39).
30. M.E. Baumgartner and Ch.J.Raub, Platinum Metals Rev., 1988,32, (4), 188-197.
31. G. Grube and D. Beischer. Z. Eletrochem., 1933, 30, 38- 45; G. Grube and H . Rienhardt. Z.Elektrochem., 1931, 37, 307-20.
32. Galvanotechnik (ex Pfanhauser), 1949,940.
33. W. Keitel and H.E.Zschiegner. Trans. Electrochem. Soc., 1953, 59,273.
- 34.R. Tripler,K. Beach and S. Faust. U.S.A.E., BMI, 1097, 11 pp, 1956.
35. E.C.Davies and A.R.Powell. T. Electrodep. Tech. Soc., 1937,13, No,26,7.
36. S. Wernick. "Electrolytic Polishing and Bright Plating of Metals" Alvin Redman Ltd, 1951,115.
37. E.H. Laiser. Metal Industry, 1954, 85, 427-9; 469-70.
38. DNS Platinum Plating Solution, Johnson Matthey & Co. Ltd; N. Hopkin and L.F. Wilson . Platinum Metals Review,

1960, April; Summarized in electroplating and Metal Finishing, 1960, 13, No 4, 133.

39. ENGELHARD Sales Ltd, Special Chemical Division Valley Rd, Cindeford, Gloucestershire GL14 2PB.

40. M.J.N.Poubaix, J.Van Muylder and N.de Zouboy, Centre Belge d Etude de la Corrosion , Brussels.

41. A.J.Haley, Characteristics of Platinum Coated Anodes, Intrepid Industries, Inc. 19L Gardner Rd, Fairfield, N.J.07006.

42. J.C.Norris, Brush plating, SIFCO Selective plating, Cleveland. OH, p323-336.

Johnson, E.L., Stevenson, R., Basic Liquid Chromatography, 1978 by Varian Associates, Palo Alto, Ca, 116.

44. C.Horvath, W.Melander, I.Molnar, P.Molnar, Enhancement of Retention by Ion-Pair Formation in Liquid Chromatography with Nonpolar Stationary Phases, Analytical Chemistry, Vol. 49, No.14, Dec 1977, 2295.

45. W.R.Melander, k.Kalghatgi, C.Horvah, Formation of Ion Pairs under conditions Employed in Reversed-phase Chromatography. Journal of Chromatography, 201, (1980) 201-209.

46. H.Small, T.Stevens, and W.Bauman, Novel Ion Exchange Chromatographic Method Using Conductimetric Detection. Anal, Chem, 47, 1801 (1975).

47. A.Iskandarani and D.J.Pietrzyk, Ion Interactio Chromatography on a Poly(Styrene-divinylbenzene) Adsorbant in the Presence of Tetraalkylammonium Salts. Anal.Chem. 54, 1065-1071(1982).

48. B.A.Bidlingmeyer, S.N.Oeming, W.D.Price JR., B.Sachok, and M.Petrusek, Retention Mechanism for Reversed Phase Ion-pair Liquid Chromatography. J. Chromatogr. 186, 419-

434 (1979).

49. N. Ibl, J. Puippe and H.Agerer, Surf. Technol, 6 (1978) 287.

50. J.Cl.Puippe and N.Ibl, Plat and Surf. Fin, 67,68 (June 1980).

51. D.L.Rehrig, H.Leidheiser, Jr, and et al Plat. Surf.Fin, 64(12) (1977) 40.

52. J.Puippe and N.Ibl, Plat.Surf.Technol, 4(1976) 339.

53. N.Kubota, E.Sato, Industrial Research Institute of Kumamoto Prefecture, Utsunomiya University. J.Met.Finish Soc Jpn, Apr 1988,39,(4), 185-188.

54. H.Hoskawa, et al, Department of Industrial Chemistry Kyushu Institute 'Electroplating of precious Metals by Current Pulses', March 1982.

55. "Plating with Periodic Pulse". Part 1, Oct 1983, Holtzman.

56. K.I.Popov, 'Fundamental Aspects of Pulsating Current Metal' Surface Tech, 1980.

57. N.Ibl, 'Some Theoretical Aspects of Pulse Electrolysis' Surface Tech, 1980.

58. R.I.Gurovich, and A.K.Krivtsov, Issled, Poelektroosazhdi Rastvor. Metallov, 1971, 174.

59. M. Viswanathan and C.J. Raub, 'Pulse Plating of Nickel-Gold Alloys', Surf.Tech, 1976.

60. J.M.Licarnini and N.Ibl. "pulse plating of Palladium" v15, March 1982.

61. T.Hayashi, H. Kitanishi nad Y.Fukumoto, "morphology and Crystallographic features of silver deposits in the pulse current electrolysis", v15, March 1982.

62. K.I.Popov, M.D.Maksimovic and R.M.Stevanovic, The

effect of pause-to pause ratio on micro-throwing power of metal deposition, Surf.Tech, 22,(1984) 10, 155-158.

63. C.J.Raub and Knodler, "The electrodeposition of Gold by pulse plating", Dec 1977.

64. H.Dahms and I.M.Croll, J.Electroanal.Chem., 70,233 (1976).

65. D.R.Gabe, and J.M.West, "Internal stress and cracking in electrodeposited chromium", Trans. Inst. Metal Finishing 40, 197 (1963).

66. R.J.Morrissey, Technical Inc, Production, Rl, "Platinum Plating", 1977, P 272-277.

67. L.D.Burke, and M.B.C.Roche, J.Electroanal Chem. Interfacial Electrochem, 25 Apr, 1984, 164, (2), 315-334.

68. A.M.Feltham and M.Spiro, Chem. Rev., 71(9171)177

70. S.D.James, J.Electrochem, Soc., 116(1969)1131

71. R.Woods in A.J.Bard(Ed), Electroanalytical Chemistry, Vol 9, Marcel Dekker , New York, 1976, pp, 1-144

72. S.Shibata, J.Electroanal. Chem., 89(1978)37

73. L.D.Burke, M.E.Lyons and D.P.Whelan, J.Electroanal. Chem., 139(1982) 131

74. L.D.Burke, O.j.Murphy, J.F.O Neil and S.Venkatesan. J.Chem. Soc. Faraday 1, 73(1977)1659

75. L.D.Burke, j.k. Mulcahy and D.P. Whelan, J.Electroanal. Chem., 163(1984)117

76. D.A.J.Rand and R.Woods, J.Electroanal Chem., 35(1972)209

77. S.Shibata and M.P.Sumino, Electrochim. acta, 26(1981)1587.

78. S.Shibata, Electrochim, Acta, 17(1972)395

79. J.S.Hammond and N.Winorad, J.Electroanal, Chem.,

78(1977)55.

80. M.Baumgartner and C.J.Raub, Plat. Met, Rev., 32, 188, (1988).

81. M.Puspavanam and S.R.Natarajan, Central Electrochemical Research Institute, Karaikudi, India. "Platinum Plating for decorative and functional applications", Sept 1988.

82. OMI International (G.B) Ltd, Forsythe Road, Sheerwater, Woking, Surrey, England.

83. D. Pletcher and F.C. Walsh, 'Industrial Electrochemistry, 2nd Edn, Chapman and Hall, London, 1990, ISBN 0-9517307-0-3.

84. D.Pletcher, A First Course in Electrode Processes, The Electrochemical Consultancy, Romsey, 1992.

85. E.Raub and K.Muller, Fundamentals of Metal Deposition, Elsevier, Amsterdam, 1967.

86. J.S.Newman, Electrochemical Systems, Prentice-Hall, Englewood Cliffs, New Jersey, 1973.

87. P.H. Reiger, Electrochemistry, Prentice-Hall, Englewood Cliffs, New Jersey, 1987; ISBN 0-13249138-9.

88. F.C.Walsh, Applied Electrochemistry Group, The Kinetics of Electrode Reactions, The Institute of Metal Finishing, May 1992, p95-99.

TABLE I
The physical properties of platinum and palladium (compiled from references 12-14)

Property	Platinum	Palladium
Atomic number	78	46
Atomic weight (relative to ¹² carbon = 12)	195.09	106.4
Density (g/cc at 20°C)	21.45	12.02
Crystal lattice	Face-centered cubic	Face-centered cubic
Lattice cell (Å)	3.9158	3.8825
Atomic radius (Å)	1.387	1.375
Allotropic forms	None known	None known
Melting point (°C)	1773.5	1554
Boiling point (°C, estimated)	4530	3980
Thermal conductivity (cal/cm/cm ² /sec/°C)	0.17	0.17
Linear thermal coefficient of expansion at 0°C (per °C)	8.9×10^{-6}	11.67×10^{-6}
Specific heat at 0°C (cal/g/°C)	0.0314	0.0584
Electrical resistivity at 20°C (micro ohm-cm)	10.6	10.8
Hardness (annealed—Brinell Hardness number)	42	46
Tensile strength (annealed—ton/in ²)	9	13.8
Young's modulus (annealed—ton/in ²)	1.1×10^6	$(8-8.8) \times 10^5$

TABLE 2

Property requirements of coating
system for gas turbine aerofoil
applications.

Property	Requirements
Corrosion and oxidation resistance	<ul style="list-style-type: none"> (i) Initial rapid formation of a thin, uniform adherent and continuous protective oxide film (ii) slow subsequent rate of scale growth (iii) highly stable and adherent scale (iv) high concn of scale-forming elements in coating (v) acceptable rate of corrosion/oxidation
Erosion resistance	<ul style="list-style-type: none"> (i) ductile and adherent oxide scale (ii) moderate coating ductility
Coating and alloy interfacial stability	<ul style="list-style-type: none"> (i) low rates of diffusion across interface (ii) minimum compositional changes, particularly w.r.t brittle phases
Coating adhesion	<ul style="list-style-type: none"> (i) matched/similar coating and substrate properties (ii) clean alloy/ coating interface
Mechanical properties	<ul style="list-style-type: none"> (i) ability to withstand all strain-temperature cycles encountered by the component during service (ii) appropriate coating ductility (iii) little or no effect upon substrate properties
Aerodynamic properties	<ul style="list-style-type: none"> (i) best possible surface finish (ii) acceptable thickness and uniformity on aerofoil (iii) minimum loss of surface smoothness during service
Coating process	<ul style="list-style-type: none"> (i) optimised for composition, structure, thickness (and thickness distribution if required) (ii) ability to coat complex shapes eg aerofoils (iii) cost effectiveness

<u>Coating Technique</u>	<u>Coating Type</u>			
	<u>Metal</u>	<u>Metallic</u>	<u>Paint</u>	<u>Organic</u>
<i>Electrodeposition</i>	<i>Yes</i>			
<i>Electroless</i>	<i>Yes</i>			
<i>Electrophoretic</i>	<i>Yes</i>	<i>Yes</i>	<i>Yes</i>	
<i>Hot dipping</i>	<i>Yes</i>		<i>Yes</i>	
<i>Spraying</i>	<i>Yes</i>	<i>Yes</i>	<i>Yes</i>	<i>Yes</i>
<i>Cladding</i>	<i>Yes</i>	<i>Yes</i>	<i>Yes</i>	<i>Yes</i>
<i>Vaccum/Vapour</i>	<i>Yes</i>			<i>Yes</i>
<i>Vapour dissociation</i>	<i>Yes</i>			
<i>Cementation and diffusion</i>	<i>Yes</i>	<i>Yes</i>		
<i>Fusion</i>		<i>Yes</i>		
<i>Roller Coating</i>				<i>Yes</i>
<i>Conversion coatings</i>		<i>Yes</i>		

TABLE 3

Coating techniques used for
metallic materials. (Courtesy of
Loughborough University, Dept
IPTME , Dr.D.Gabe)

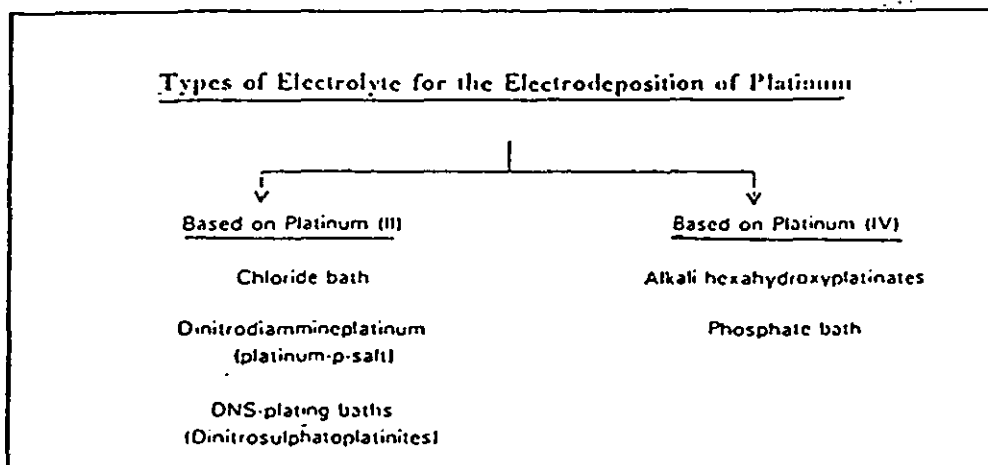


TABLE 4

Types of electrolyte for the electrodeposition of platinum.

TABLE 5

Survey of electrolytes producing
different cathode current effi-
ciencies.

Baths for Platinum Electrodeposition

Type of bath Reference		Chloride		Dinitrodiammineplatinum						DNS	Alkali hexahydroxyplatinales				Phosphate
		(10)	(11)	(13)	(16)	(17)	(18)	(19)	(1)	(20)	(21)	(24)	(25)	(26)	(4)
Concentrations, g/l															
Chloroplatinic acid	H_2PtCl_6	10-50													
Ammoniumhexachloro- platinite	$(NH_4)_2PtCl_6$		15												
Platinum-p-salt	$Pt(NH_2)_2(NO_2)_2$			8-16.5	20	6-20	8	6-20	16.5						
Dinitrosulphate- platinous acid	$H_2Pt(NO_2)_2SO_4$									10					
Sodium hexahydroxy- platinite	$Na_2Pt(OH)_6 \cdot 2H_2O$										20	18.5			
Hexahydroxyplatinic acid	$H_2Pt(OH)_6$												20		
Potassium hexahydroxy- platinite	$K_2Pt(OH)_6$													20	
Platinum chloride	$PtCl_4 \cdot 5H_2O$														7.5
Ammonia (28%)	NH_3			50											
Hydrochloric acid	HCl	180-300													
Sodium citrate	$Na_3C_6H_5O_7 \cdot 2H_2O$		100												
Ammonium chloride	NH_4Cl		4-5												20-25
Ammonium nitrate	NH_4NO_3			100											
Sodium nitrite	$NaNO_2$			10											
Fluoroboric acid	HF_4				50-100										
Sodium fluoroborate	$NaBF_4$				80-120										
Sulphamic acid	NH_2SO_3H					20-100									
Phosphoric acid	H_3PO_4						80	10-100							
Sulphuric acid	H_2SO_4							10-100		pH 2					
Sodium acetate	$NaCH_3COO$								70						
Sodium carbonate	Na_2CO_3								100						
Sodium hydroxide	$NaOH$										10	5.1			
Sodium oxalate	$Na_2C_2O_4$											5.1			
Sodium sulphate	Na_2SO_4											30.8			
Potassium hydroxide	KOH												15		
Diammonium hydrogen phosphate	$(NH_4)_2HPO_4$														20
Disodium hydrogen phosphate	Na_2HPO_4														100
Potassium sulphate	K_2SO_4														40
Temperature, °C		45-90	80-90	90-95	70-90	65-100	75-100	75-100	80-90	30-70	75	65-80	75	70-90	70-90
Current density, A/dm^2		2.5-3.5	0.5-1.0	0.3-2.0	2-5	0.2-2	0.5-3.0	0.5-3	0.5	2.5	0.8	0.8	0.75	0.3-1	0.3-1
Current efficiency, per cent		15-20	70	10	14-18	15	15	15	35-40	10-15	100	80	100	10-50	10-50

TABLE 6

Dinitrodiammine platinum or ('P'
Salt) composition.

<i>Dinitrodiammine Platinum</i>		
<i>(Pt 10 g/l)</i>	<i>Pt(NH₃)₂(NO₃)₂</i>	<i>16.5 g/l</i>
<i>Ammonium Nitrate</i>	<i>NH₄NO₃</i>	<i>100 g/l</i>
<i>Sodium Nitrite</i>	<i>NaNO₂</i>	<i>10 g/l</i>
<i>Ammonia (28% solution)</i>	<i>NH₄OH</i>	<i>50 ml/l</i>
<i>Anodes</i>	<i>Platinum</i>	

TABLE 7

Sodium Hexahydroxyplatinate or
('Q' Salt) composition.

<i>Sodium Hexahydroxyplatinate</i>	
<i>Sodium Platinate</i>	<i>20 g/l</i>
<i>Sodium Hydroxide</i>	<i>5.6 g/l</i>
<i>Sodium Oxalate</i>	<i>5.6 g/l</i>
<i>sodium Sulphate</i>	<i>33.7 g/l</i>

TABLE 8

Different compositions of platinum which manufactured by Engelhard company.

PLATINUM 209

OPERATING CONDITIONS

<u>BARREL PLATING</u>	<u>UNIT</u>	<u>RANGE</u>	<u>OPTIMUM</u>
Platinum concentration	g/l	8-12	10
Alkaline pH	pH	8-9	8
Temperature	°C	80-90	85
Current Density	A/dm ² A/ft ²	2.0-2.5 18-22	2.2 20

<u>VAT PLATING</u>	<u>UNIT</u>	<u>RANGE</u>	<u>OPTIMUM</u>
Platinum concentration	g/l	8-12	10
Alkaline pH	pH	8-9	8
Temperature	°C	80-90	85
Current Density	A/dm ² A/ft ²	2.2-8.8 20-80	* *
Agitation		None	

* Current density depends on plating requirements.

PLATINUM 3745

<u>OPERATING CONDITIONS</u>	<u>UNIT</u>	<u>RANGE</u>	<u>OPTIMUM</u>
Platinum Concentration	g/l	8-15	12.5
Current Density	A/dm ² A/ft ²	0.5-1 5-10	0.7 7.0
Temperature	°C	75-85	80

Deposition Rate: 1 micron is deposited in 9.8 minutes at 0.7A/dm².

TABLE 9

Typical Brush plating solutions
for brush plating techniques.

Typical Brush Plating Solutions

Group I Preparatory Solutions

Cleaning(for materials)

Etching(for aluminium alloys, steels and cast iron)

Desmutting(for cast iron, carbon and alloy steels and copper alloys)

Etching & Activating(for high-temperature, nickel-base materials and stainless steel)

Etching(for Babbit)

Activating(for activating industrial hard chromium)

Cadmium activator

Chromium activator(for activating decorative chromium)

Group II Plating Solutions For Ferrous and Non-Ferrous Metals

Antimony

Lead(alkaline)

Bismuth

Lead(for alloying)

cadmium(acid)

Nickel(dense)

Cadmium(alkaline)

Nickel(alkaline)

Cadmium(no bake)

Nickel(acid strike)

Chromium(dense trivalent)

Nickel(neutral, for heavy build-up)

Chromium(hexavalent)

Nickel(ductile, for corrosion protection)

Cobalt(for heavy build-up)

Nickel(sulphate, soft, low stress)

Copper(acid)

Nickel(sulphamate, moderate hardness)

Copper(alkaline)

Nickel(sulphamate, hard, low stress)

Copper(neutral)

Tin(alkaline)

Copper(high-speed acid)

Zinc(neutral)

Copper(high-speed alkaline for heavy build-up)

Zinc(acid)

Iron

Zinc(bright)

Typical Brush Plating Solutions	
Group II plating Solutions for Precious Metals	
Gallium	Platinum
Gold(alkaline)	Rhenium
Gold(neutral)	Rhodium
Gold(acid)	Silver(soft)
Indium	Silver(hard)
Palladium	Silver(noncyanide)
Group II plating Solutions For Alloys	
Brass	
Nickel-cobalt	Nickel-tungsten
Tin-indium	Babbitt SAE 11
Tin-lead-nickel	Babbitt Navy Grade 2
Cobalt-tungsten	Cadmium-tin
Group III Special Purpose Solutions	
Anodizing(chromic)	Chromate treatment
Anodizing(sulphuric)	Electropolishing solution
Anodizing(hard coat)	

TABLE 10

Typical Brush plating solutions
for brush plating techniques.

TABLE 11

Historical Milestone developments
in Liquid Chromatography

TABLE 12

Historical Milestone developments
in Ion Chromatography.

Historical Milestone in Liquid Chromatography		
Year	Name	Developments
1903	Tswett	Invented development Chromatography
1941	Martin & Synge	Partition Chromatography(won Nobel prize for their work)
1948	Stein & Moore	Amino acid separation using ion exchange Chromatography
1952	Martin & James	Gas Chromatography
1953	Wheaton & Bauman	Exclusion principle observed
1959	Porath & Flodin	Gel permeation Chromatography(soft polydextrans)
1962	Moore	Gel permeation (rigid polystyrene gels)
1965		High pressure liquid Chromatographs are marketed

Historical Milestone Ion Chromatography	
Year	Developments
1971	IC [†] is first performed at Dow Chemical.
1972	First prototype Ion Chromatograph is built using a conductivity cell.
1975	First IC research report is published: 'Novel Ion Exchange Chromatographic Method Using Conductimetric Detection' by Small, Stevens, and Bauman in Analytical Chemistry, Vol. 47, No. 11, 1975, pp. 1891-1809.
1975	Dionex Corporation is formed under Dow License.
1975	First commercially available Ion Chromatograph introduced.
1977	First EPA Symposia on IC analysis-environmental pollution.
1977	Small, Stevens, and Bauman win the 1977 Pittsburgh Conference award for the most significant advance in applied analytical chemistry.

* IC- Ion Chromatograph

SUMMARY OF SEPARATION MODES

	Predominant Separation Mechanism	Resin Functionality	Standard Eluents	Useful For:
HPIC	Ion Exchange			
Anion	"	$-N^+-R_3$	$Na_2CO_3/NaHCO_3$	Cl^- , NO_3^- , Br^- , SO_4^{2-} , PO_2^{3-} , PO_3^{3-} , CrO_4^{2-} , AsO_4^{3-}
Cation	"	$-SO_3^-$	HCl	Li^+ , Na^+ , NH_4^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}
Metals	"	$-N^+-R_3$ or $-SO_3^-$	Oxalic and Citric Acid	Fe^{3+} , Fe^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} , Mn^{2+} , Cd^{2+} , Al^{3+}
MPIC	Ion Pairing and Adsorption	Neutral		
Anion	"	"	Tetrabutyl NH_4OH (TBAOH) CH_3CN	$Au(CN)_2^-$, $Au(CN)_4^-$, $Co(CN)_6^{3-}$ Alkyl sulfonates and sulfates DF_4^-
Cation	"	"	Hexane sulfonic acid (HSA) CH_3CN	Alkyl and quaternary amines
HPICE	Ion Exclusion	Totally functional $-SO_3^-$	HCl	Formate, citrate, tartrate, succinate, lactate, carbonate, borate

TABLE 13

Shows the summary of separation modes for Ion Chromatography techniques

DETECTION MODES

	Principle	Most Useful For:
Suppressed Conductivity	Electrical conductivity	Anions or cations with pK_a or pK_b values < 7 eg. Cl^- , SO_4^{2-} , Na^+
Amperometric	Oxidation or reduction at Ag or Pt electrodes	CN^- , S_2^{2-} , mercaptans, OCl^- , hydrazine
Pulsed Amperometric	Oxidation or reduction at Ag, Pt, Au, or glassy carbon electrodes	Phenolics, carbohydrates, nitro aromatics
Direct UV VIS after PCR	Ultraviolet light absorption Visible light absorption after reaction with a post column reagent	Aromatic organics and select anions Transition and heavy metals after post column reaction with 4-(2-pyridylazo)-resorcinol (PAR) Polyvalents after reaction with $Fe(NO_3)_3$
Fluorescence after PCR	Excitation and Emission	Amino acids after reaction with o-phthalaldehyde

TABLE 14

Shows the summary of detection
modes for Ion Chromatography
techniques

TABLE.15

LIST OF COMPONENT USED FOR PULSE-PLATING(P.P) & CONVENTIONAL PLATING(C.P)

1. Power Mosfets.
2. Double beam oscilloscope.
3. Power supply.
4. Pulse generator
5. Potentiostat (only used for conventional plating).
6. Pump-generator.
7. pH-meter.
8. Voltmeter and Ammeter.
9. The magnetic stirrer.
10. Chart recorder.
11. Amp-hour meter (used only for measuring the efficiency of the cell).

TABLE.16.

STEPS WHICH WERE USED FOR PLATINUM PLATING AND ITS ALLOYS
WITH FRESH AND OLD SOLUTION FORMULATIONS

1. Visual inspection for either mild-steel or nimonic specimens.
2. Shot blasting.
3. Cleaning the sample.
4. Cathodic clean (five minute per sample).
5. Wash the sample before the plating.
6. Weight the sample before the plating.
7. Platinum, rhodium or nickel plating.
8. Wash the sample after plating.
9. Dry the sample.
10. Weight the sample after drying.
11. Keep the sample in desiccator.

TABLE 17

Shows the solution make-up and
its composition for plating tanks
used by C.U.K Ltd.

Solution Make-up

Solution; Platinum Plate

Controlling

Secification: 01-078 App.24

Tanks: A,E Volume 335 Litres

B,C,D Volume 170 Litres

Substance	Weight/Volume	
	170 litre tank	335 litre tank
Platinum 'p' salt	425g (Pt)	837g (Pt)
Disodium Hydrogen Orthophosphate	14.0g Kg	27.0 Kg
Di-sodium Hydrogen Orthophosphate	2.8 Kg	5.5 Kg

Make up Instructions

Half fill tank with deionised water. Add Disodium Hydrogen Orthophosphate, and Diammonium Hydrogen Orthophosphate, heat solution.

Once salts have dissolved add platinum 'p' salt, followed by 10 litres of

Ammonia solution for 170 litre tank, 20 litres for 335 litre tank.

Top up with deionised water.

TABLE 18

Shows the solution make-up and
their composition for bath No.1
and 2.

Bath Compositions used for Platinum Plating

Bath No.1

Platinum as 'P' Salt, g/l	4-5
Diammonium Hydrogen Orthophosphate, g/l	79
Disodium Hydrogen Orthophosphate, g/l	393
Temperature, °C	84-87
pH	7.5-8.0

Bath No.2

Platinum as 'P' Salt, g/l	8-10
Diammonium Hydrogen Orthophosphate, g/l	79
Disodium Hydrogen Orthophosphate, g/l	393
Temperature, °C	84-87
pH	7.5-8.0

TABLE 20

Shows the solution make-up and
their composition for bath No.5
,6 and 7.

Bath No.5

Platinum as 'P' Salt, g/l	8-10
Ammonium Nitrate, g/l	100
Sodium Nitrate, g/l	10
Ammonium to adjust the pH	7.5
Temperature, °C	65-70

Bath No.6

Platinum as Dinitritosulphato Platinum Complex, g/l	5
pH	1.2-2.0
Temperature, °C	25-30

Bath No.7

Platinum as 'P' Salt, g/l	8-10
Potassium Nitrite, g/l	25
Ammonium Nitrite, g/l	250
Temperature, °C	84-87
pH	7.5

TABLE 21

Shows the solution make-up and their composition for bath Nos (8-10).

Bath No.8

Platinum as 'P' Salt, g/l	8-10
Potassium Nitrite, g/l	25
Ammonium Nitrite, g/l	250
Potassium Hydroxide, g/2l	5
Temperature, °C	84-87
pH	7.6

Bath No.9

Platinum as 'P' Salt, g/l	8-10
Potassium Nitrite, g/l	25
Ammonium Nitrite, g/l	250
Potassium Hydroxide, g/2l	15
Temperature, °C	84-87
pH	8.6

Bath No.10

Platinum as 'P' Salt, g/l	8-10
Potassium Hydroxide, g/2l	20
Temperature, °C	84-87
pH	8.8

TABLE 22

Shows the solution make-up and
their composition for bath Nos
(11-15).

Bath No.11

Platinum as 'P' Salt, g/l	8-10
Potassium Hydroxide, g/2l	30
Temperature, °C	84-87
pH	8.8

Bath No.12

Platinum as 'P' Salt, g/l	8-10
Potassium Hydroxide, g/2l	35
Temperature, °C	84-87
pH	9.7

Bath No.13

Platinum as 'P' Salt, g/l	8-10
Potassium Hydroxide, g/2l	35
Temperature, °C	65-70
pH	13

Table 22. Continued

Bath No.14

Platinum as 'P' Salt, g/l	8-10
Sodium Oxalate, g/l	5-6
Potassium Sulphate, g/l	30
Temperature, °C	65-70
pH	13

Bath No.15

Platinum as 'P' Salt, g/l	8-10
Sodium Oxalate, g/l	5-6
Potassium Sulphate, g/l	30
Potassium Nitrate, g/2l	5
Temperature, °C	65-70
pH	13

TABLE 23

Shows the solution make-up and their composition for bath Nos (16-17).

Bath Composition used for Platinum Plating

Bath No.16

Platinum as 'P' Salt, g/l	5
Sodium Acetate, g/l	70
Sodium Carbonate, g/l	100
Temperature, °C	84-88
pH	11.3

Bath No.17

Platinum as 'P' Salt, g/l	5
Sodium Acetate, g/l	25
Sodium Carbonate, g/l	36
Temperature, °C	84-88
pH	11.5

TABLE 24

Shows the solution make-up and their composition for bath Nos(18-19).

Bath No.18

Platinum as 'P' Salt, g/l	5
Sodium Citrate, g/l	25
Sodium Carbonate, g/l	36
Temperature, °C	84-88
pH	11.5

Bath No.19

Platinum as 'P' Salt, g/l	5
Sodium Sulphate, g/l	40
Sodium Chloride, g/l	5
Temperature, °C	84-88
pH	11.5

The composition and operating conditions

<i>Ni Sulphamate</i>		<i>Ni Chloride Strike</i>	
<i>Ni-sulphamate</i>	<i>600g/l</i>	<i>Ni-chloride 240g/l</i>	
<i>Ni-chloride</i>	<i>10g/l</i>		
<i>Boric acid</i>	<i>30g/l</i>	<i>hydrochloric acid 86ml/l</i>	
<i>pH</i>	<i>3.75-4.0</i>	<i>pH</i>	<i>0.75-1.0</i>
<i>Temperature</i>	<i>58-60°C</i>	<i>Temperature</i>	<i>Room temp</i>

TABLE 25

Shows the composition and operating conditions for throwing power (Localised plating).

TABLE 26

Shows the Applied current, average thickness, cathode current efficiency, surface appearance, ratio of anode to cathode and finally temperature of plating for bath No.s (1-3).

Applied Current mA/cm^2	Average Thickness (μm)	Cathode Current Efficiency (%)	Surface Appearance at Given Temperature	Ratio of Anode to Cathode	Temperature $^{\circ}\text{C}$	pH
Bath No.1						
30	6.5	7.3 \pm 1.1	Dull & Dark	2:1	87	7.5
30	7.1	7.0 \pm 0.7	Dull & Dark	2:1	87	7.5
30	7.1	6.5 \pm 1.3	Slightly Peeled-off	2:1	87	7.5
30	7.4	9.3 \pm 0.6	Dull	2:1	97	7.5
30	8.0	7.6 \pm 1.2	Uniform Thickness & Dull	4:1	87	7.5
40	5.2	4.0 \pm 1.6	Very Dark, Porous & Burnt	2:1	87	7.5
Bath No.2						
30	9.0	13 \pm 1.5	Dull & Dark	2:1	87	7.5
Bath No.3						
30	10	13.6 \pm 0.8	Semi-bright	2:1	87	7.5

TABLE 27

Shows the Applied current, average thickness, cathode current efficiency, surface appearance, ratio of anode to cathode and finally temperature of plating for bath Nos.(1-9).

Applied Current mA/cm ²	Average Thickness(um)	Cathode Current Efficiency (%)	Surface Appearance at Given Temperature	Ratio of Anode to Cathode	Temperature °C	pH
Bath No.4						
30	8.2	12.5±0.5	Semi-bright	2:1	87	7.5
Bath No.5						
30	5.0	4.3±1.7	Bright	2:1	69	7.5
30	5.2	6.8±1.1	Bright	2:1	87	7.5
Bath No.6						
30	0.25	0.3±0.9	Very Bright	2:1	30-45	2.0
30	1.7	1.4±0.5	Very Bright	2:1	30-45	2.0
Bath No.7						
30	6.4	6.1±1.3	Bright	2:1	86	7.5
Bath No.8						
30	6.7	6.2±0.8	Bright	2:1	86	7.6
Bath No.9						
30	6.8	6.4±1.1	Bright	2:1	86	8.6
40	6.4	6.0±1.5	Semi-bright	2:1	86	8.6

TABLE 28

Shows the Applied current, average thickness, cathode current efficiency, surface appearance, ratio of anode to cathode and finally temperature of plating for bath Nos.(10-15).

Applied Current mA/cm ²	Average Thickness(um)	Cathode Current Efficiency (%)	Surface Appearance at Given Temperature	Ratio of Anode to Cathode	Temperature °C	pH
<i>Bath No.10</i>						
30	6.6	6.3±1.1	Bright	2:1	86	8.8
<i>Bath No.11</i>						
30	6.6	36±2.2	Highly stressed & peeled off	2:1	86	8.8
<i>Bath No.12</i>						
30	6.6	19±1.7	Slightly peeled off	2:1	86	9.7
<i>Bath No.13</i>						
30	6.8	10.6±0.8	Dull&Dark	2:1	70	13
<i>Bath No.14</i>						
30	6.8	10.7±1.3	Dull&Dark	2:1	85-88	13
<i>Bath No.15</i>						
30	6.8	31.8±3.0	One side is highly stressed and another side is bright and adherent	2;1	85	

Applied Current mA/cm ²	Average Thickness(um)	Cathode Current Efficiency (%)	Surface Appearance at Given Temperature	Ratio of Anode to Cathode	Temperature °C	pH
<i>Bath No.16</i>						
15	5.7	18.6±2.7	Bright	2:1	84-88	11.3
<i>Bath No.17</i>						
15	6.1	40±5.2	Very Bright	2:1	84-88	11.5
15	6.4	41±3.3	Bright	2:1	84-88	11.5
<i>Bath No.18</i>						
15	6.7	52±4.7	Bright	2:1	84-88	11.5
<i>Bath No.19</i>						
15	5.9	38.4±2.3	Bright	2:1	84-88	11.5

TABLE 29

Shows the Applied current, average thickness, cathode current efficiency, surface appearance, ratio of anode to cathode and finally temperature of plating for bath Nos.(16-19).

TABLE 30

'Q'Salt from Johnson Matthey
solution shows higher cathode
efficiency with effect of lower
current density.

TABLE 31

'Q'Salt from Johnson Matthey
solution shows slightly lower
cathode efficiency with effect of
higher current density.

<i>Current Density</i> <i>(mA/cm²)</i>	<i>Weight Gain</i> <i>(g)</i>	<i>Efficiency</i> <i>(%)</i>
2	0.0218	77.6
3	0.0545	109
3	0.0418	119
4	0.0483	54
5	0.0744	82.7

<i>Current Density</i> <i>(mA/cm²)</i>	<i>Weight Gain</i> <i>(g)</i>	<i>Efficiency</i> <i>(%)</i>
4	0.0483	54
4	0.0597	90.45
5	0.0372	43.25
5	0.077	81.9

TABLE 32

Shows the amount of nitrite before and after plating and that amount has diminished and the cell efficiency was lower compared with standard fresh solution which is around (7-9)%.

TABLE 33

Shows the level of phosphates in tank No.s B,C and D present in plating shop containing platinum solution.

Addition of Nitrite NO_2 (20g/1.5l)	Efficiency(%)	PO_4 (g/l)	NO_3 (g/l)	NO_2 (g/l)
Before Plating	---	58.6	0.6	12.05
After Plating	2.1	63	0.3	6.8

Plating Tanks No	PO_4 (g/l)					
	17.7.89	31.7.89	7.8.89	14.8.89	1.9.89	27.9.89
B	75.6	88.4	79.6	75.7	78	68.1
C	81.3	75.7	80.3	72.7	80.2	68.5
D	46.3	77.1	80.3	71.1	78.9	67.45

TABLE 34

Shows the variation of cathode current efficiency for tank No.C with addition of different amount of phosphates.

Plating Tank No	Additions	pH Before Plating	Temperature, °C	pH After Plating	Cathode Current Efficiency (%)
C	(a) Sample from Tank.18 with PO_4 level of 75.7g/l	7.1	86	6.5	2.75 \pm 0.9
C	(b) 130 ml from above tank, plus 19 ml fresh 'P'Salt to make 400 ml of solution	7.1	86	6.5	3.7 \pm 1.1
C	(c) 130 ml from above tank, plus 19 ml fresh 'P' Salt, Plus 16.6g Disodium+3.9g Diammonium Orthophosphates	7.1	86	6.5	5.0 \pm 1.4
C	(d) 200 ml from above tank, Plus 12.3g Disodium+2.9g Diammonium Orthophosphates	7.1	86	6.6	3.75 \pm 0.8
C	(e) Sample after above conditions	7.1	86	6.6	3.65 \pm 0.6

TABLE 35

Shows the cathodic polarization values of phosphate base solution and tank No.A.

Cathode Potential(mV)	Anode Potential(mV)	Current Density(mA/cm ²)	pH after Plating
<i>Phosphates(Only)</i>			
-500	90	0.083	7.0
-600	100	0.083	7.0
-700	150	0.2	7.0
-800	900	3.13	7.0
-850	1150	6.32	7.0
-900	1200	10	7.0
-1000	1300	18	7.0
-1100	1320	28	7.0
<i>Plating Tank A</i>			
-500	710	0.7	7.0
-600	930	4.8	7.0
-650	1072	8.2	7.0
-700	1087	2.8	7.0
-750	1119	5.2	6.9
-800	1155	10.65	6.9
-900	1179	23	6.8
-984	1193	33.7	6.8

TABLE 36

Shows the cathodic polarization values of platinum solution with an addition of 130ml of NaOH for a 2 litres solution of tank No.A.

Cathode Potential(mV)	Anode Potential(mV)	Current Density(mA/cm ²)	pH after Plating
Plating Tank A with adjusted pH to 7.0 with 130 ml of NaOH			
-500	720	0.8	7.2
-600	916	5.2	7.2
-650	1060	8.3	7.2
-700	1093	2.8	7.2
-750	1127	4.8	7.2
-800	1146	10.7	7.2
-850	1158	16	7.2
-900	1164	22.52	7.0
-950	1171	29.65	7.0
-979	1120	33.5	7.0
Plating Tank A with adjusted pH to 8.6 with 20g of NaOH			
-500	0.0	0.1	7.2
-600	136	0.5	7.2
-650	750	2.6	7.2
-700	971	6.0	7.2
-750	940	2.5	7.2
-800	940	2.0	7.2
-850	992	5.4	7.2
-900	1022	10.9	7.0
-950	1038	16.7	7.0
-1000	1050	22.86	7.0

Bath Composition and Operating Conditions

	Ratios		
	7:1	4:1	1:1
Pt as 'P' Salt(28.01g/l)	214	214	214
Sodium Nitrite, g/l	102	102	102
Disodium Hydrogen Orthophosphate, g/l	213	187	85.2
Diammonium Hydrogen Orthophosphate, g/l	39.6	63.4	158
pH	7.65	7.7	7.7
Temperature, C	84-86	84-86	84-86

TABLE 37

Shows the bath composition and operating conditions with different solutions having phosphate ratios, using constant platinum content of 3.0 g/l.

TABLE 38

Shows the cathodic and anodic polarization values of the solutions having phosphate ratios of 1:1 and 4:1 using constant platinum content.

Cathode Potential(mV)	Anode Potential(mV)	Current Density(mA/cm ²)	pH after Plating
Ratio 1:1			
-600	744	0.4	7.65
-650	1072	1.0	7.65
-700	1450	6.0	7.65
-750	1828	14.3	7.65
-800	1877	10.7	7.65
-850	1947	16.8	7.65
-900	2010	23.0	7.65
-950	2071	29.5	7.65
Ratio 4:1			
-600	1252	1.5	7.45
-650	1484	6.4	7.45
-700	1837	13	7.45
-750	1903	18	7.45
-800	1979	8.8	7.45
-850	1994	15	7.45
-900	2055	21	7.45
-950	2117	27.4	7.45

Cathode Potential(mV)	Anode Potential(mV)	Current Density(mA/cm ²)	pH after Plating
<i>Ratio 7:1</i>			
-600	1413	4.0	7.55
-650	1742	9.5	7.55
-700	1815	16	7.55
-750	1877	20.5	7.55
-800	1936	25.4	7.55
-850	1994	30.6	7.55
-900	2023	18	7.55
-950	2086	24.3	7.55

TABLE 39

Shows the cathodic and anodic polarization values of the solutions having phosphate ratio of 7:1 compared with other ratios using constant platinum content.

TABLE 40

Shows the cathodic and anodic polarization values of the solutions having phosphate ratios 4:1, 7:1 and 1:1 as well as cell efficiency comparison using constant platinum content.

Cathode Potential (mV)	Weight Gain(g)	Current Density(mA/cm ²)	Cathode Current Efficiency (%)	pH after Plating
<i>Ratio 4:1</i>				
-600	0.00	0.11	--	7.5
-700	0.012	9.0	6.6±1.2	7.5
-800	0.038	22.0	8.6±1.4	7.5
-900	0.064	20.5	15.8±1.5	7.5
<i>Ratio 7:1</i>				
-600	0.00	0.083	--	7.7
-700	0.009	7.0	6.2±0.9	7.7
-800	0.04	25.6	8.0±1.2	7.7
-900	0.061	19.45	15.9±2.1	7.7
<i>Ratio 1:1</i>				
-600	0.00	0.083	--	7.7
-700	0.00	0.7	--	7.7
-800	0.011	10.0	5.6±1.2	7.7
-900	0.055	24.6	11.35±2.3	7.7

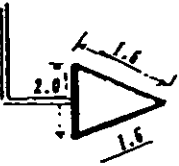


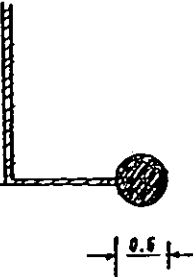
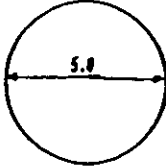
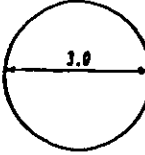
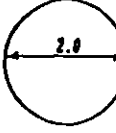
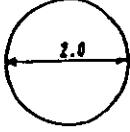

<i>Ni-Strike</i>				
<u>Anode Shape(cm)</u>	<u>Current Applied (Amp)</u>	<u>Interel ectrode Separat ion(mm)</u>	<u>Plating Duration (min)</u>	<u>Deposit Shape(cm)</u>
Medium Triangle Anode Size				
	1.0	5	5	
	1.57	5	5	
Spherical Anode Size				
	1.0	5	5	
	1.56	5	5	
	0.52	5	5	
	0.56	5	5	
	0.38-0.56	5	5	

TABLE 41

Shows the effects of parameters such as applied current, interelectrode separation and plating time upon the characteristic and shape deposits using medium triangle and spherical anode size.

<i>Ni-Strike</i>				
<u>Anode Shape (cm)</u>	<u>Current Applied (Amp)</u>	<u>Interel ectrode Separat ion (mm)</u>	<u>Plating Duration (min)</u>	<u>Deposit Shape (cm)</u>
Medium Ellipse Anode size				
	1.56	5	5	
	1.36	5	5	
	0.49-0.5	5	5	
	0.65-0.7	5	5	
Rectangular Anode Size (Horizontal Position)				
	1.55	5	5	
	1.0	5	5	
	0.5-0.54	5	5	
	0.53-0.63	5	5	

TABLE 42

Shows the effects of parameters such as applied current, interelectrode separation and plating time upon the characteristic and shape deposits using medium ellipse and rectangular anode size.

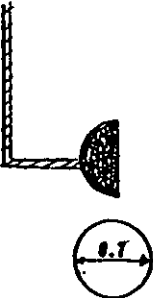
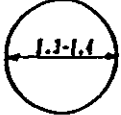
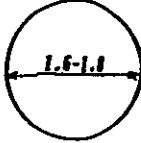
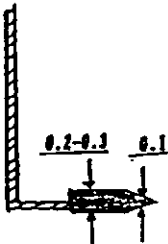


<i>Ni Sulphamate</i>				
<u>Anode Shape(cm)</u>	<u>Current Applied (mAmp)</u>	<u>Interel ectrode Separat ion(mm)</u>	<u>Plating Duration (min)</u>	<u>Deposit Shape(cm)</u>
<i>Circular Size Anode</i>				
	53	5	5	
	51	3	5	
<i>Cone Size Anode</i>				
	45-50	3	5	
	35-48	5	5	

TABLE 43

Shows the effects of parameters such as applied current, interelectrode separation and plating time upon the characteristic and shape deposits using circular and cone anode size.

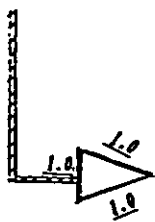
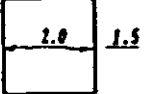
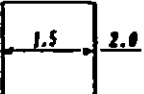

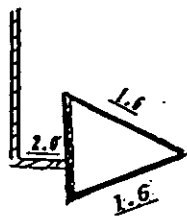
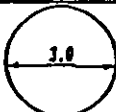

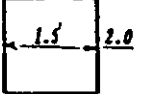
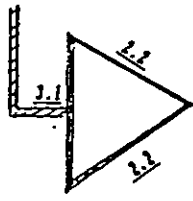
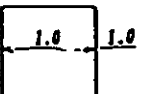
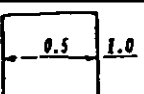
Ni Sulphamate				
<u>Anode Shape (cm)</u>	<u>Current Applied (mAmp)</u>	<u>Interel ectrode Separation (mm)</u>	<u>Plating Duration (min)</u>	<u>Deposit Shape (cm)</u>
<i>Small Triangle Size Anode</i>				
	110	1	1	
	150	1	1	
	141	1	1	
<i>Medium Triangle Size Anode</i>				
	56-73	5	5	
	55-65	3	5	
	240-250	1	1	
<i>Large Triangle Size Anode</i>				
	111	1	1	
	111	1	1	

TABLE 44

Shows the effects of parameters such as applied current, interelectrode separation and plating time upon the characteristic and shape deposits using small, medium and large triangle anode size.

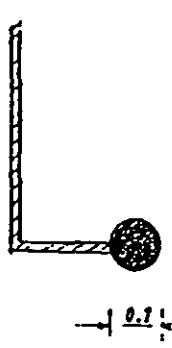

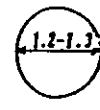


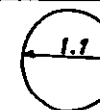
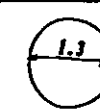
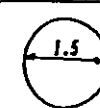
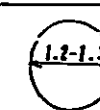
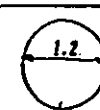

<i>Ni Sulphamate</i>				
<u>Anode Shape (cm)</u>	<u>Current Applied (mAmp)</u>	<u>Interel ectrode Separation (mm)</u>	<u>Plating Duration (min)</u>	<u>Deposit Shape (cm)</u>
Spherical Size Anode				
	53-56	5	5	
	52-67	3	5	
	58-86	5	10	
	56-67	1	10	
	127-140	1	1	
	100	1	1	
	54	1	1	
	56	1	1	
	50	1	1	
	33-41	1	1	

TABLE 45

Shows the effects of parameters such as applied current, interelectrode separation and plating time upon the characteristic and shape deposits using spherical anode size.

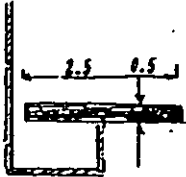
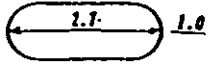
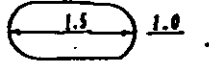
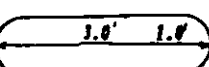
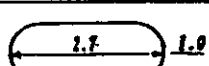
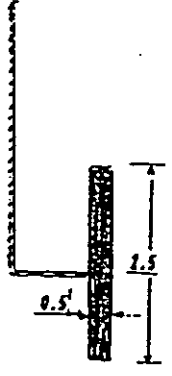
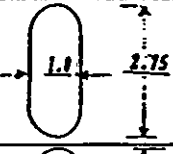
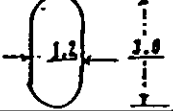
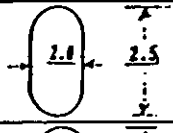
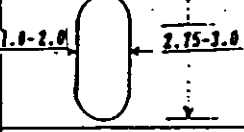
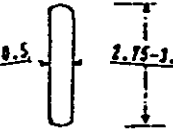
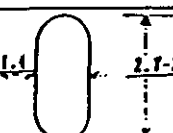
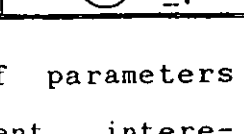
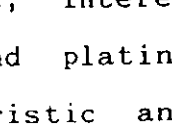
<i>Ni Sulphamate</i>				
<i>Anode Shape (cm)</i>	<i>Current Applied (mAmp)</i>	<i>Inter electrode Separation (mm)</i>	<i>Plating Duration (min)</i>	<i>Deposit Shape (cm)</i>
Rectangular Size Anode (Horizontal Position)				
	50-56	5	5	
	52	5	3	
	54-64	5	10	
	55	3	10	
Rectangular Size Anode (Vertical Position)				
	223-290	1	3	
	330-430	5	4	
	500-550	6	3	
	400-450	1-2	3	
	300-400	1-2	3	
	180-450	1	3	
	370-500	1	2	
	200-350	1	3	

TABLE 46

Shows the effects of parameters such as applied current, inter-electrode separation and plating time upon the characteristic and shape deposits using rectangular anode size in horizontal and vertical positions .

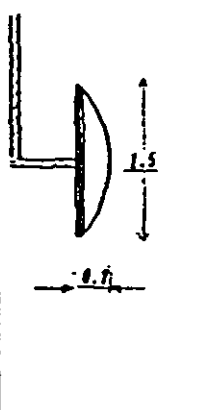
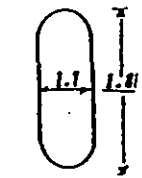
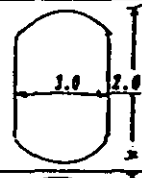
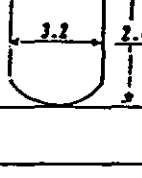
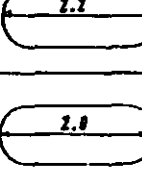
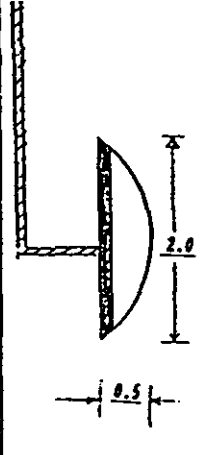
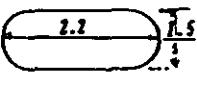
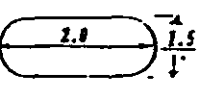

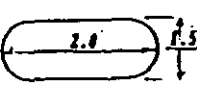
<i>Ni Sulphamate</i>				
<i>Anode Shape (cm)</i>	<i>Current Applied (mAmp)</i>	<i>Inter-electrode Separation (mm)</i>	<i>Plating Duration (min)</i>	<i>Deposit Shape (cm)</i>
<i>Small Ellipse Size Anode</i>				
	54	5	5	
	60-65	5	5	
	125-130	3	5	
	240-254	3	5	
<i>Medium Ellipse Size Anode</i>				
	67-74	5	10	
	53-69	3	10	
	55-76	5	5	
	66-90	5	5	

TABLE 47

Shows the effects of parameters such as applied current, inter-electrode separation and plating time upon the characteristic and shape deposits using small ellipse and medium ellipse anode size .

Table 48

Serial No.	Comments
OF 1011R	Satisfactory
IN 10251R	Evidence of stop off overspill on to trailing edge
FA 568R	Minor cratering noted along edge
IN 19534R	Local area on convex aerofoil exhibits lack of aluminising due to stop off overspill
IN 19372R	Local area on concave aerofoil exhibits lack of aluminising due to stop off overspill
FA 751R	Reworked blade, visual evidence of original defect observed convex platform aerofoil radius
IN 19801R	Local area on concave aerofoil exhibits lack of aluminising due to stop off overspill
IN 12831	Satisfactory
OF 1009R	Coating satisfactory. Blades exhibits breaking of coating

Table 49

<i>Serial No.</i>	<i>Comments</i>
<i>K01526</i>	<i>Satisfactory</i>
<i>K04099</i>	<i>Satisfactory</i>
<i>K01664</i>	<i>Satisfactory</i>
<i>K04092</i>	<i>Satisfactory</i>
<i>K04025</i>	<i>Local areas of non aluminising due stop off overspill</i>
<i>K04098</i>	<i>Satisfactory</i>
<i>K04063</i>	<i>Satisfactory</i>
<i>K04102</i>	<i>Satisfactory</i>
<i>K04019</i>	<i>Satisfactory</i>
<i>K04103</i>	<i>Satisfactory, stop off overspill on leading edge adjacent to platform</i>
<i>K02015</i>	<i>Satisfactory</i>
<i>K04045</i>	<i>Satisfactory</i>

Table 50

<i>1st Stage</i>		<i>2nd Stage</i>	
<i>Serial No.</i>	<i>Hardness HRC</i>	<i>Serial No.</i>	<i>Hardness HRC</i>
<i>IN 10251R</i>	<i>38.0</i>	<i>K04045</i>	<i>36.2</i>
<i>IN 12831R</i>	<i>38.4</i>	<i>K04025</i>	<i>40.6</i>
<i>IN 19372R</i>	<i>33.2</i>	<i>K04063</i>	<i>40.0</i>
<i>IN 19807R</i>	<i>36.5</i>	<i>K04098</i>	<i>43.4</i>
<i>FA751R</i>	<i>35.1</i>	<i>K04102</i>	<i>42.2</i>
<i>IN 19534R</i>	<i>36.8</i>	<i>K02015</i>	<i>36.0</i>
<i>OF 1009R</i>	<i>32.8</i>	<i>K04103</i>	<i>43.6</i>
<i>OF 1011R</i>	<i>36.2</i>	<i>K01526</i>	<i>44.6</i>
<i>FA 568R</i>	<i>34.8</i>	<i>K04013</i>	<i>43.6</i>
		<i>K04019</i>	<i>43.2</i>
		<i>K04099</i>	<i>41.4</i>
		<i>K04092</i>	<i>41.2</i>
		<i>K01664</i>	<i>39.4</i>

Table 51

Stress Rupture Testing Results to date (Material U500)

<i>Component</i>	<i>Position</i>	<i>Duration</i>	<i>E1%</i>	<i>R of A%</i>
<i>1st Blade</i>	<i>Aerofoil</i>	<i>Test Held</i>		
	<i>Root</i>	<i>Specimen stripped threads</i>		
<i>2nd Blade</i>	<i>Upper Aerofoil</i>	<i>Rupture on loading</i>	<i>37.5</i>	<i>37.6 Fail</i>
	<i>Lower Aerofoil</i>	<i>Specimen stripped threads</i>		
	<i>Root</i>	<i>Specimen stripped threads</i>		
<i>Blank</i>	<i>Blank 1</i>	<i>Rupture on loading</i>	<i>35.4</i>	<i>41.1 Fail</i>
	<i>Blank 2</i>	<i>Rupture on loading</i>	<i>39.3</i>	<i>61.1 Fail</i>

Table 52

<i>TG20 1st Stage Vane</i>	
<i>Serial No.</i>	<i>Comments</i>
<i>IH5022</i>	<i>Satisfactory</i>
<i>IH1684</i>	<i>Satisfactory</i>
<i>IH981</i>	<i>Evidence of cratering defects on aerofoil and platform</i>
<i>IH1511</i>	<i>Satisfactory</i>
<i>IHF2661</i>	<i>Evidence of rework present convex aerofoil inner radius</i>
<i>IH5042</i>	<i>Evidence of rework convex aerofoil</i>
<i>IH1119</i>	<i>Crater present on leading edge remainder satisfactory</i>
<i>IH9538</i>	<i>Satisfactory</i>
<i>IH5181</i>	<i>Evidence of rework (satisfactory)</i>
<i>IH1798</i>	<i>Satisfactory</i>
<i>IH4970</i>	<i>Satisfactory</i>

Table 53

TG20 2nd Stage Vane	
Serial No.	Comments
IHI KEU04	Chip defect on leading edge vane 2 mechanical damage evidence of rework visible in radii. Rough surface finish between aerofils.
SER 6280	Evidence of rework present. Rough surface finish on concave aerofoil.
IHF KE203	Evidence of rework present. Some cratering vane 1 Halo plating effect visible on inner platform.
26 FSA	Some evidence of rework present roughness on surface considered acceptable
IHI KEK03	Evidence of rework on inner radii. Satisfactory
SER 6274	Concave aerofoil show rough surface finish considered acceptable. Evidence of rework on platform.
IHI KES02	Evidence of halo plating effect on inner platform. Considered acceptable.
SER 6278	Roughness on concave surfaces. Evidence of halo plating effect and blistering on inner platform.
IHI KDB02	Evidence of rework present. Satisfactory
V2H 2218	Evidence of halo plating effect inner platform considered acceptable
IHI KEK01	Evidence of rework inner platform considered acceptable.

Table 54

Component	Serial No.	Position	Time to Rupture	EI%	R of A%	
1st Vane	IH981	Outer platform	14 hrs	27.1	29 Fail	
	IH5042	Outer platform	12 hrs	24.6	27.9 Fail	
2nd Vane	IHI KF507	Outer platform Vane 1	20 hrs	40.4	54.8 Pass	
		Outer platform Vane 2	24 hrs	62.6	38.7 Pass	
	SER 6278	Outer platform Vane 1	18 hrs	62.6	70.4 Pass	
		Outer platform Vane 2	22 hrs	54.8	65.9 Pass	
	Blanks		1	52 hrs	22.3	did not break Pass
			2	34 hrs	50.6	44.6 Pass
		3	38 hrs	39.6	46.6 Pass	
		4	33 hrs	48.8	51.7 Pass	

TABLE 55

Shows the main bath composition ranges, current density, temperature, pH and finally cathode current efficiency.

	Bath No.16	Bath No.17	Bath No.18	Bath No.19
Platinum as 'P' Salt, g/l	5	5	5	5
Sodium Acetate, g/l	70	25	-	-
Sodium Carbonate, g/l	100	36	36	-
Sodium Citrate, g/l	-	-	25	-
Sodium Sulphate, g/l	-	-	-	40
Sodium Chloride, g/l	-	-	-	5
Temperature, °C	84-88	84-88	84-88	84-88
pH	11.5	11.5	11.5	11.5
C.D mA/cm ²	15	15	15	15
C.C.Efficiency (%)	18.6	41	52.4	38.4

TABLE 56

Shows the effects of various current densities upon conventional and pulse plating/longer period.

	C.D (15mA/cm ²)	C.D (30mA/cm ²)	C.D (45mA/cm ²)
	<i>Bath No.1</i>		
<i>Coventional Plating</i>	14	7.3	4
<i>Pulse Plating</i>	16.2	8.5	2.1
<i>Pulse Plating with Longer Off-period</i>	16.8	8.6	2.4
	<i>Bath No.2</i>		
<i>Coventional Plating</i>	17	13	7.1
<i>Pulse Plating</i>	16	15	7.5
<i>Pulse Plating with Longer Off-period</i>	16.4	16	7.8
	<i>Bath No.3</i>		
<i>Coventional Plating</i>	19	13.6	7.8
<i>Pulse Plating</i>	21	17	9.1
<i>Pulse Plating with Longer Off-period</i>	24.6	19.1	9
	<i>Bath No.4</i>		
<i>Coventional Plating</i>	18	12.5	6.8
<i>Pulse Plating</i>	23	16	8.2
<i>Pulse Plating with Longer Off-period</i>	22.1	19	5.6
	<i>Bath No.5</i>		
<i>Coventional Plating</i>	7	6.8	3.1
<i>Pulse Plating</i>	9	12	12.8
<i>Pulse Plating with Longer Off-period</i>	9.8	12.8	3.6
	<i>Bath No.6</i>		
<i>Coventional Plating</i>	4.1	1.4	0.5
<i>Pulse Plating</i>	2.1	0.7	0.5

Table 56. Continued

<i>Pulse Plating</i>	2.1	0.7	0.5
<i>Pulse Plating with Longer Off-period</i>	0.5	0.2	0
	<i>Bath No. 7</i>		
<i>Coventional Plating</i>	6.8	6.1	3.3
<i>Pulse Plating</i>	3.2	2.1	1.1
<i>Pulse Plating with Longer Off-period</i>	2.1	1.8	1.0
	<i>Bath No. 8</i>		
<i>Coventional Plating</i>	7.3	6.2	4.3
<i>Pulse Plating</i>	9	7.4	3.2
<i>Pulse Plating with Longer Off-period</i>	11	8.6	2.2
	<i>Bath No. 9</i>		
<i>Coventional Plating</i>	7.9	6.4	5.1
<i>Pulse Plating</i>	8.9	7.3	8.6
<i>Pulse Plating with Longer Off-period</i>	12.1	8.6	2.3
	<i>Bath No. 10</i>		
<i>Coventional Plating</i>	7.8	6.3	4.6
<i>Pulse Plating</i>	10.2	7.8	2.8
<i>Pulse Plating with Longer Off-period</i>	14	9.8	2.5

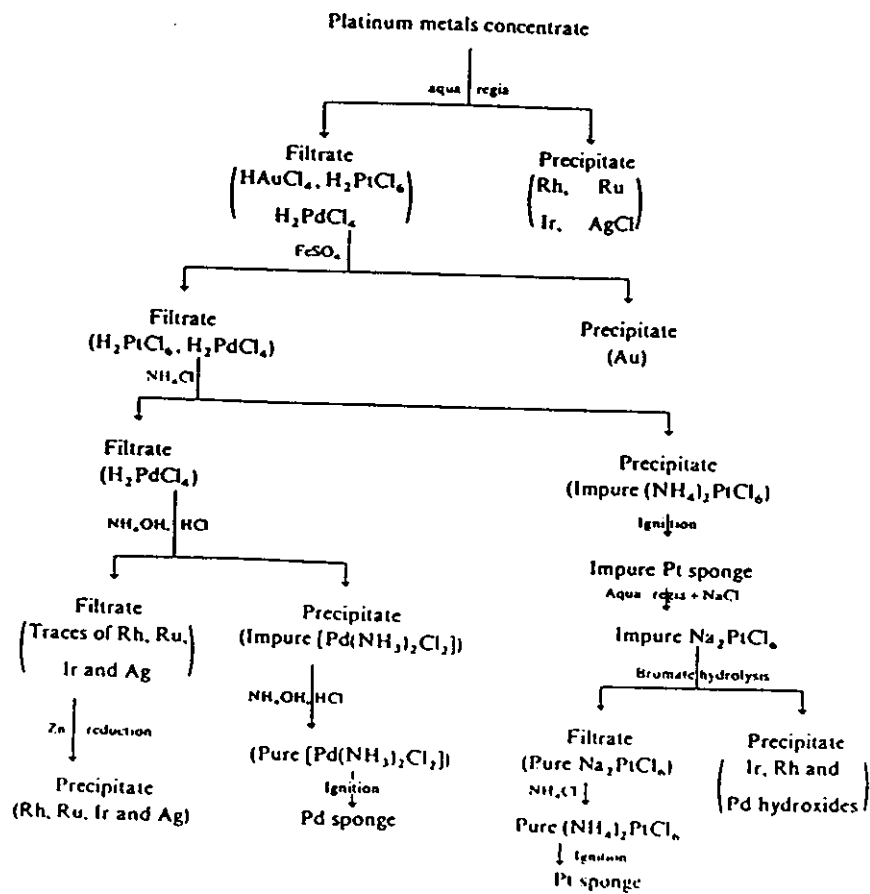


Fig. 1. Scheme for the extraction of platinum and palladium.

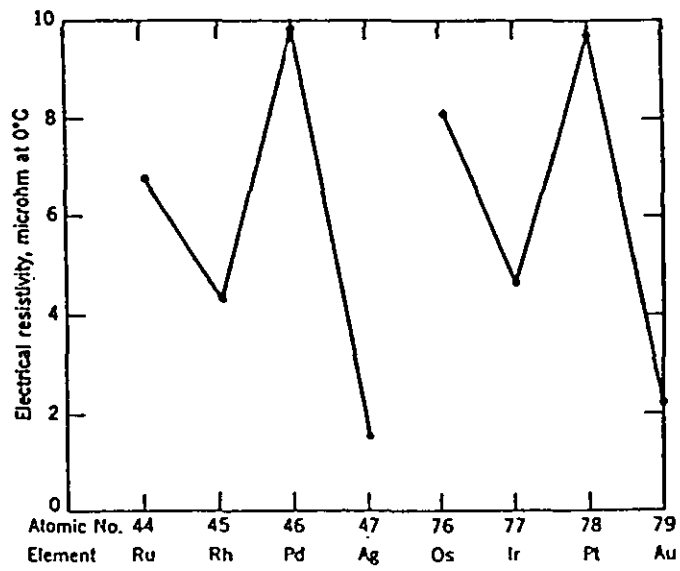
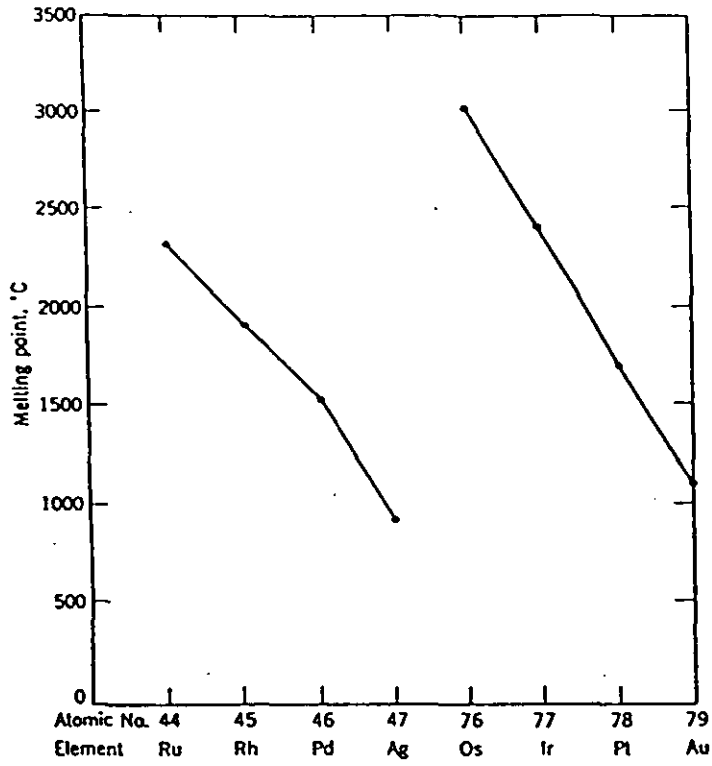
Figure 2

Shows the melting points of
precious metals(Data from INCO
Ltd).

Figure 3

Shows the electrical resistivity
of precious metals.

PLATINUM METALS



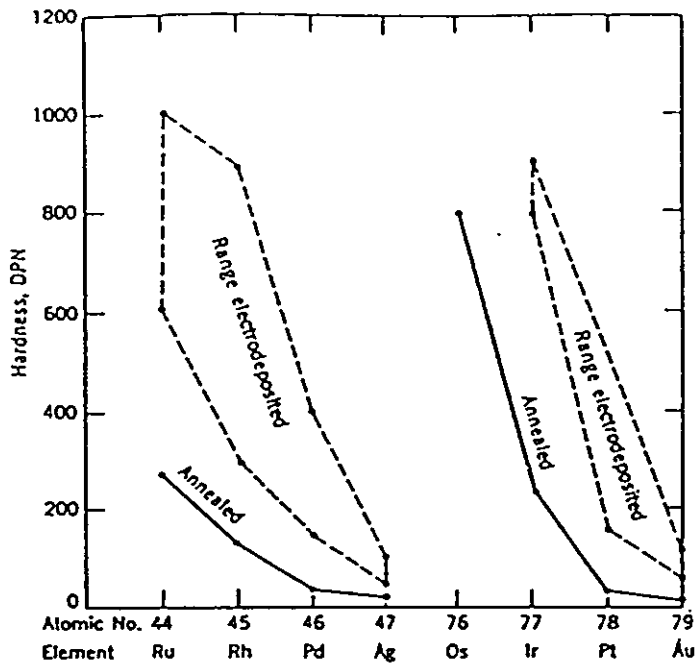


Figure 4

Shows the annealed hardness and range of hardness for electrodeposited precious metals.

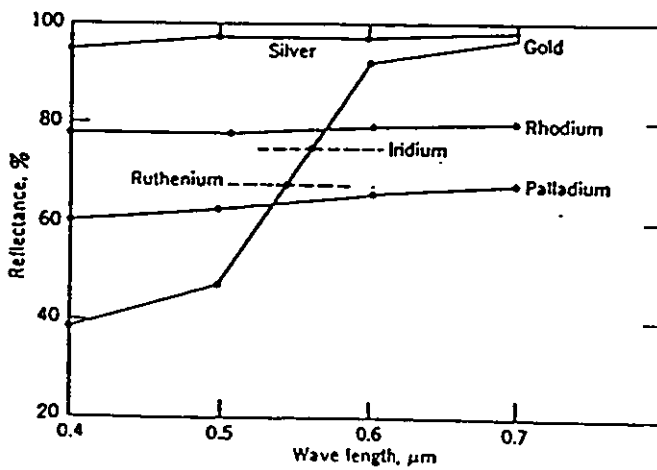


Figure 5

Shows the reflectance of precious metals.

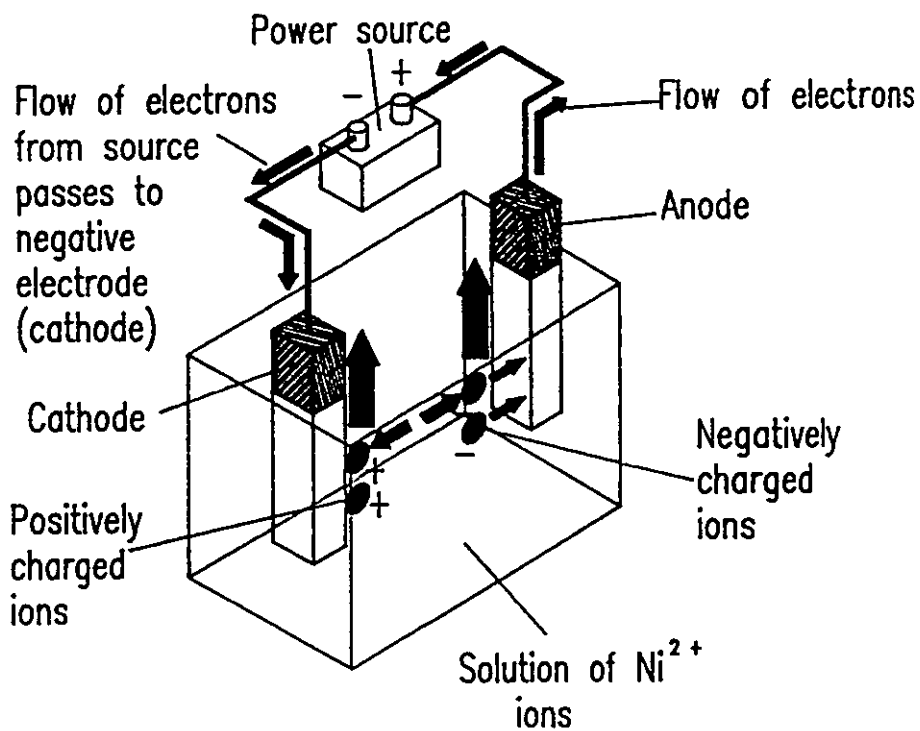


Figure 6

Schematic representation of the mechanism of potential difference across the cell due to the current source makes an excess of electrons available at the cathode.

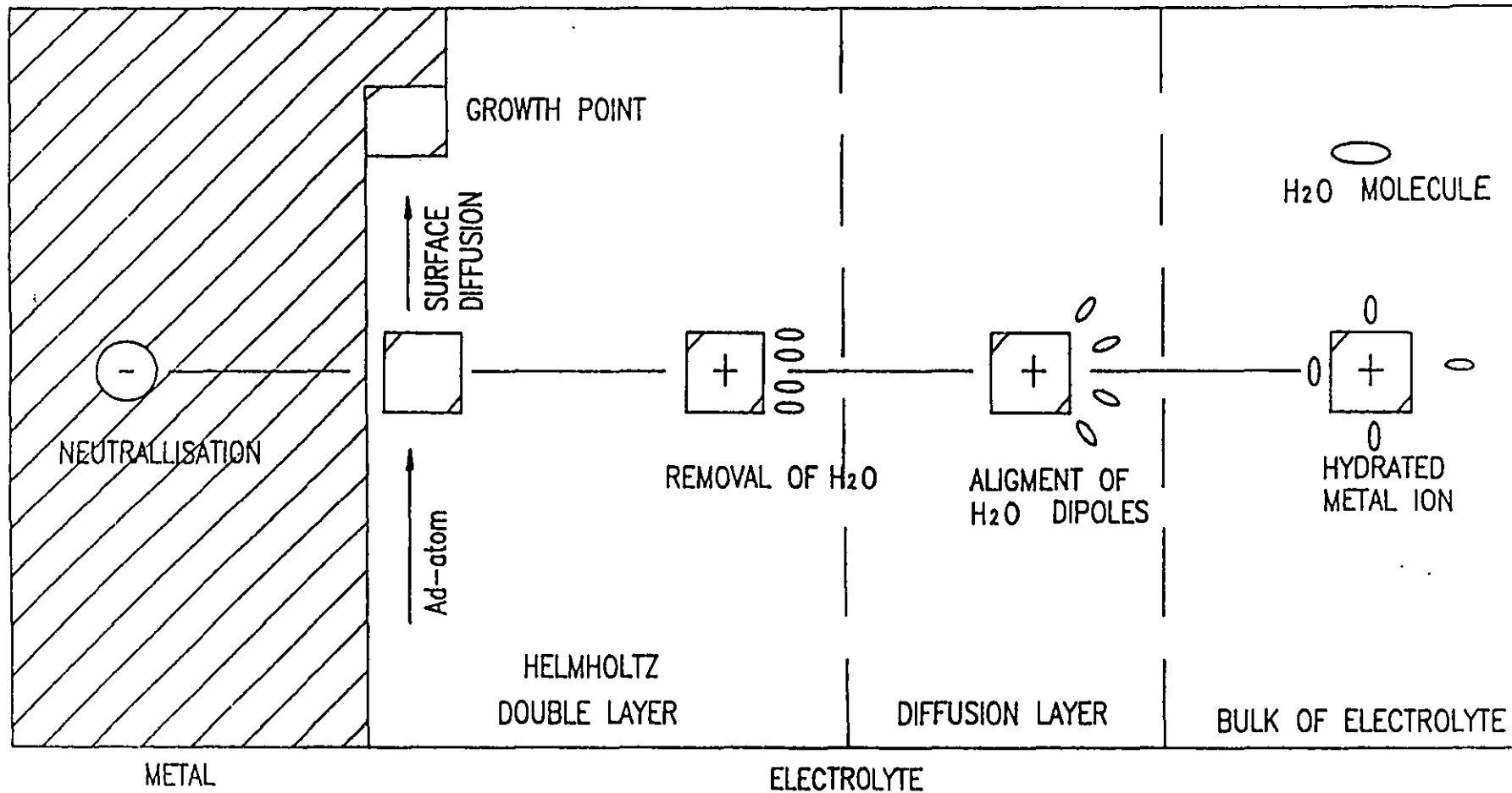


Figure 7

Schematic representation of the mechanism of cathodic metal deposition.

Figure 8

Potential and concentration gradients in the electrolytic cell $\text{Cu}/\text{CuSO}_4/\text{Cu}$.

(a) The electrodes are unpolarised; the potential difference E_{eg} and there is no concentration gradient in the diffusion layer.

(b) The electrodes are polarised; ΔE_{eq} whilst E_{p} of the cathode is more negative and concentration gradients exist across the diffusion layer; C_{e} , C_{b} are the concentrations at the electrode and in the bulk solution.

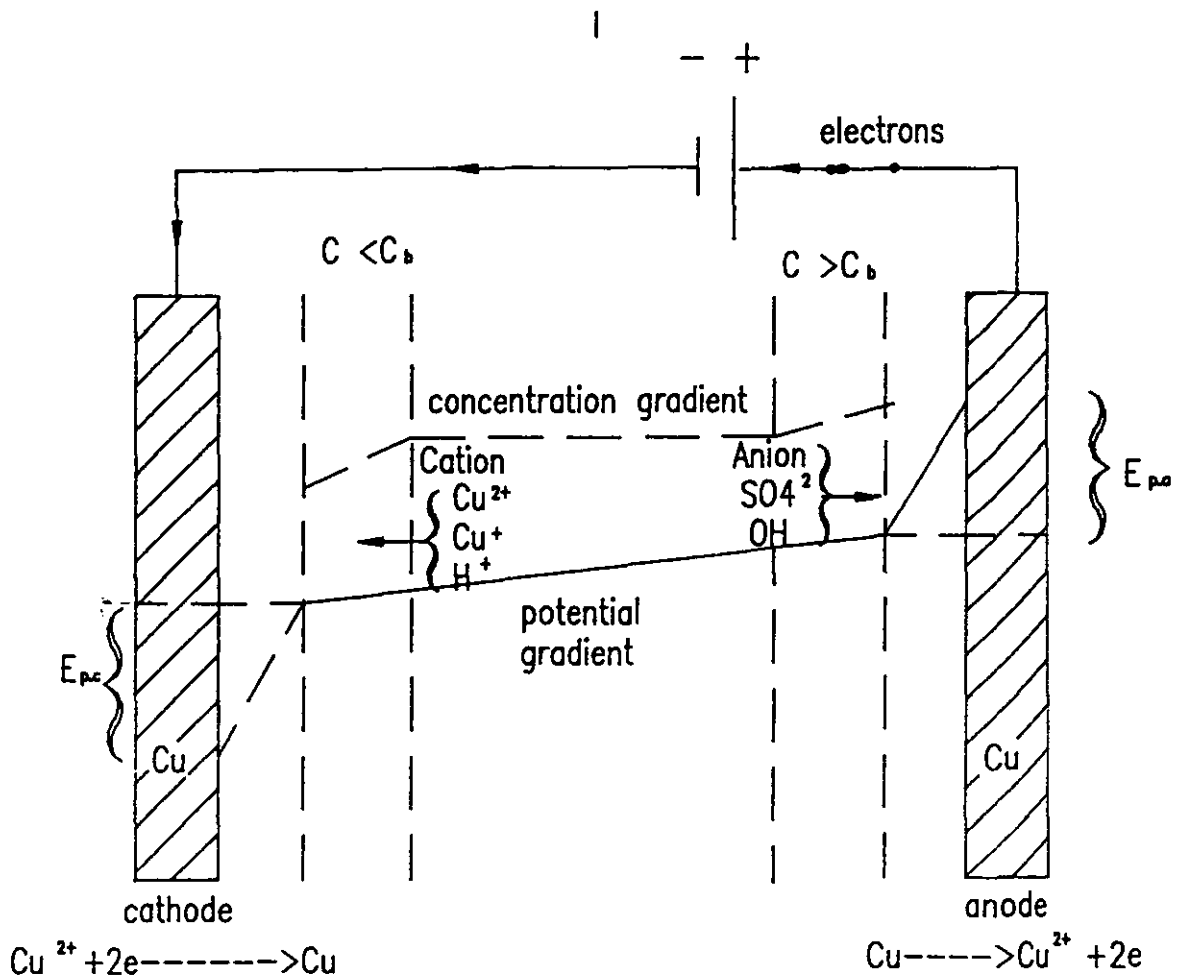
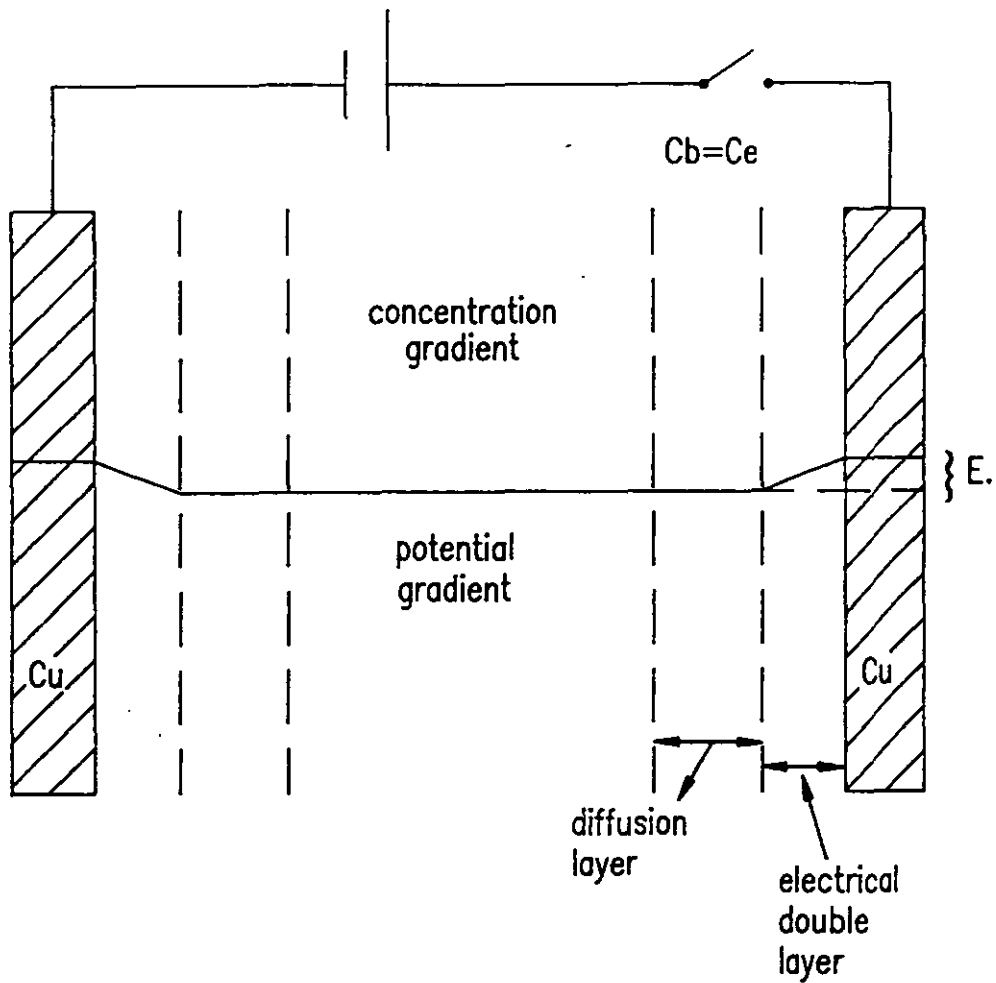


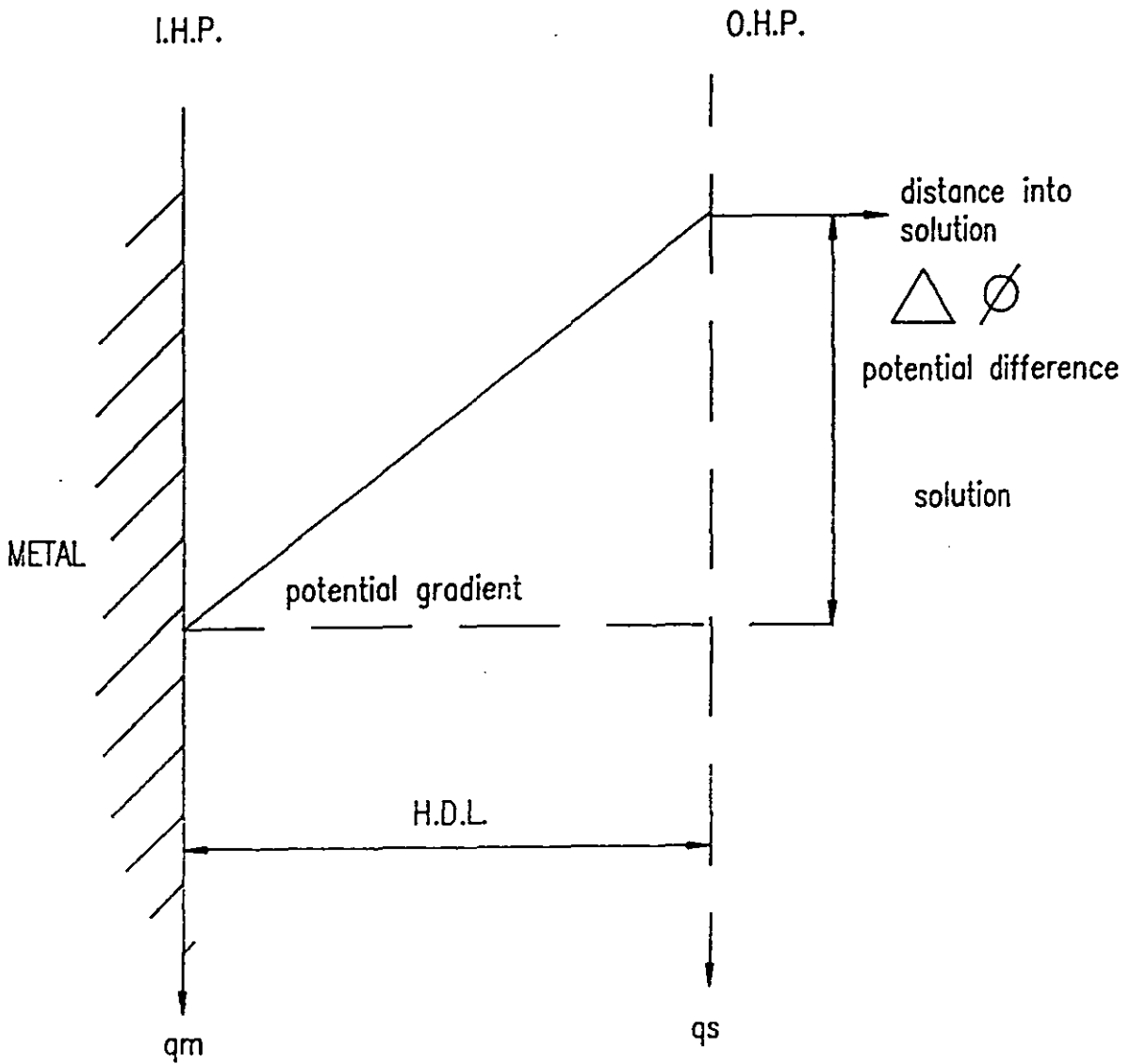
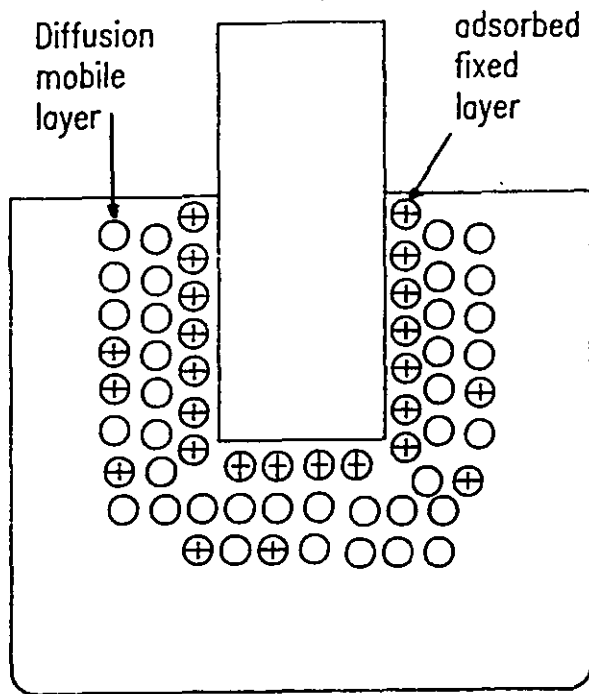
Figure 9

Schematic representation of the electrical double layer.

Double layer acts as a capacitor, with a fixed plate (the fixed layer) and a movable plate (the mobile layer).

Figure 9a

Schematic representation of the Helmholtz double layer (H.D.L) consisting of a plate of excess positive charges (cations) in solution. The double layer as a whole being electrically neutral. The double layer can be regarded as equivalent to a capacitor in which the plates are separated by a distance.

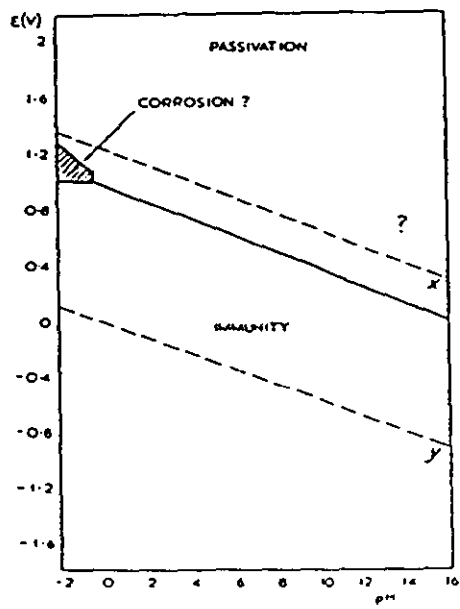
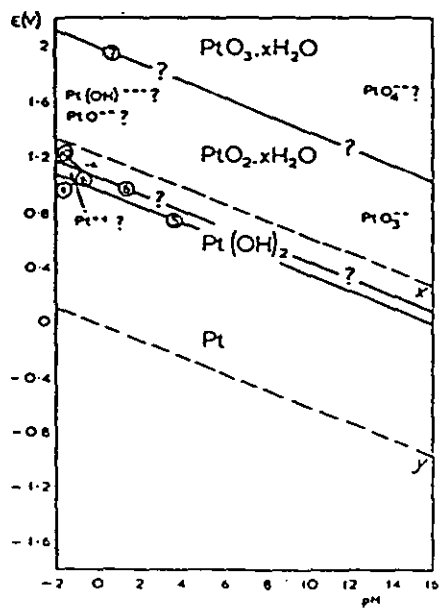
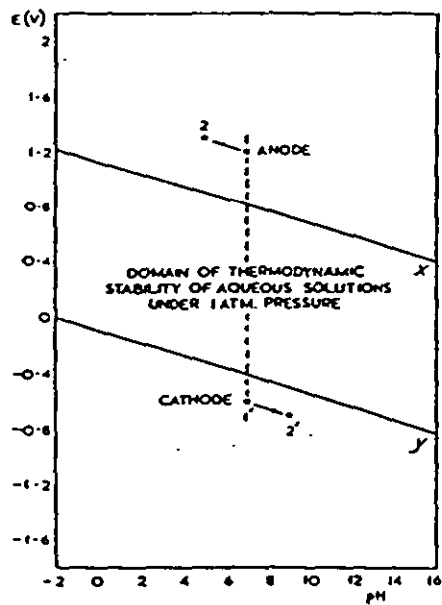
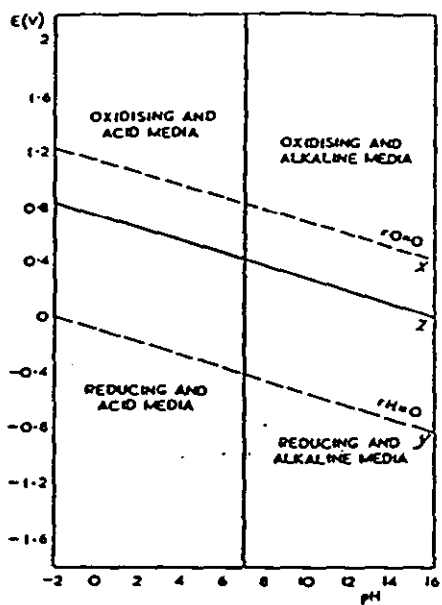


Figures 10-11

Schematic representation of the potential-pH diagrams. The dotted line x refers to the conditions of equilibrium .

Figures 12-13

Schematic representation of the metallic platinum is stable in aqueous solution at low potentials and fig 13 represents theoretical conditions for the corrosion, immunity and passivation of platinum .



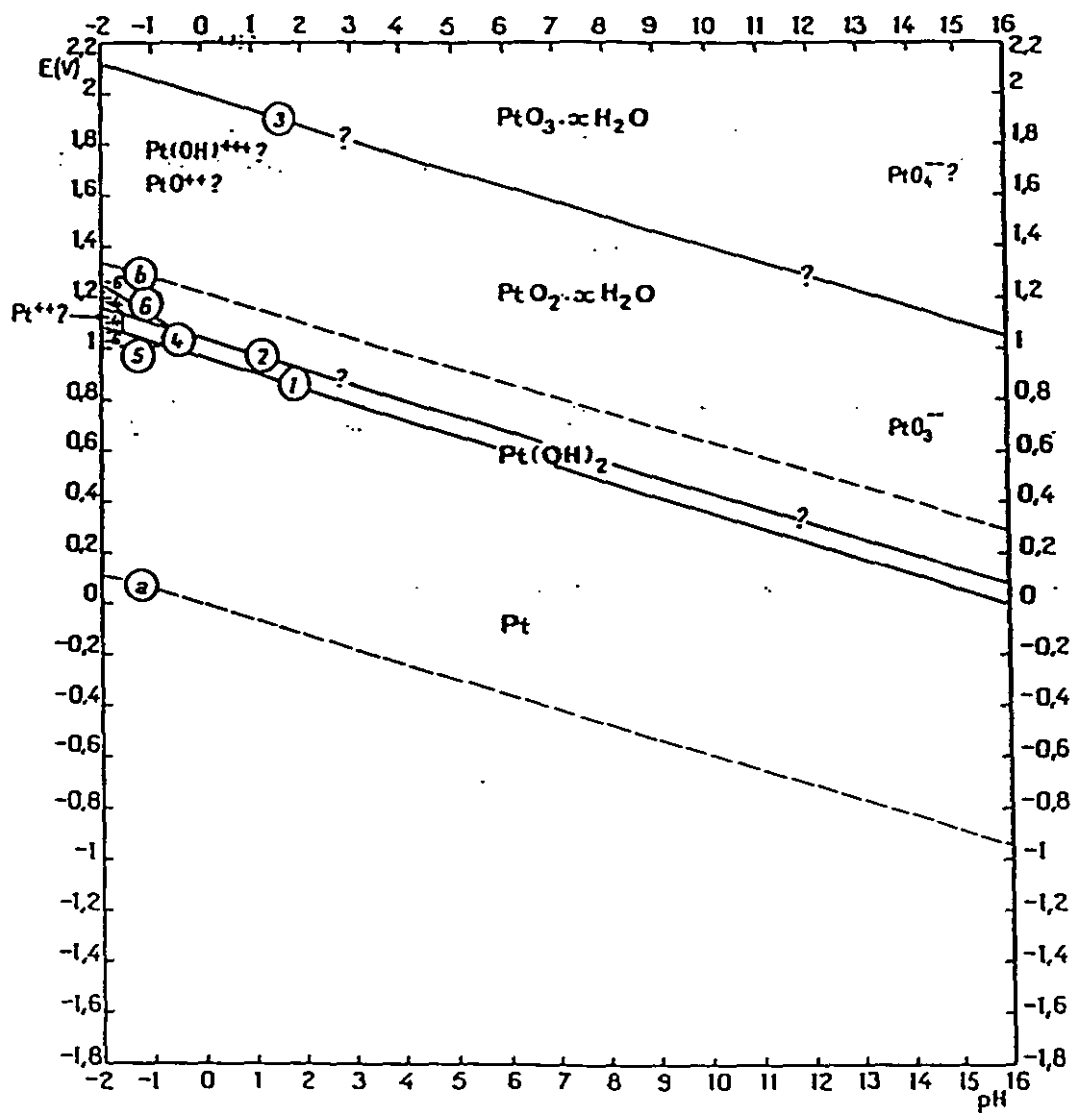


Figure 14

Schematic representation showing how metallic platinum is stable in aqueous solution at low potentials.

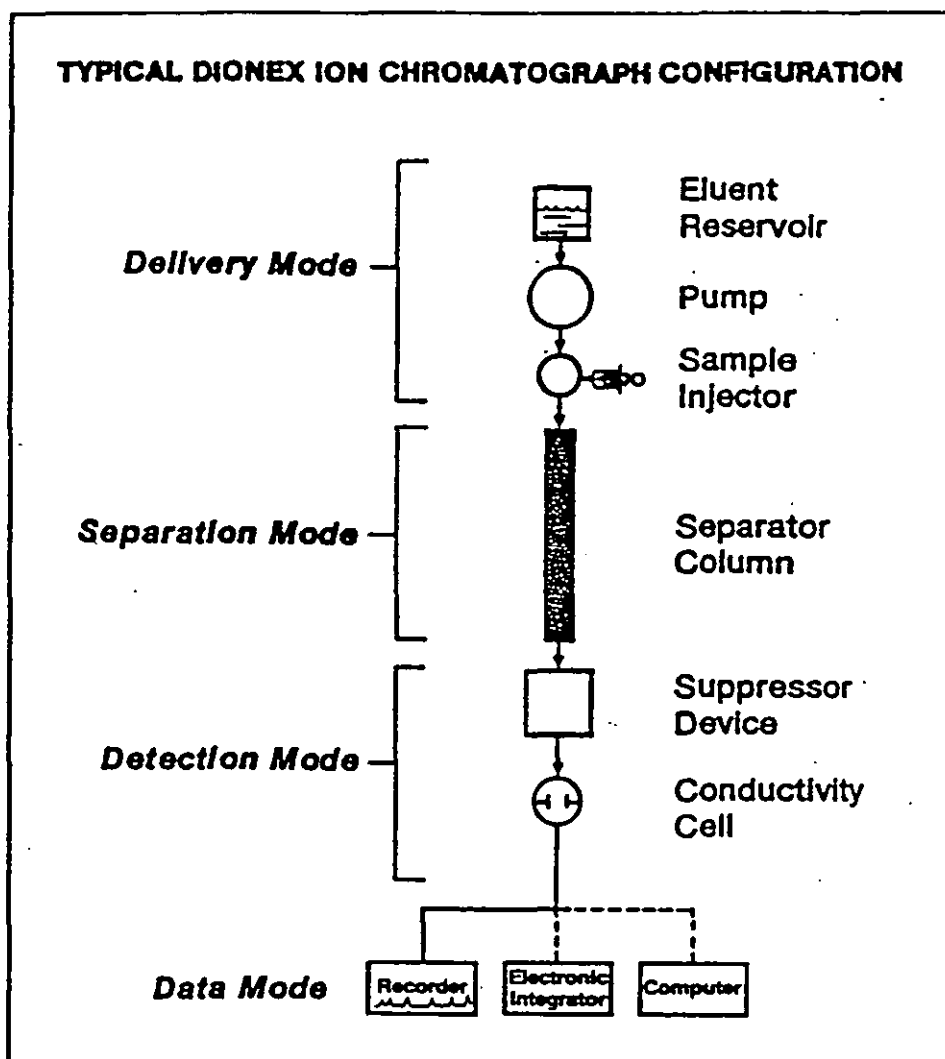


Figure 15

Shows the components of a typical Ion chromatograph are schematically indicated.

Figure 16

Schematic representation flow
path during sample loading.

Figure 17

Schematic representation flow
path during sample injection.

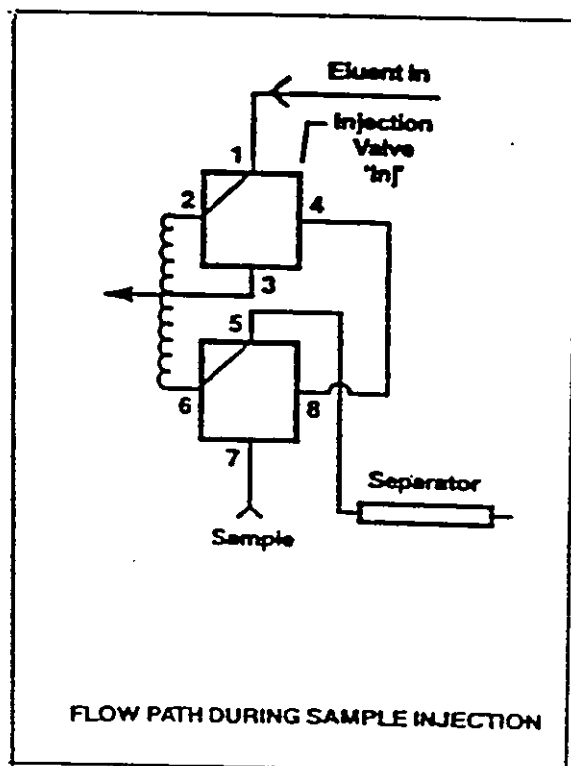
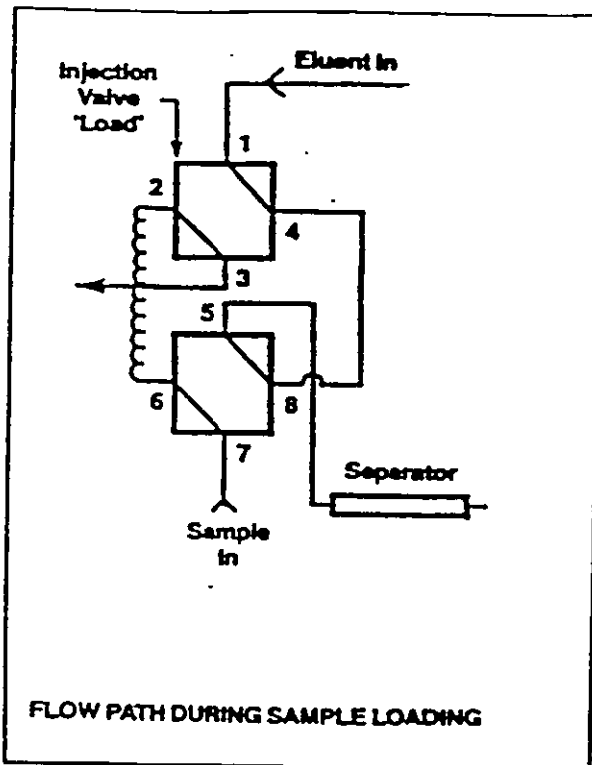


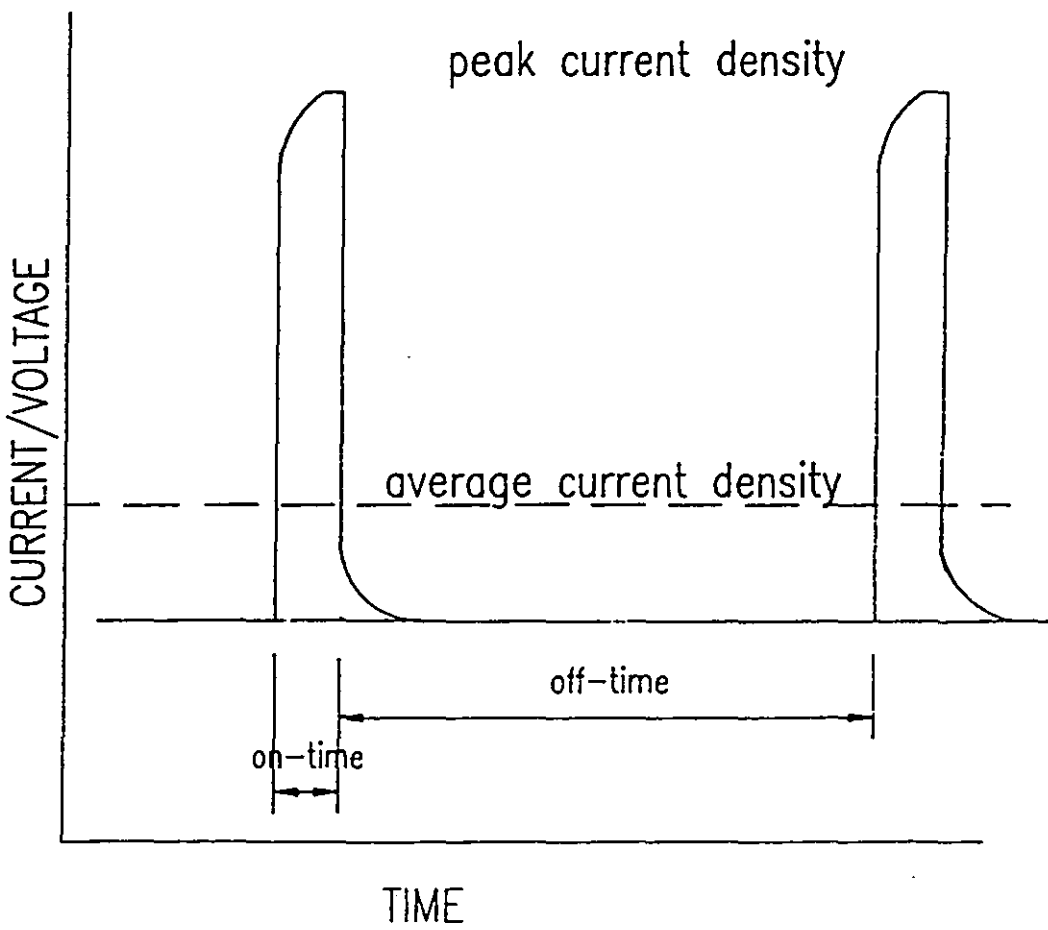
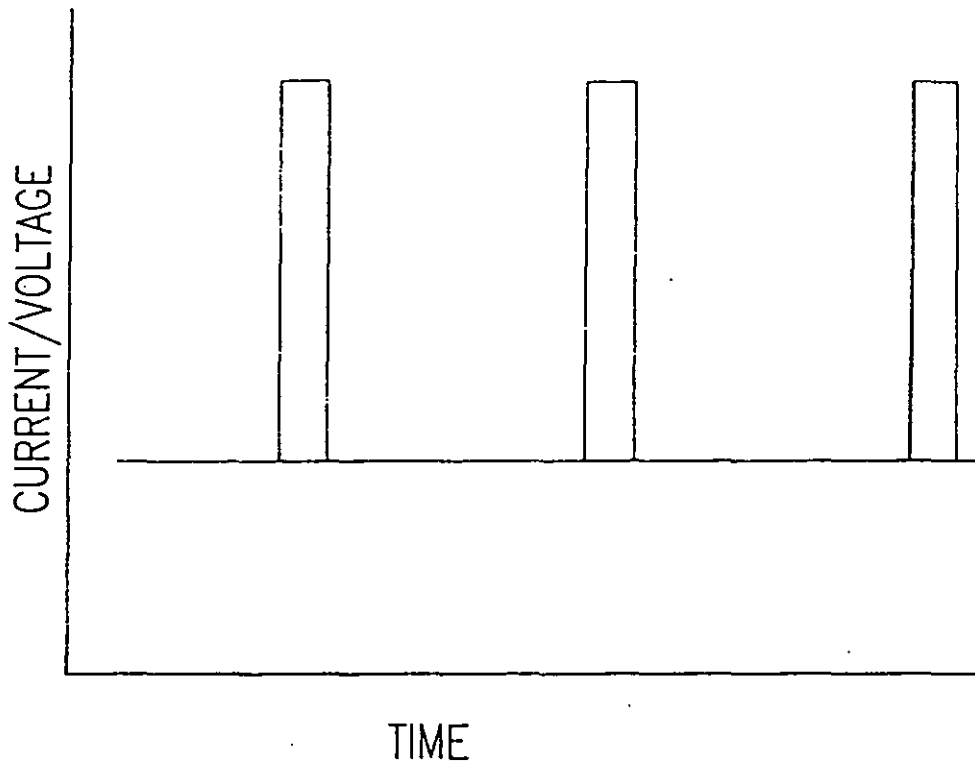
Figure 18

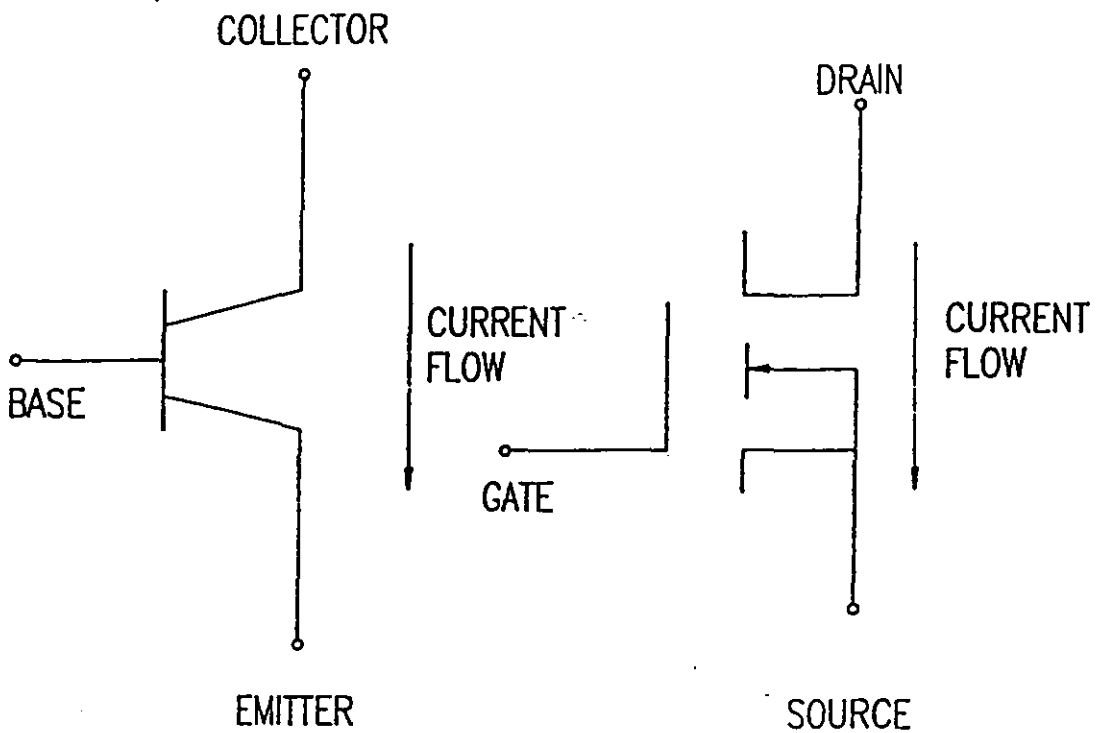
Schematic representation of a square wave pulsed current.

Figure 19

Schematic representation of a square wave pulsed current with curved flow.

It does not show a pure square because there is a gradual curvature to both the ascending and descending current flow.





(a) NPN BIPOLAR TRANSISTOR

(b) N-CHANNEL MOSFET

Figure 20

General view for bipolar and Mosfet electrical symbol. Instead of collector, emitter and base, electrical symbols for power Mosfets are; drain, source and base.

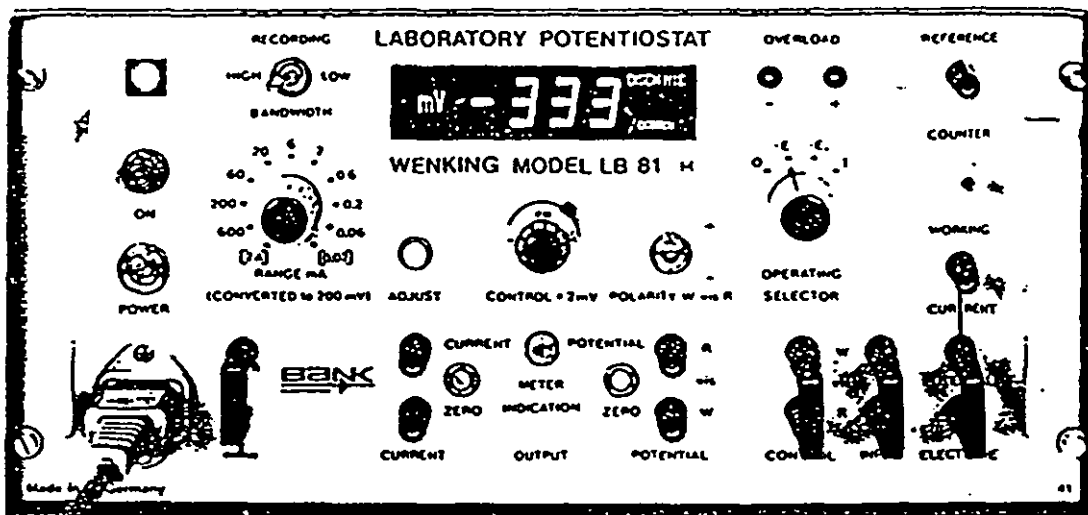


Figure 21

General view of a Laboratory Potentiostat (Wenking Model LB M).

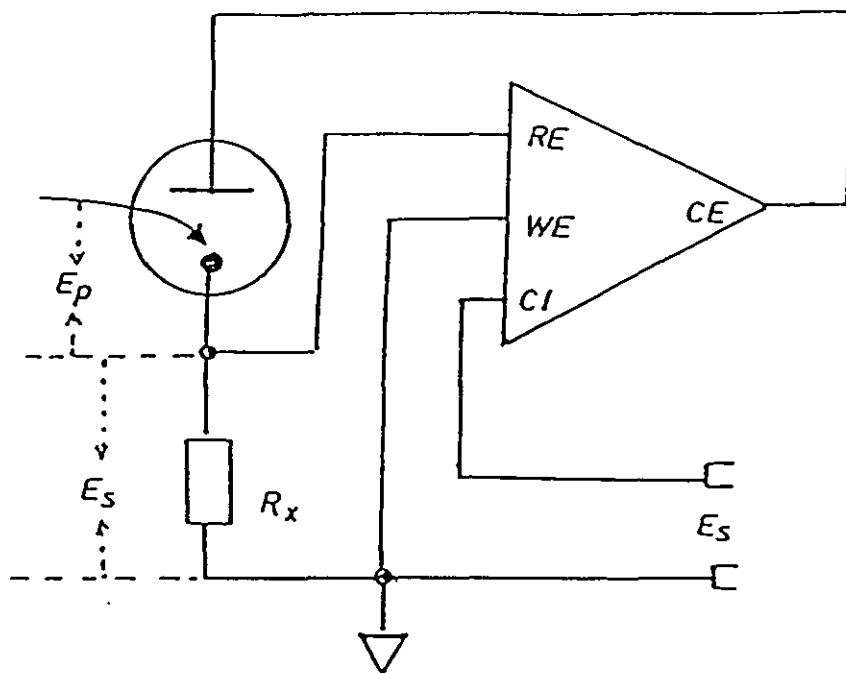
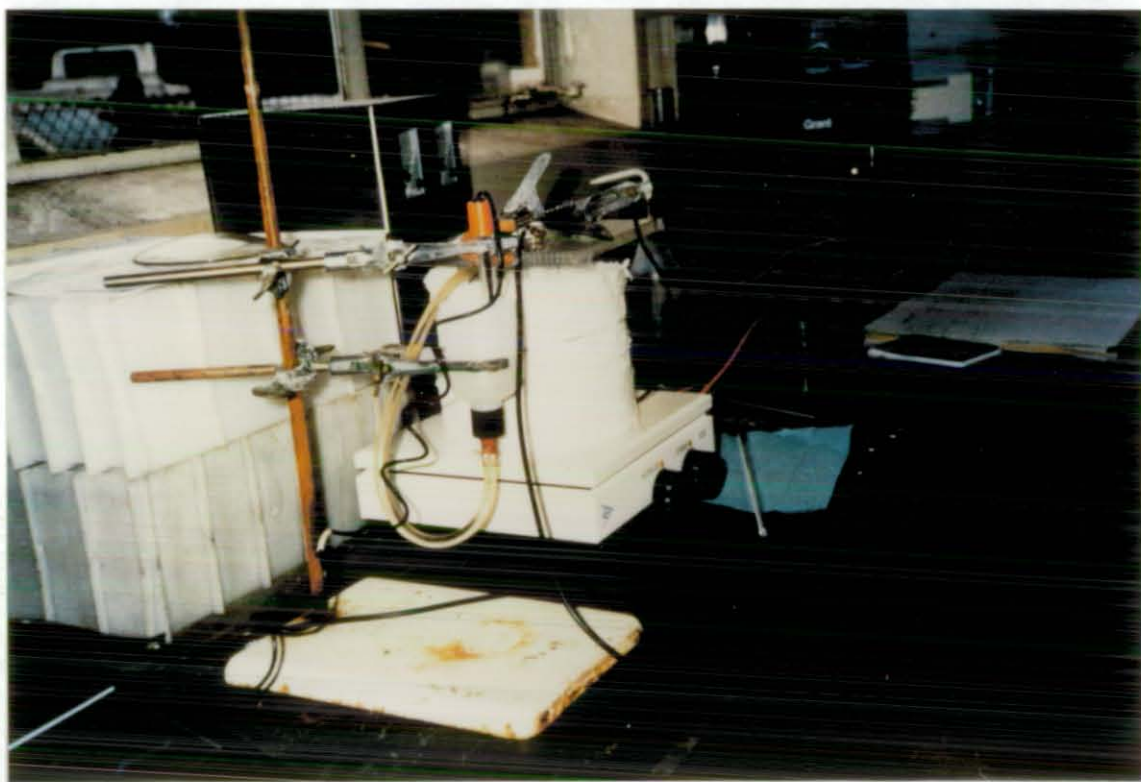


Figure 22

Shows the potential difference of the reference electrode against the working electrode. The polarity indication is therefore opposite to the normal electrochemical convention, as shown by the negative sign before position E_R .

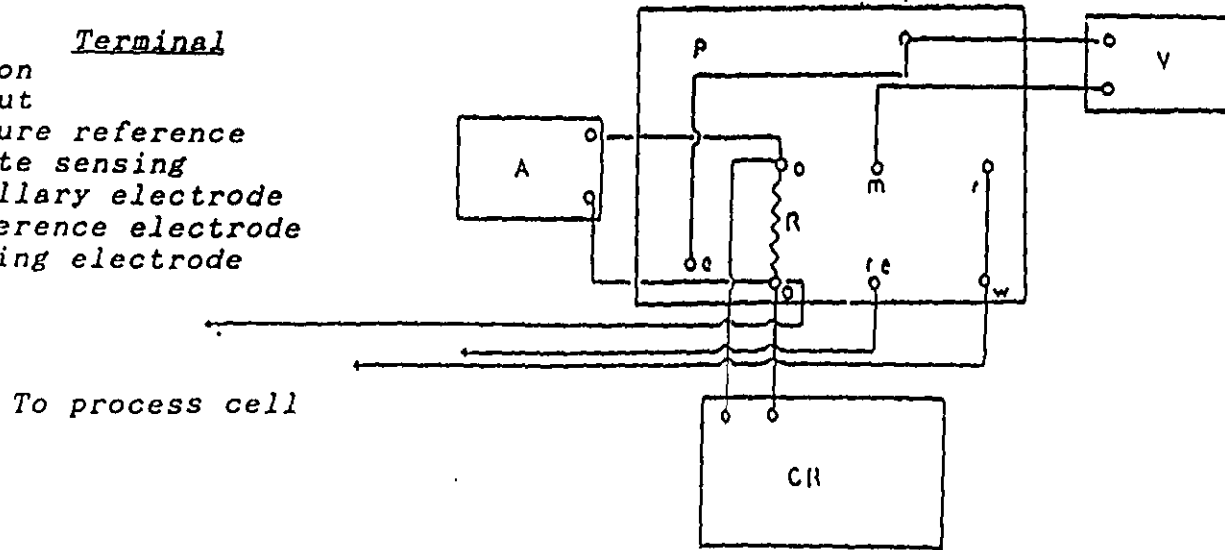
Figure 23

Shows the 2.0 litre beaker with a separate lid which had five openings facilitating the insertion and removal of various electrodes, thermometer and gas bubbler.



Key
 P- Potentiostat
 CR-Chart Recorder
 A- Digital Meter (Ammeter)
 V- Digital Meter (Voltmeter)
 R- 1 Ohm Resistor

Terminal
 c- common
 o- output
 m- measure reference
 r- remote sensing
 a- auxillary electrode
 re- reference electrode
 w- working electrode



Circuit diagram for polarisation apparatus

Figure 24
 Schematic representation of the
 circuit diagram for polarization
 apparatus.

Figure 25

Shows the solid mild steel cylinder surrounded by same shape mesh anode.

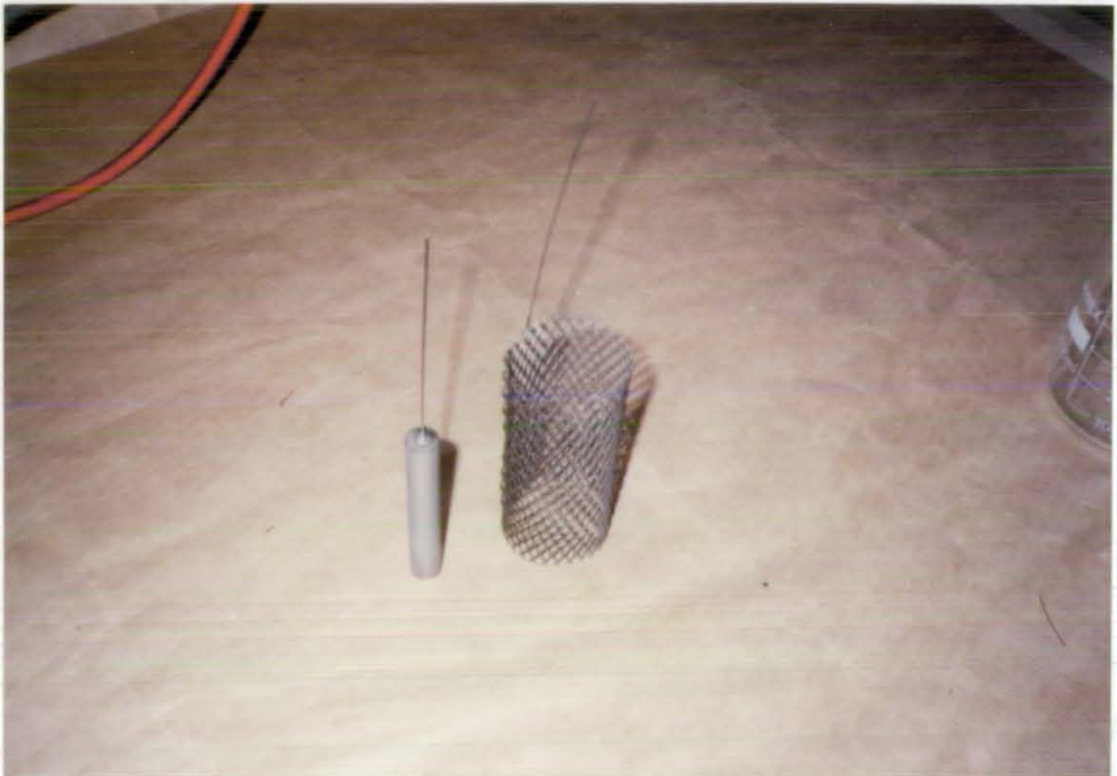
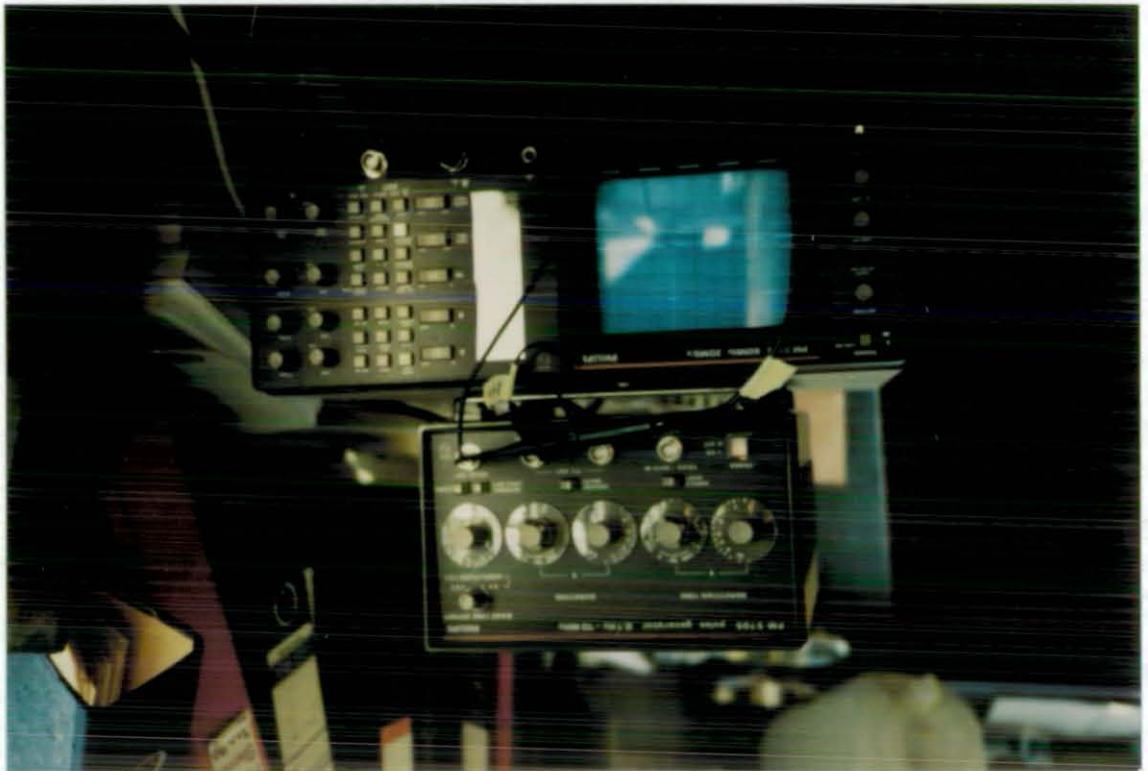


Figure 26

General view of the Pulse plating equipments containing, oscilloscope and pulse generator.



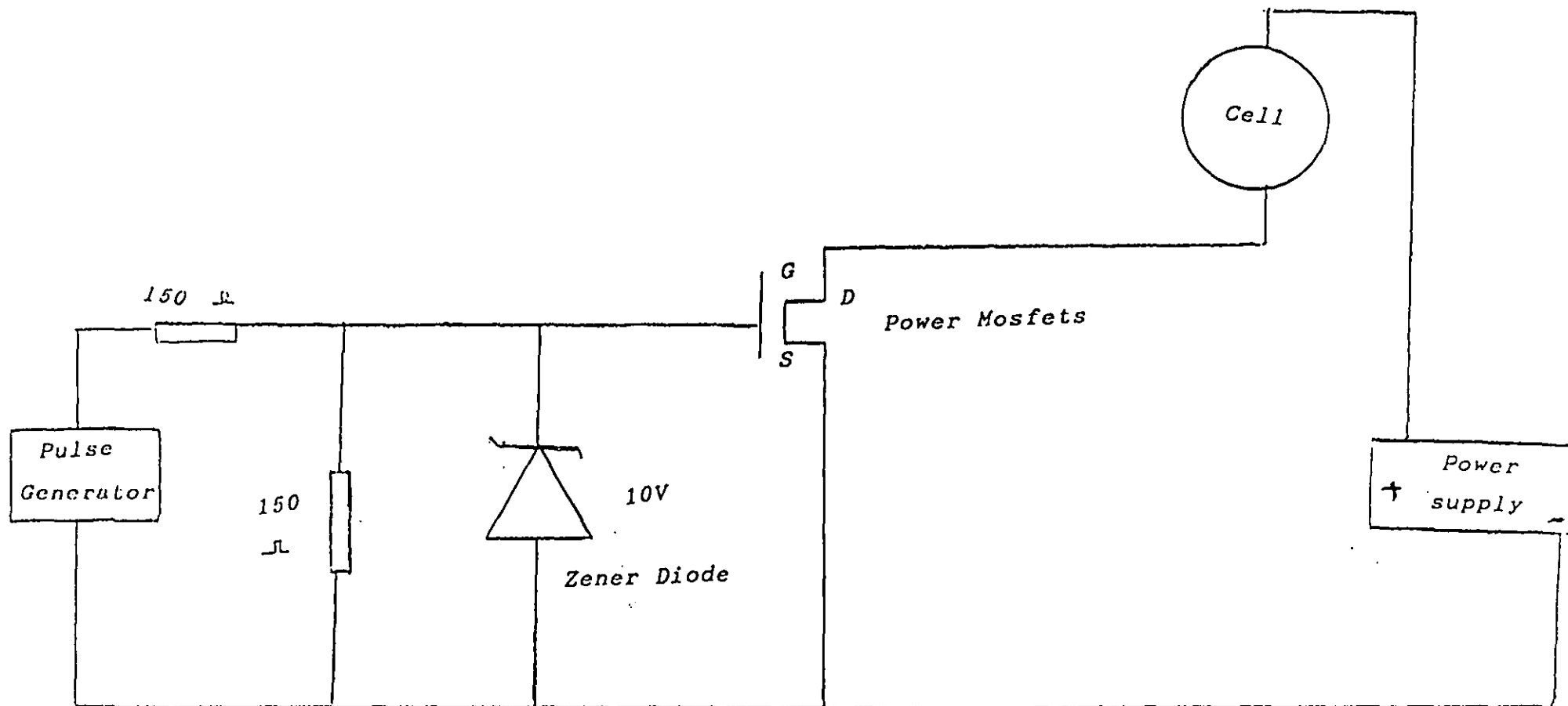


Figure 27 Schematic representation of the pulse plating technique using pulse generator, Zener Diode, power supply, power Mosfet, resistor and finally the cell.

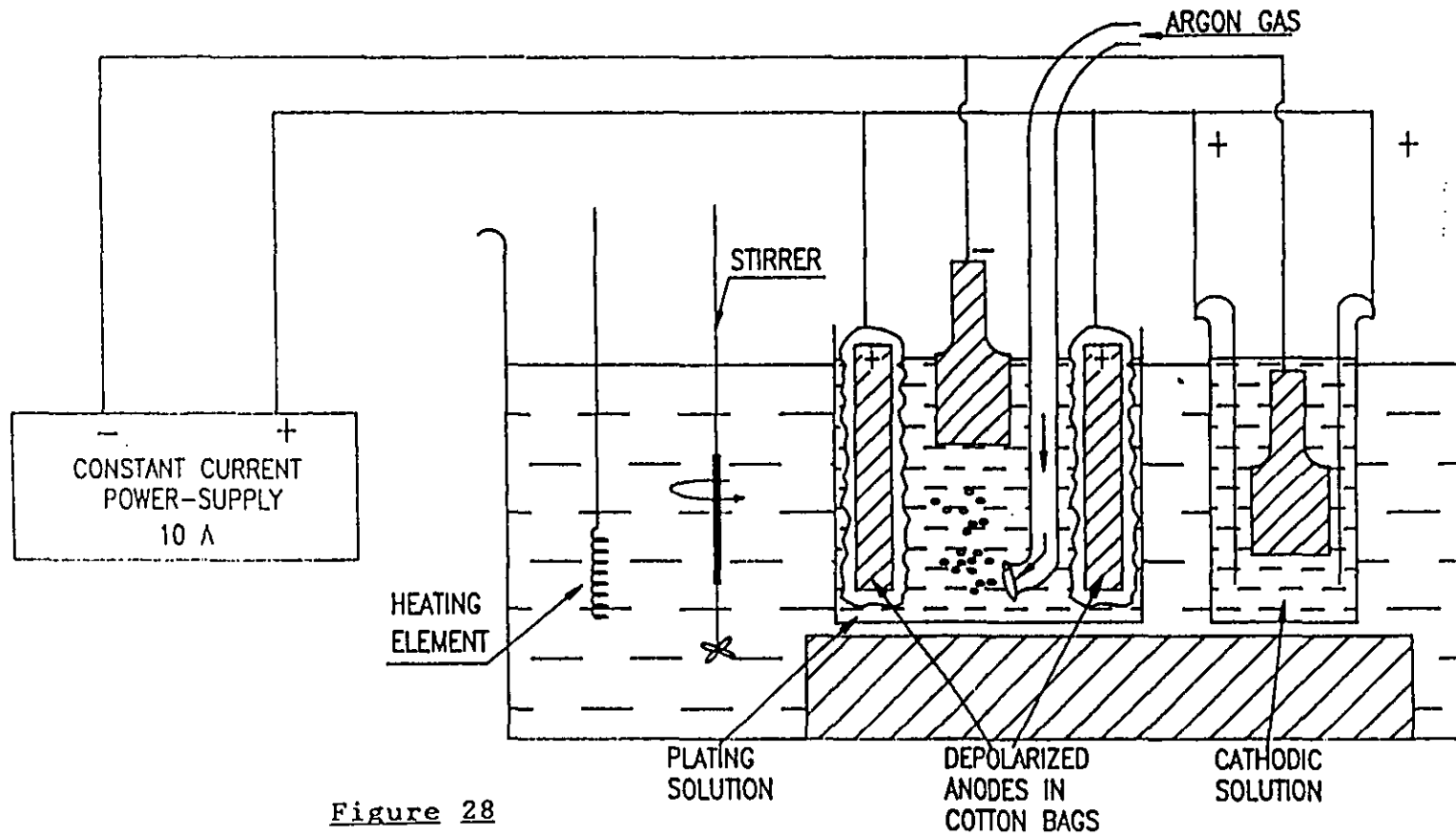


Figure 28

General view of normal plating cell and circuit showing plating bath, cathode cleaning cell, anode and finally heating method.

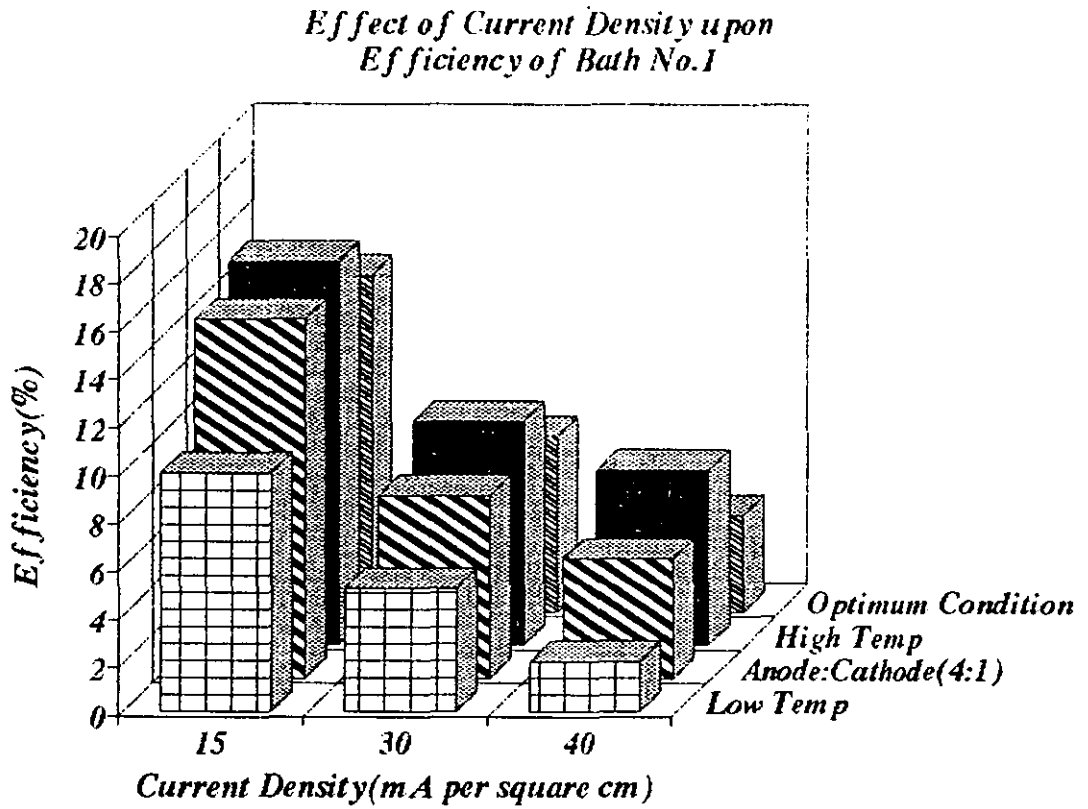


Figure 29

Effects of current density upon bath No.1 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.2*

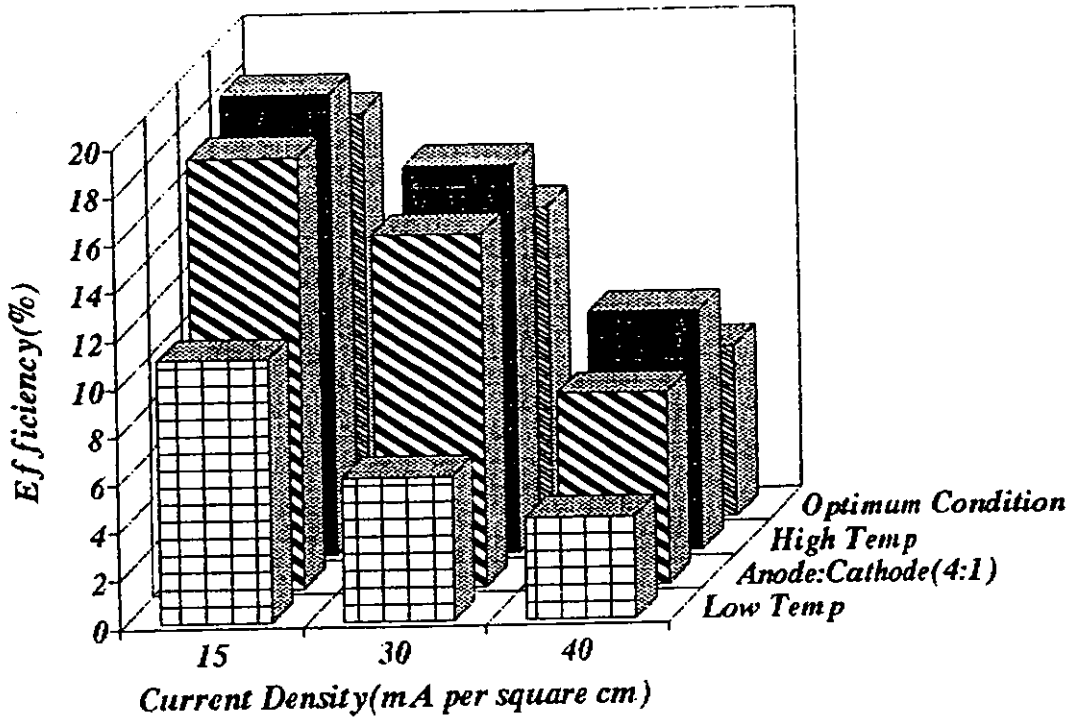


Figure 30

Effects of current density upon bath No.2 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.3*

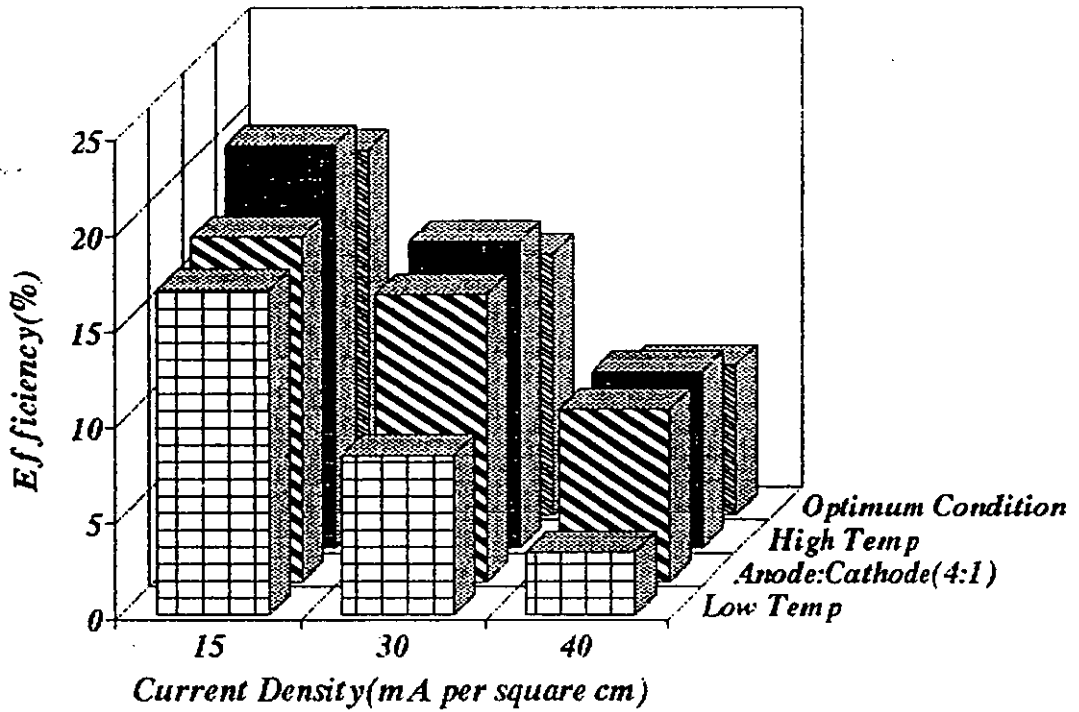


Figure 31

Effects of current density upon bath No.3 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.5*

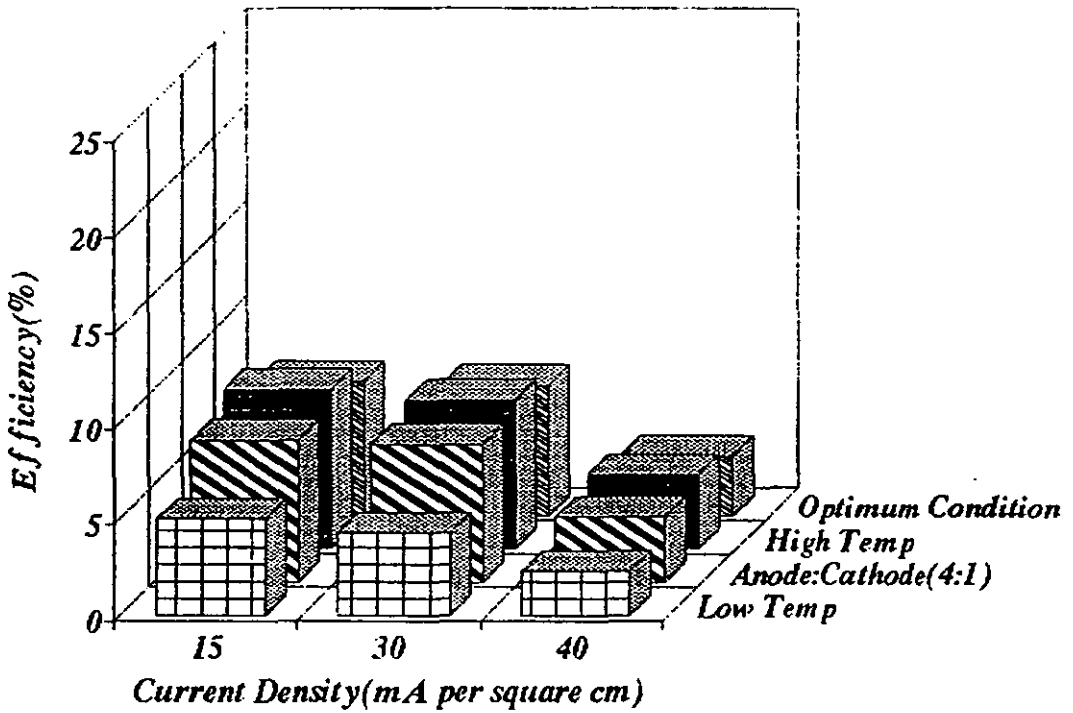


Figure 33

Effects of current density upon bath No.5 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.6*

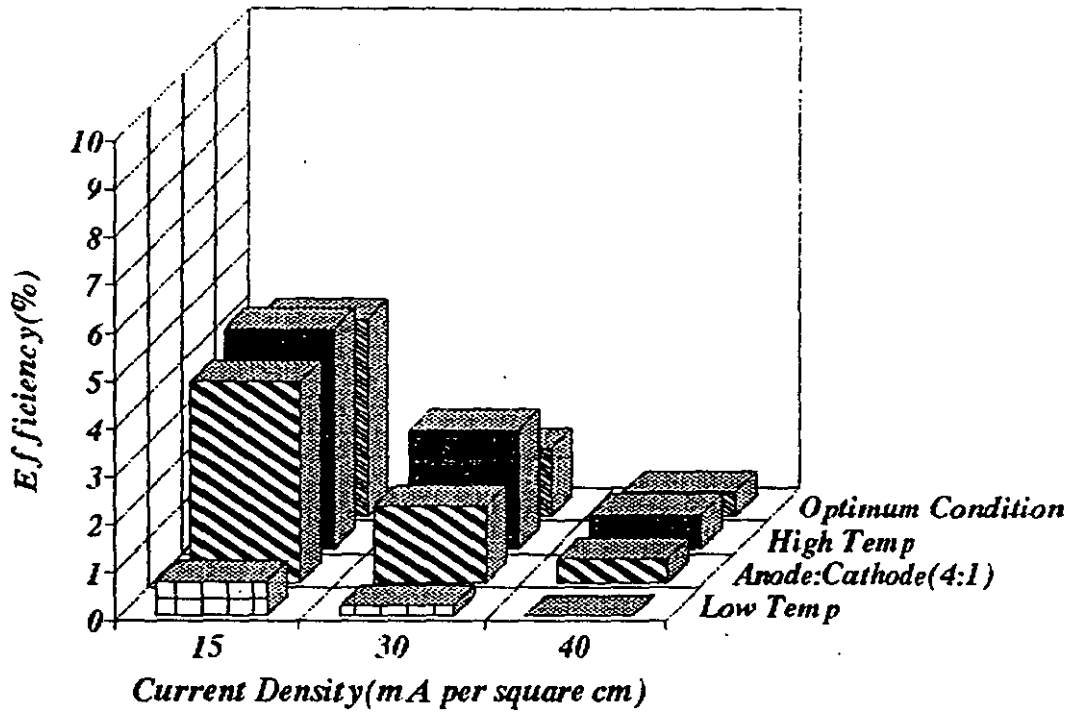


Figure 34

Effects of current density upon bath No.6 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.7*

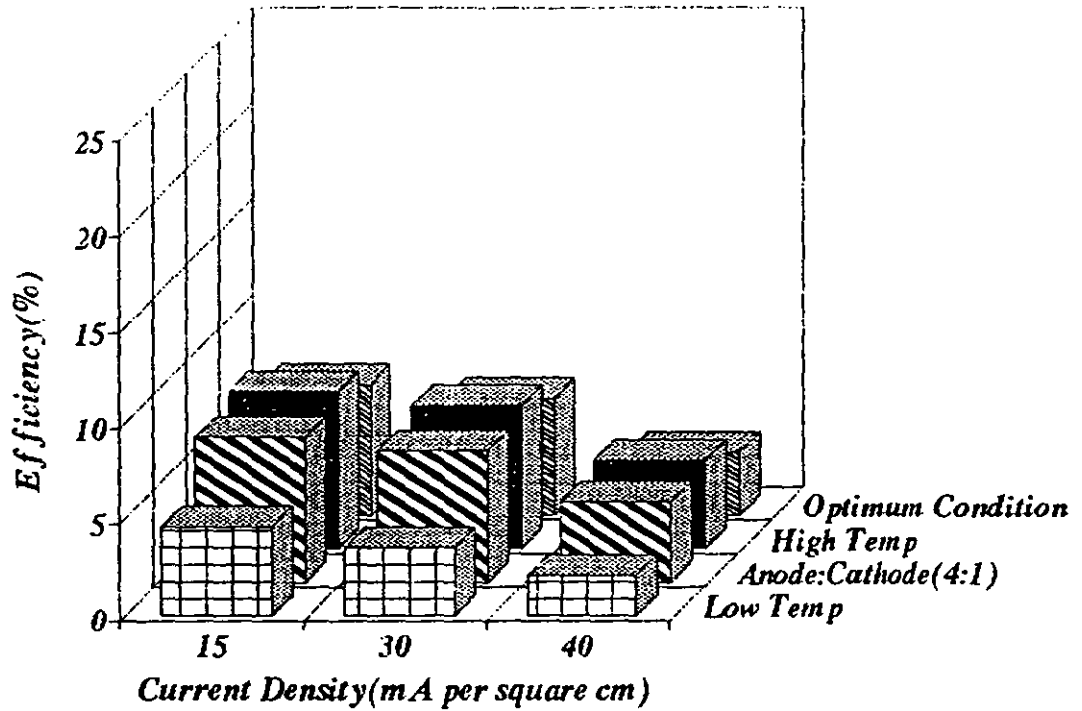


Figure 35

Effects of current density upon bath No.7 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.8*

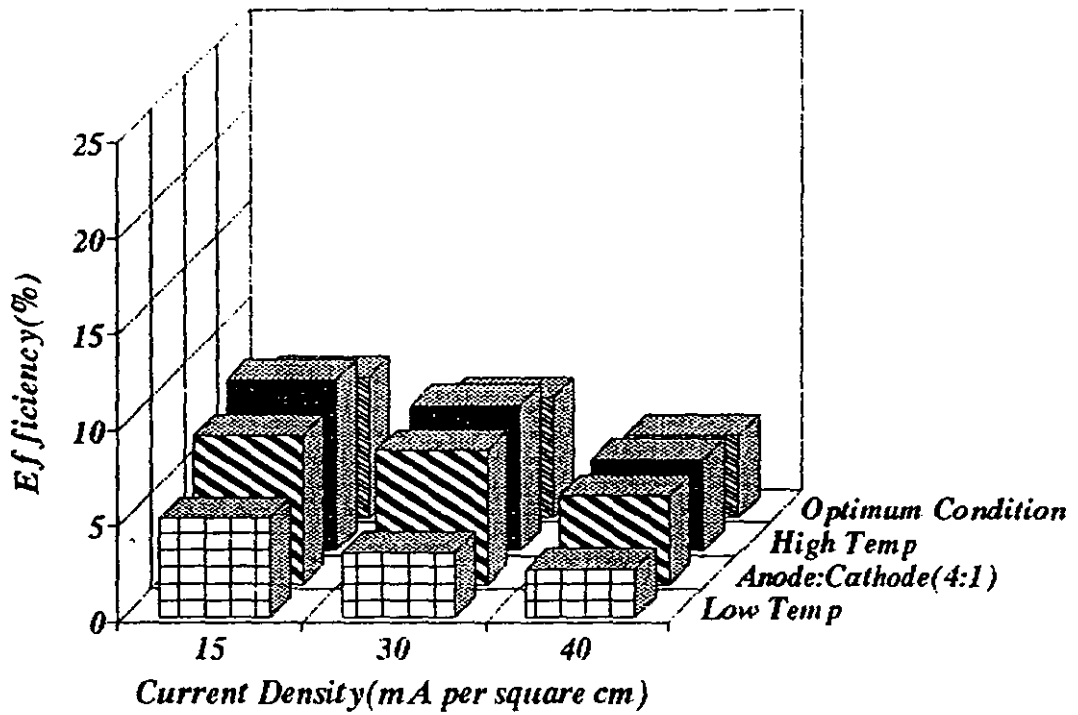


Figure 36

Effects of current density upon bath No.8 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.9*

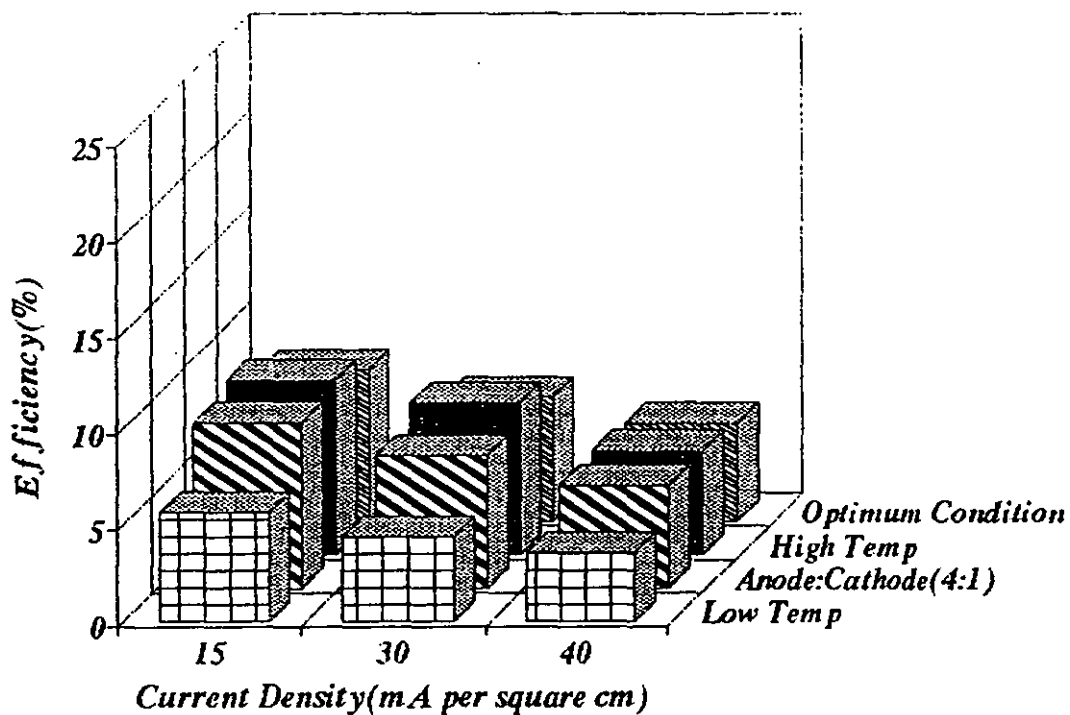


Figure 37

Effects of current density upon bath No.9 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.10*

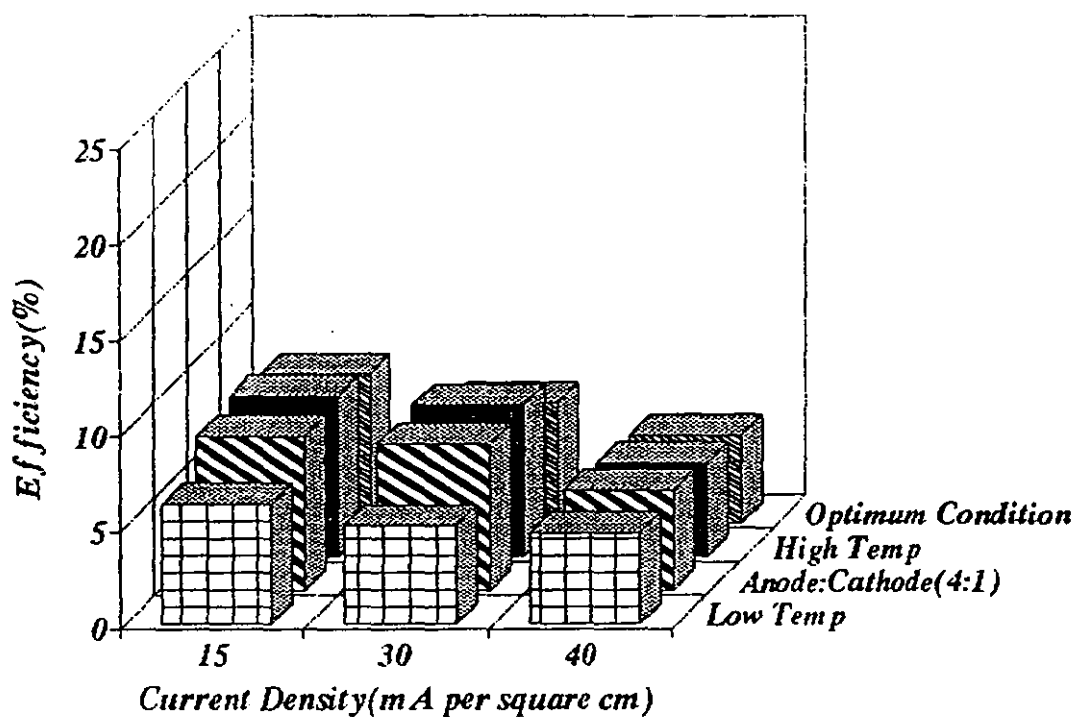


Figure 38

Effects of current density upon bath No.10 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.11*

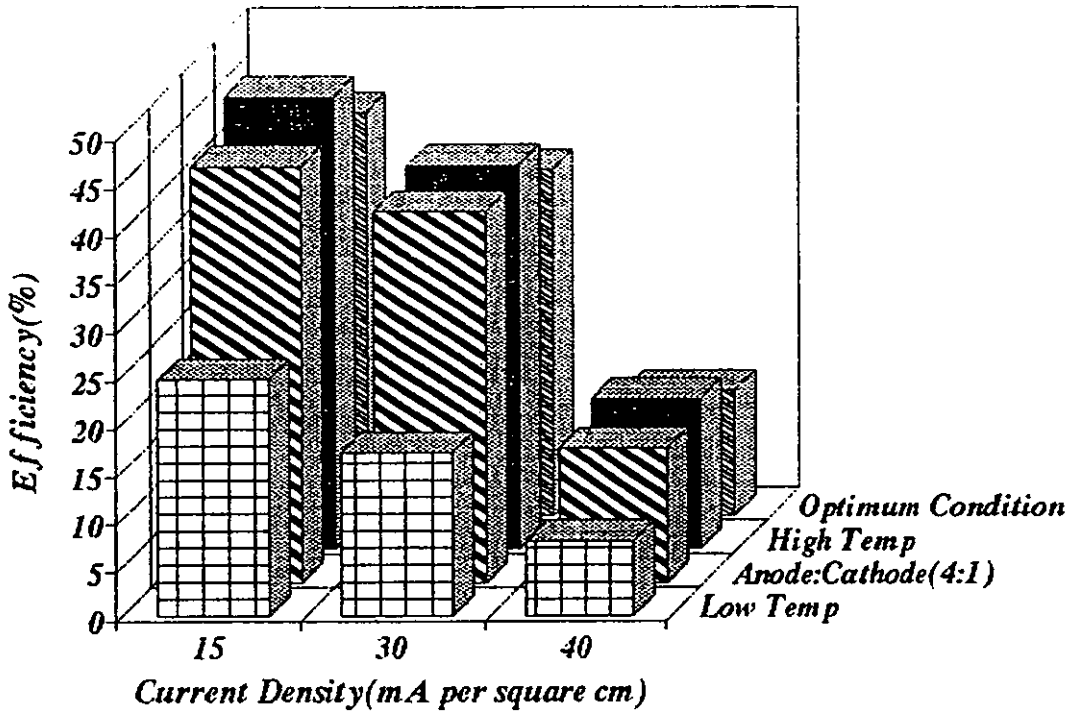


Figure 39

Effects of current density upon bath No.11 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.12*

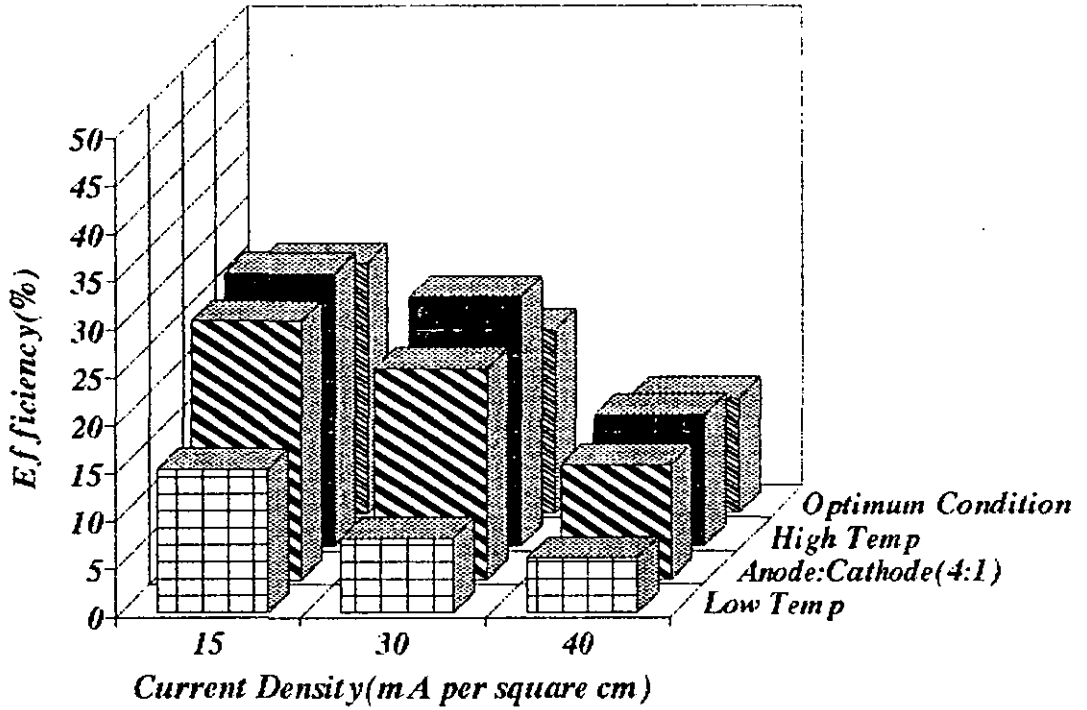


Figure 40

Effects of current density upon bath No.12 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.13*

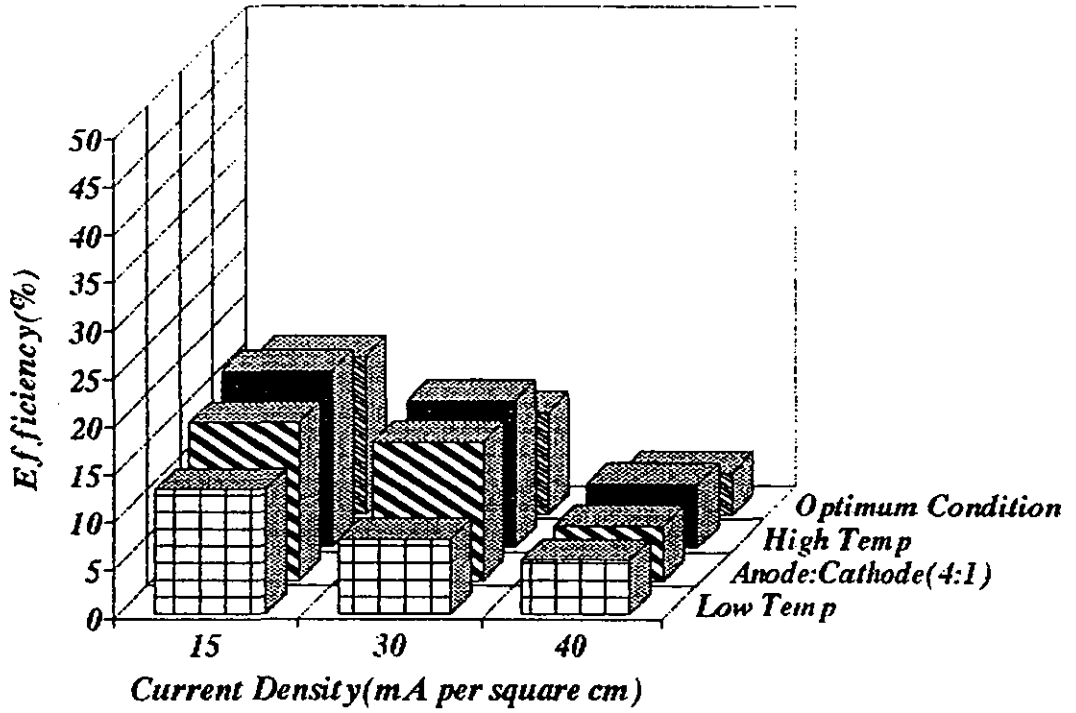


Figure 41

Effects of current density upon bath No.13 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.14*

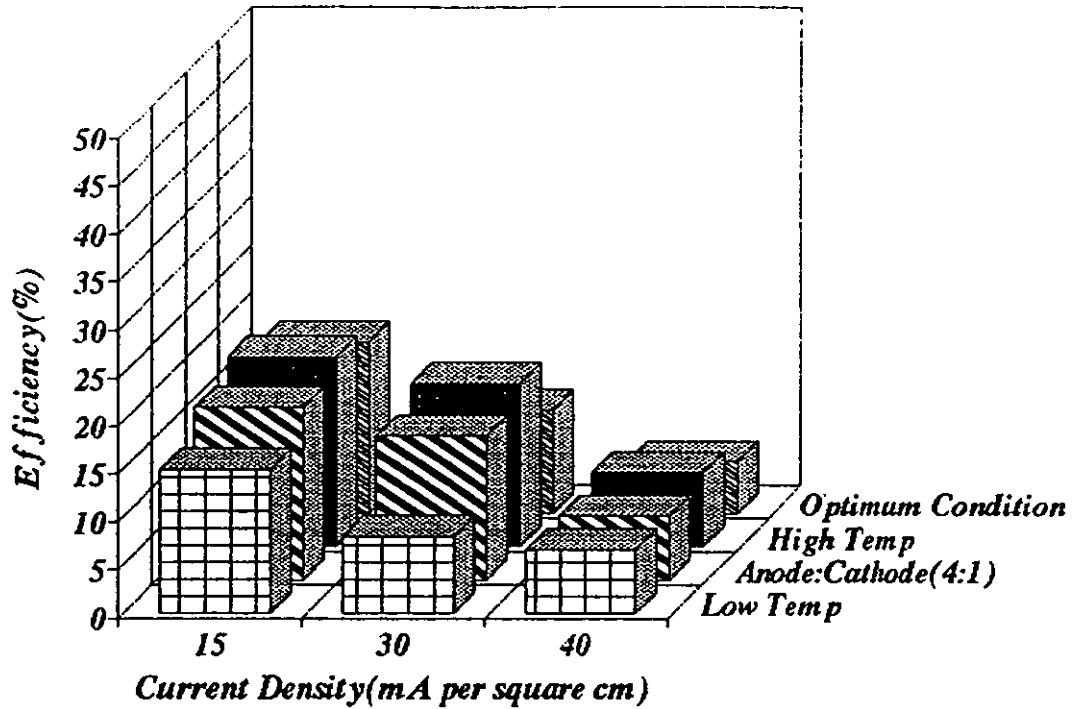


Figure 42

Effects of current density upon bath No.14 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.15*

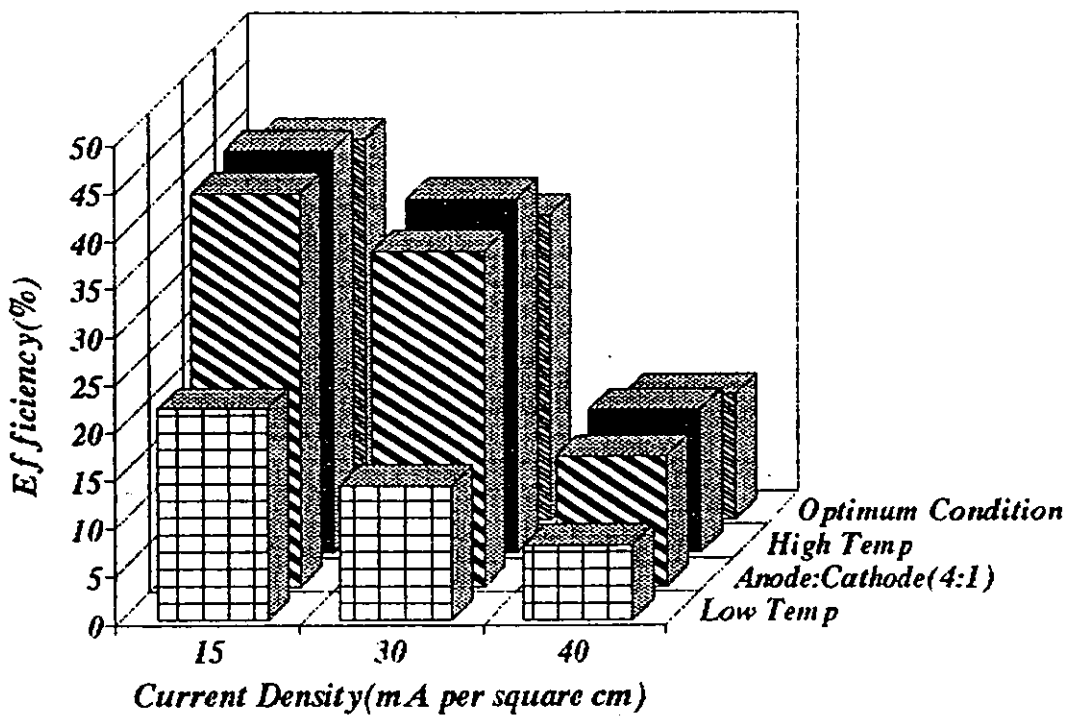


Figure 43

Effects of current density upon bath No.15 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.16*

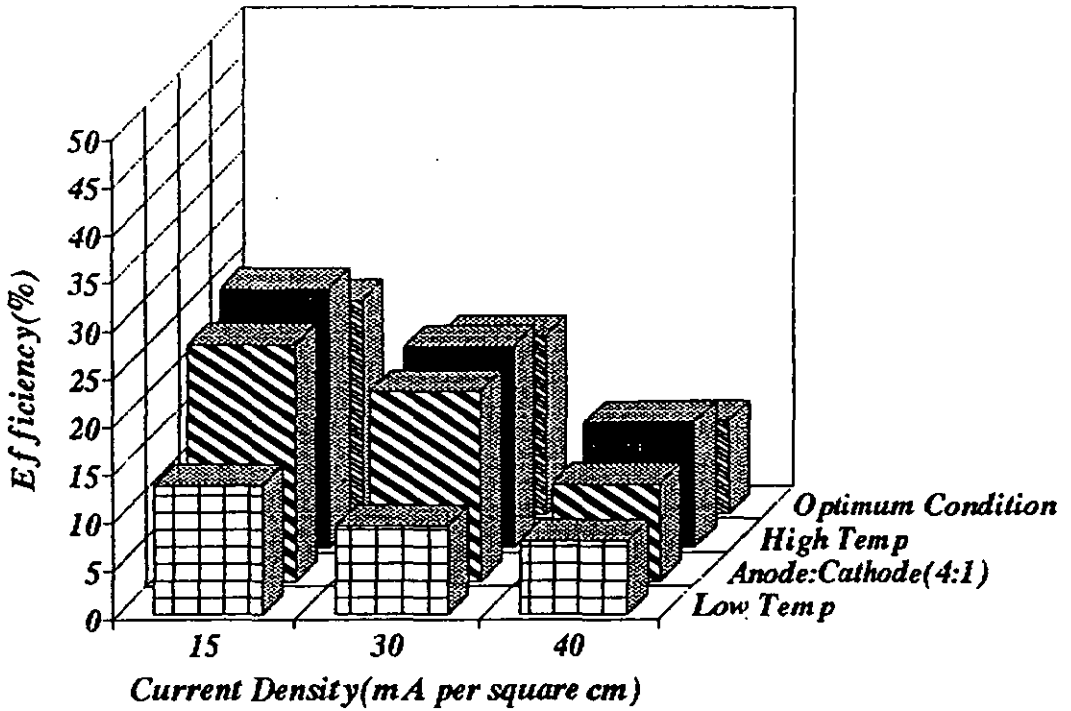


Figure 44

Effects of current density upon bath No.16 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.17*

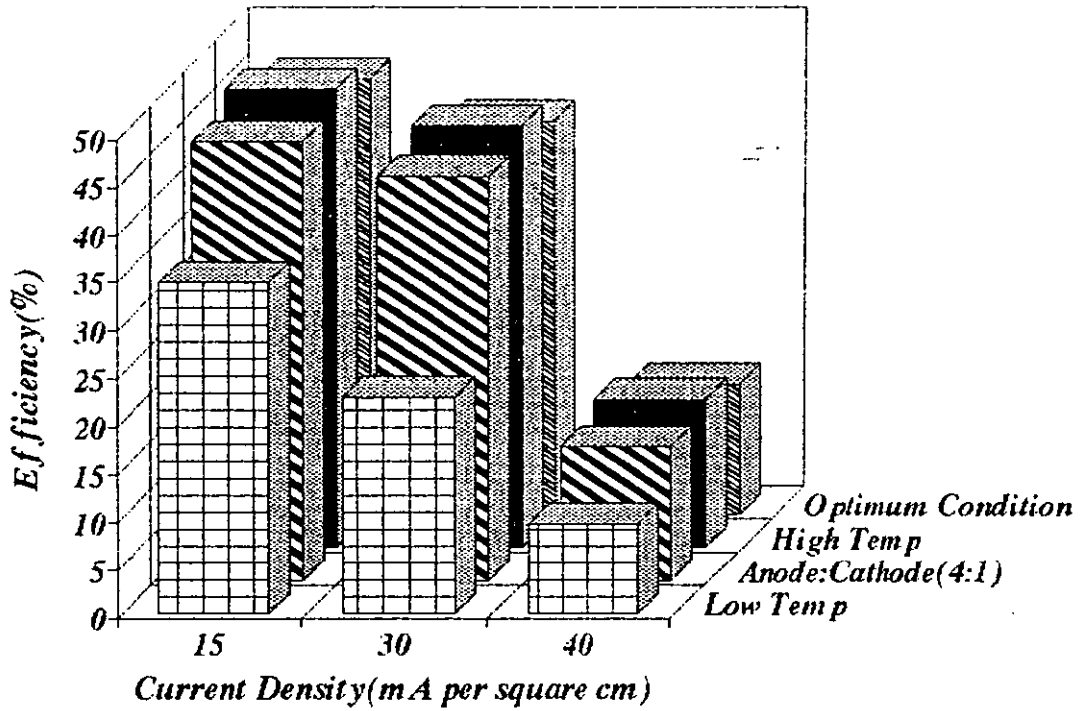


Figure 45

Effects of current density upon bath No.17 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.18*

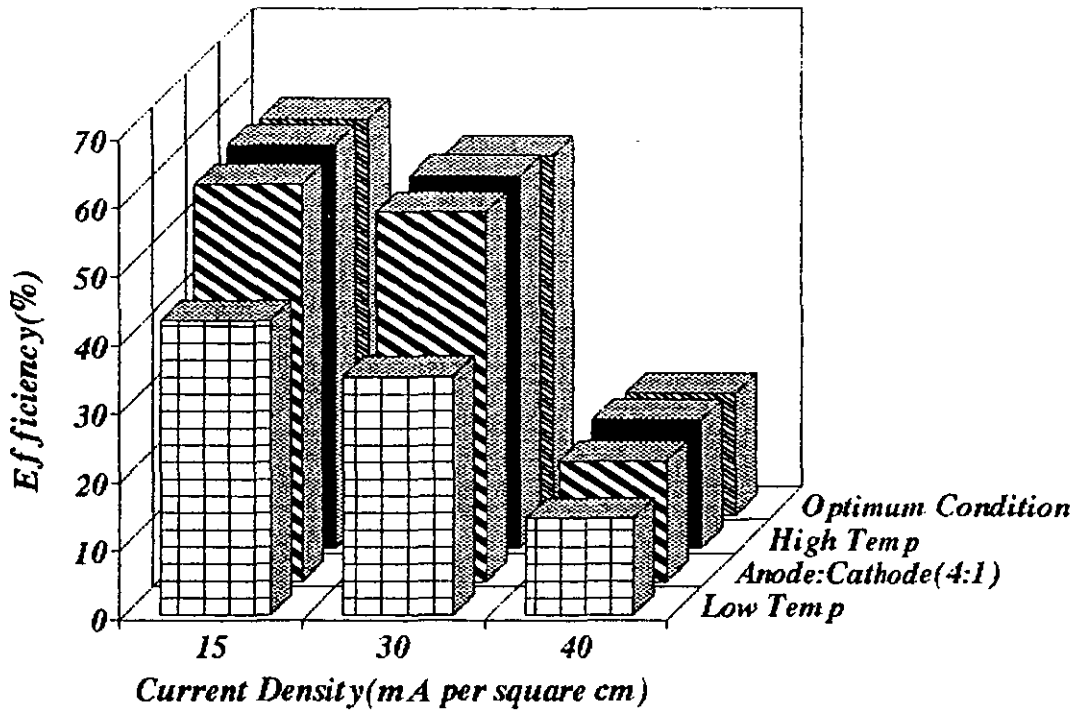


Figure 46

Effects of current density upon bath No.18 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

*Effect of Current Density upon
Efficiency of Bath No.19*

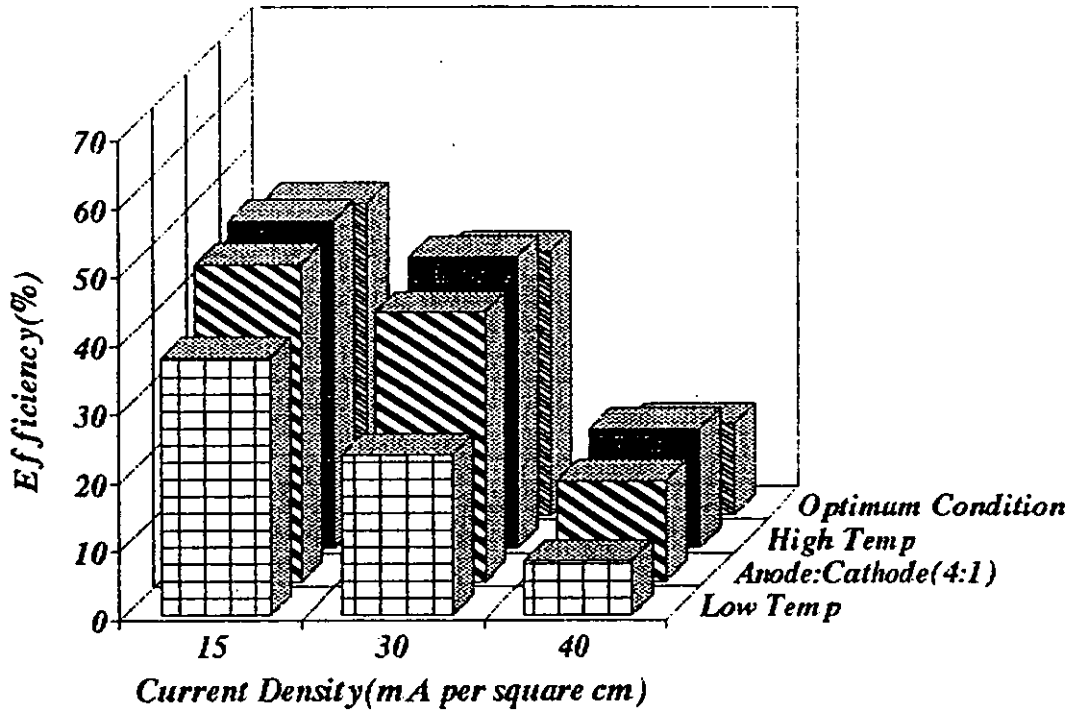


Figure 47

Effects of current density upon bath No.19 cell efficiency, optimum condition of plating, low and high temperatures and finally ratio of anode to cathode.

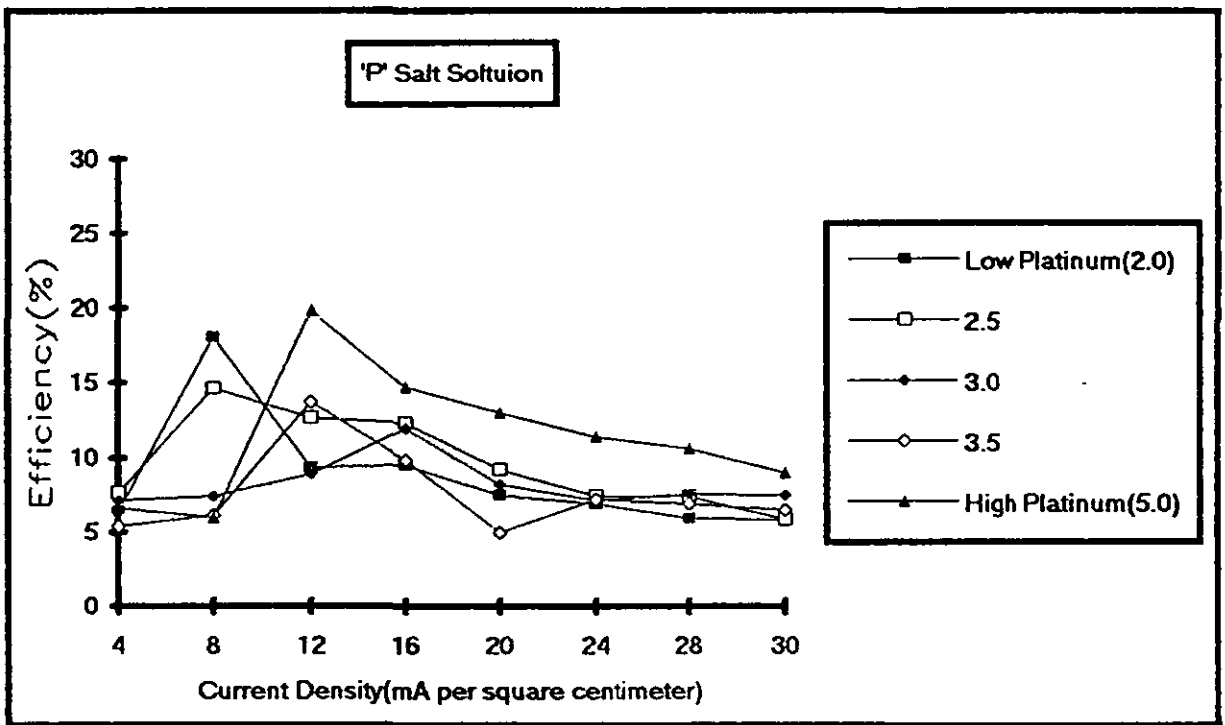


Figure 48

Effects of current density and platinum content upon cell efficiency using 'P' Salt solution.

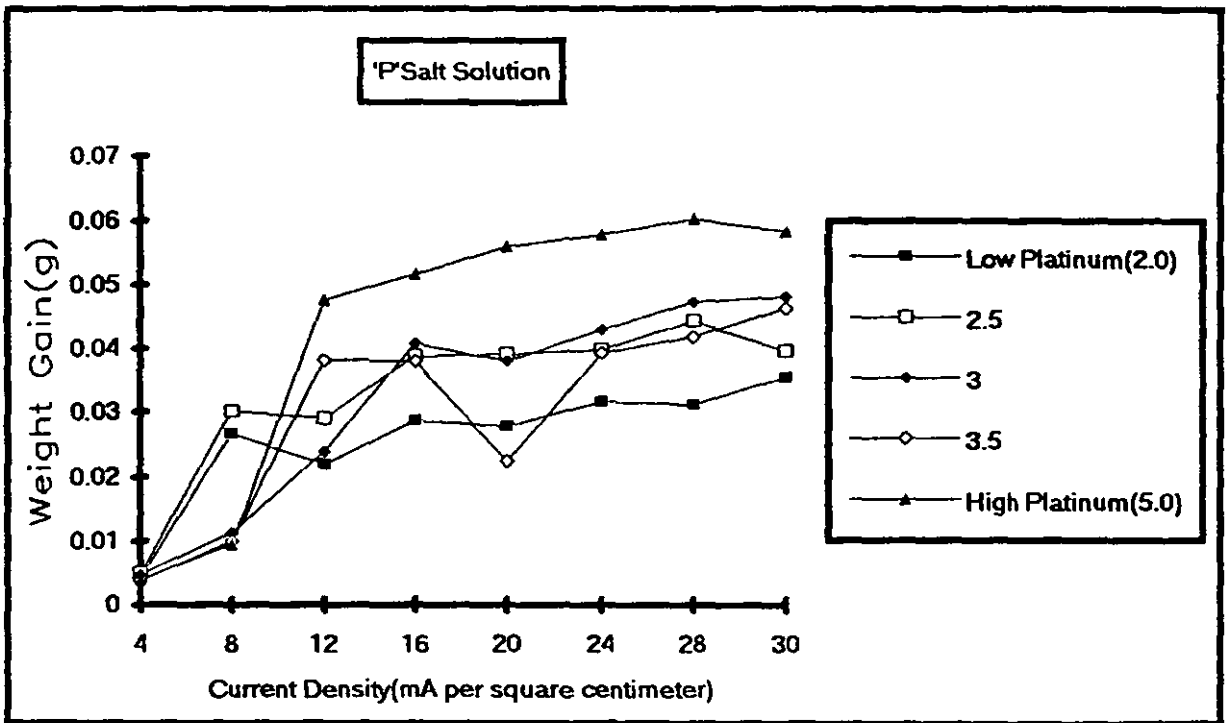


Figure 49

Effects of current density and platinum content upon cell weight gain using 'P' Salt solution.

Effect of various current densities on 'Q'salt(J.M) to produce Electroless Pt

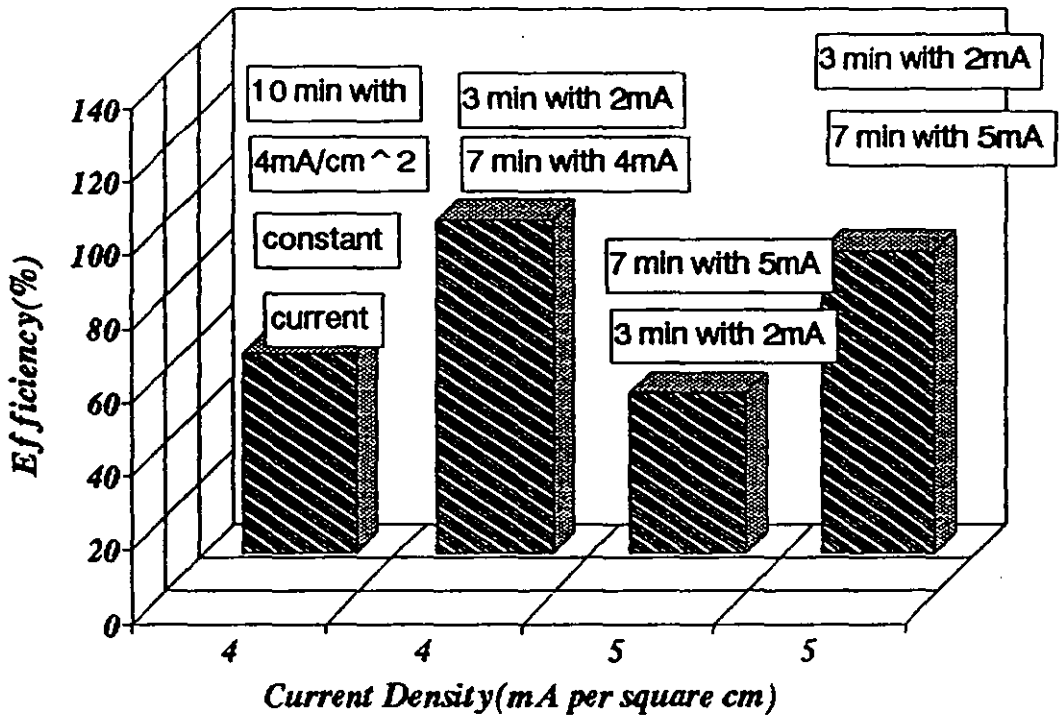


Figure 50

Effect of various current densities upon cell efficiency using 'Q' Salt(J.M) to produce electroless platinum.

Effect of various current densities on 'Q'salt(J.M) to produce Electroless Pt

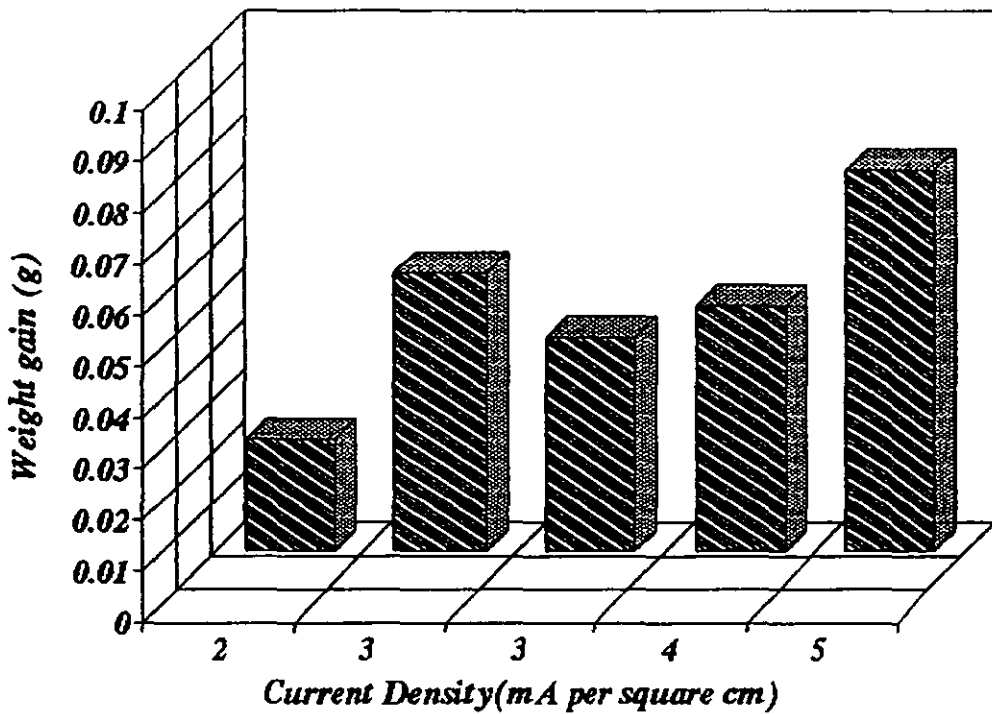


Figure 51

Effect of various current densities upon weight gain using 'Q' Salt(J.M) to produce electroless platinum.

Effect of various current densities on 'Q'salt(J.M) to produce Electroless Pt

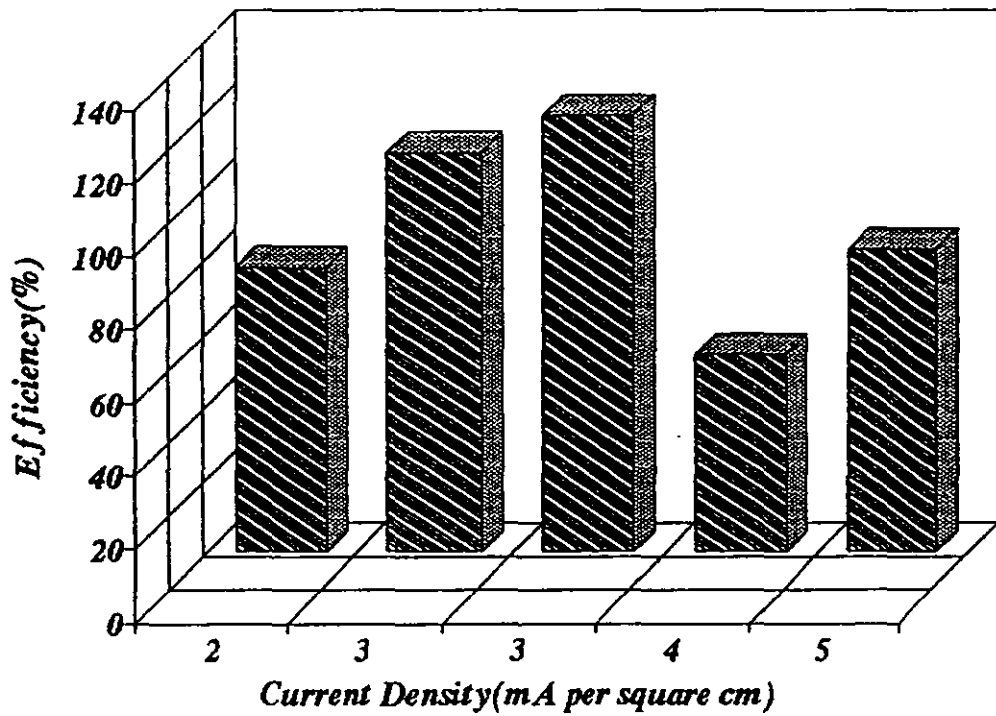


Figure 52

Effect of various current densities upon cell efficiency using 'Q' Salt(J.M) to produce electroless platinum.

Effect of various current densities on 'Q'salt(J.M) to produce Electroless Pt

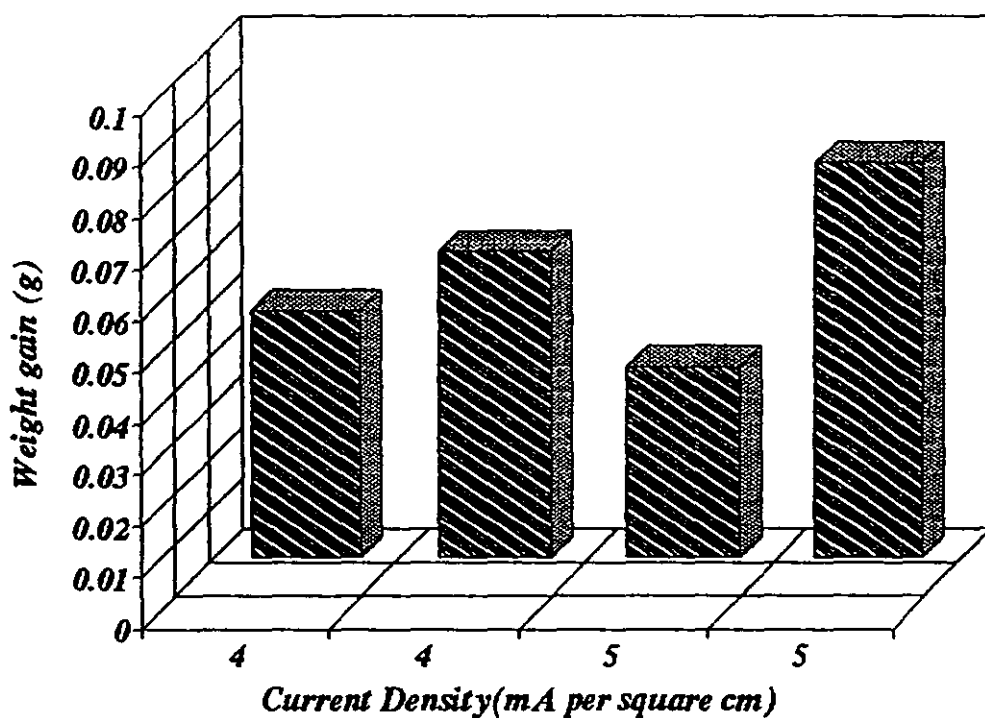


Figure 53

Effect of various current densities upon weight gain using 'Q' Salt(J.M) to produce electroless platinum.

*Effect of various current densities on
'Q'salt(J.M)*

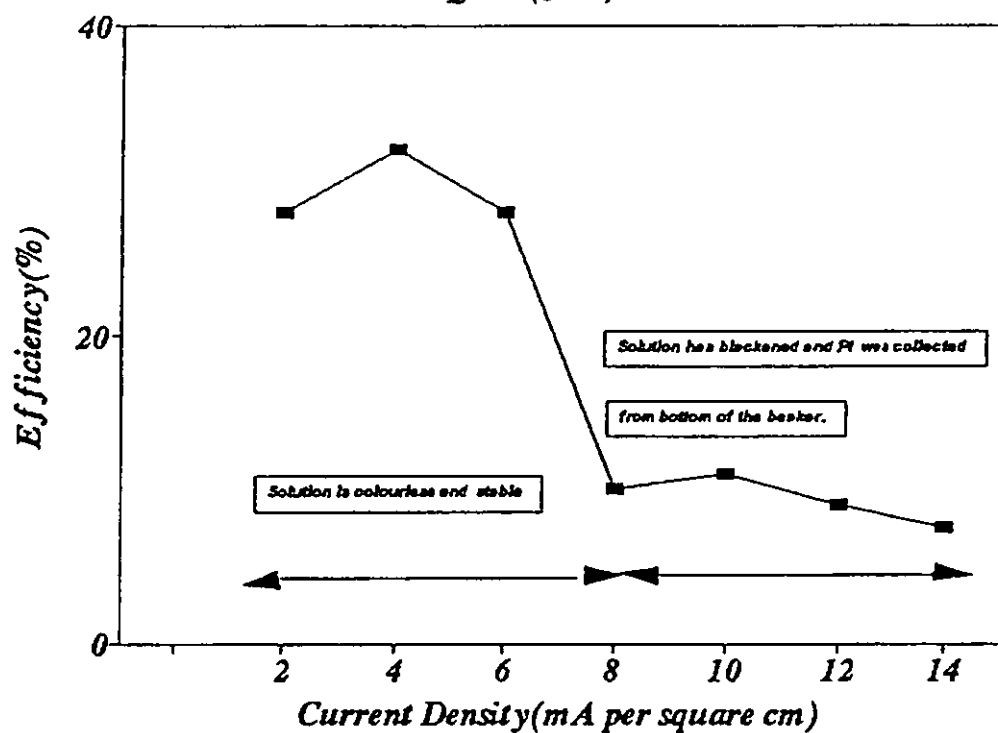


Figure 54

Effect of various current densities upon cell efficiency to investigate the stability of 'Q' Salt solution.

*Effect of various current densities on
'Q'salt(J.M)*

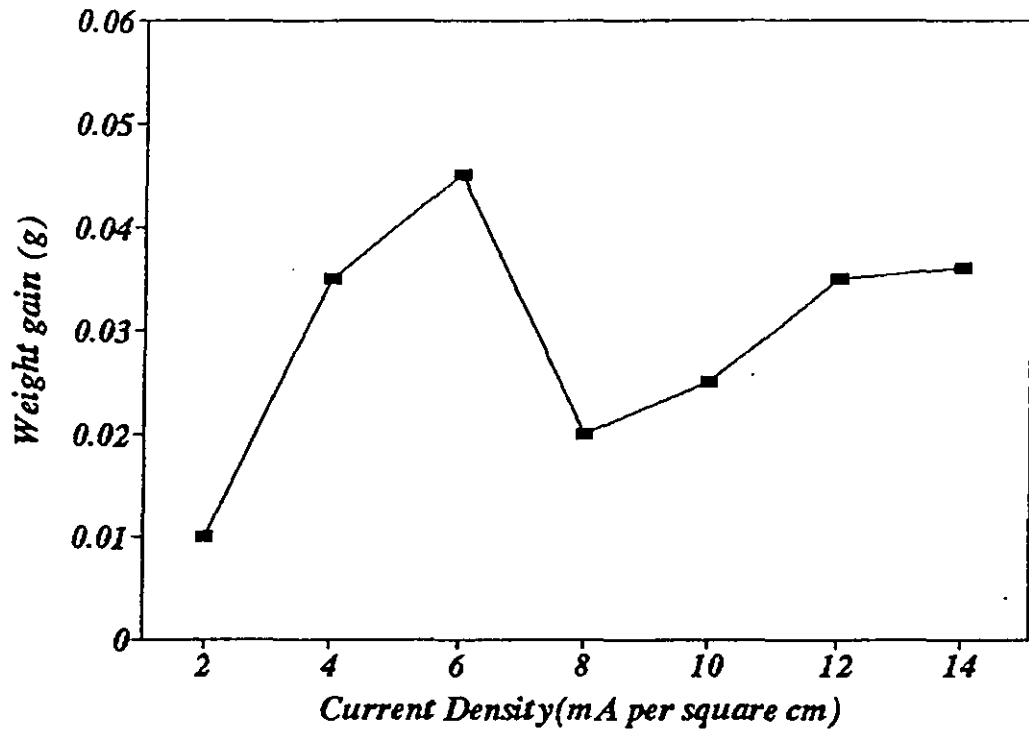


Figure 55

Effect of various current densities upon weight gain to investigate the stability of 'Q' Salt solution.

EFFECTS OF VARIOUS C.d ON 'P'SALT

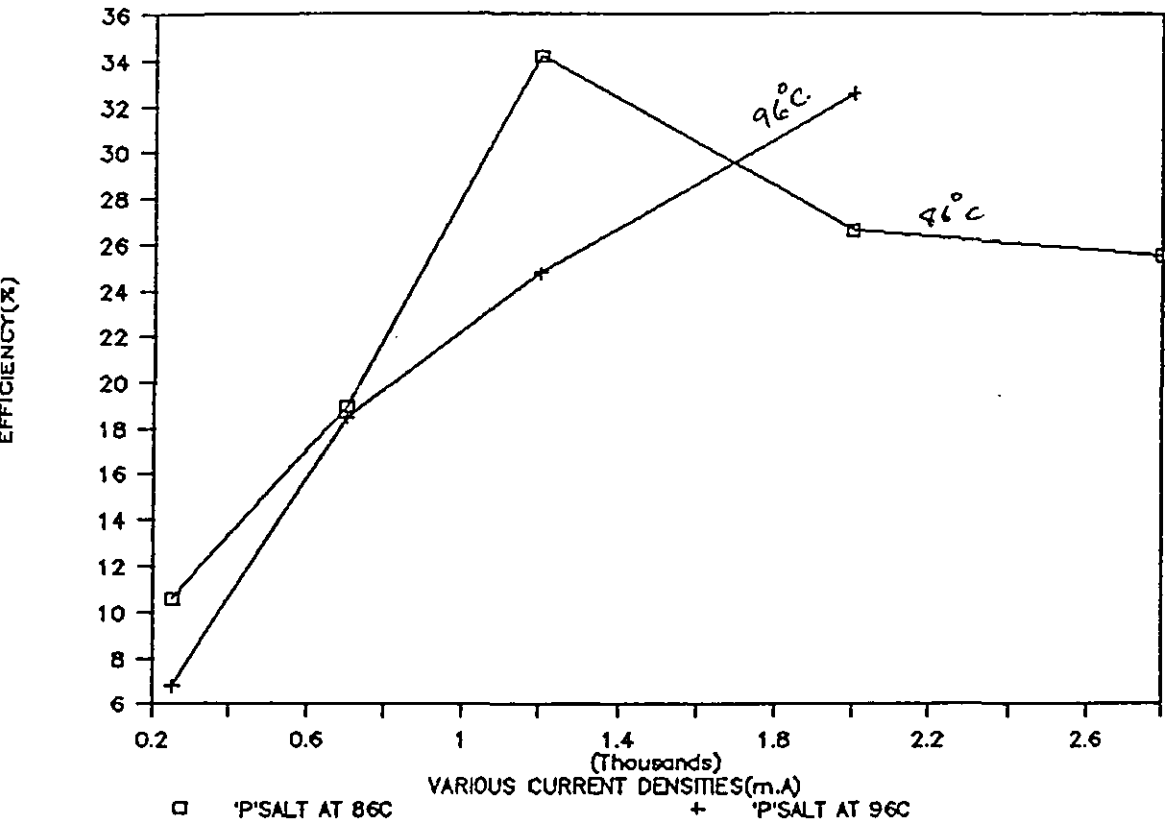


Figure 56

Effect of various current densities upon cell efficiency to compare the high temperature with low temperature using 'P' Salt solution.

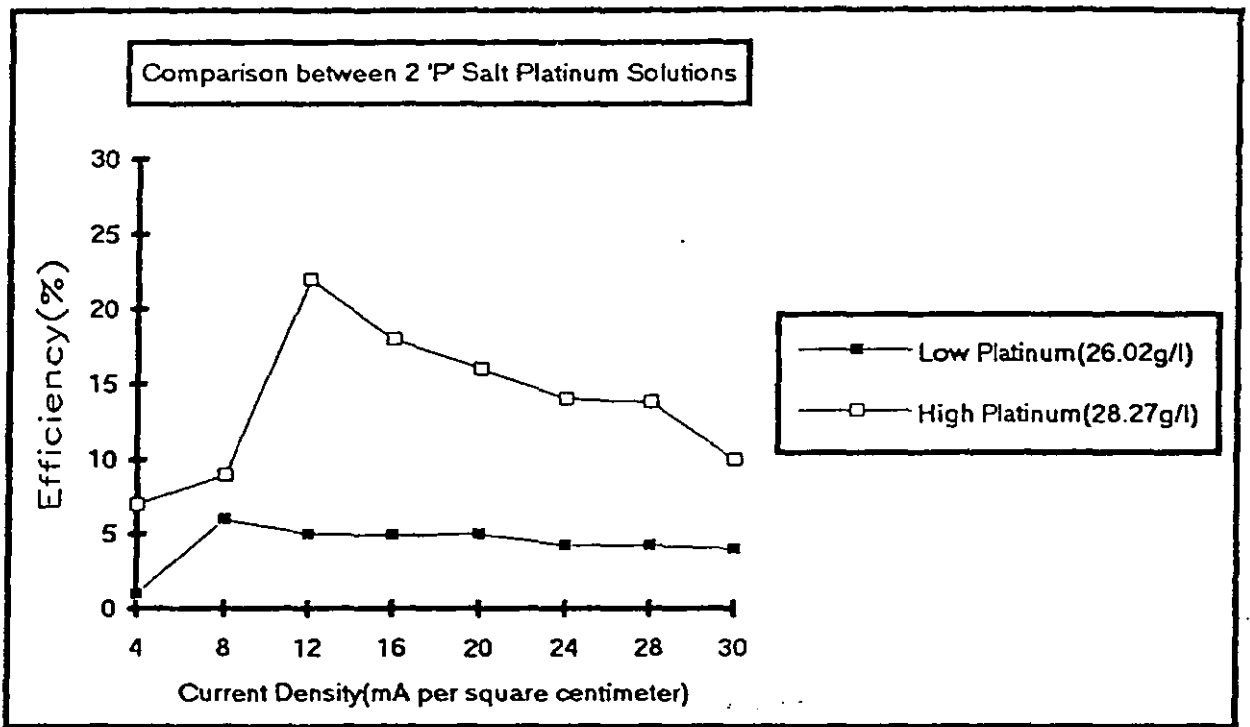


Figure 57

Effect of various current densities upon cell efficiency to compare the concentration of 2 'P' Salt solutions.

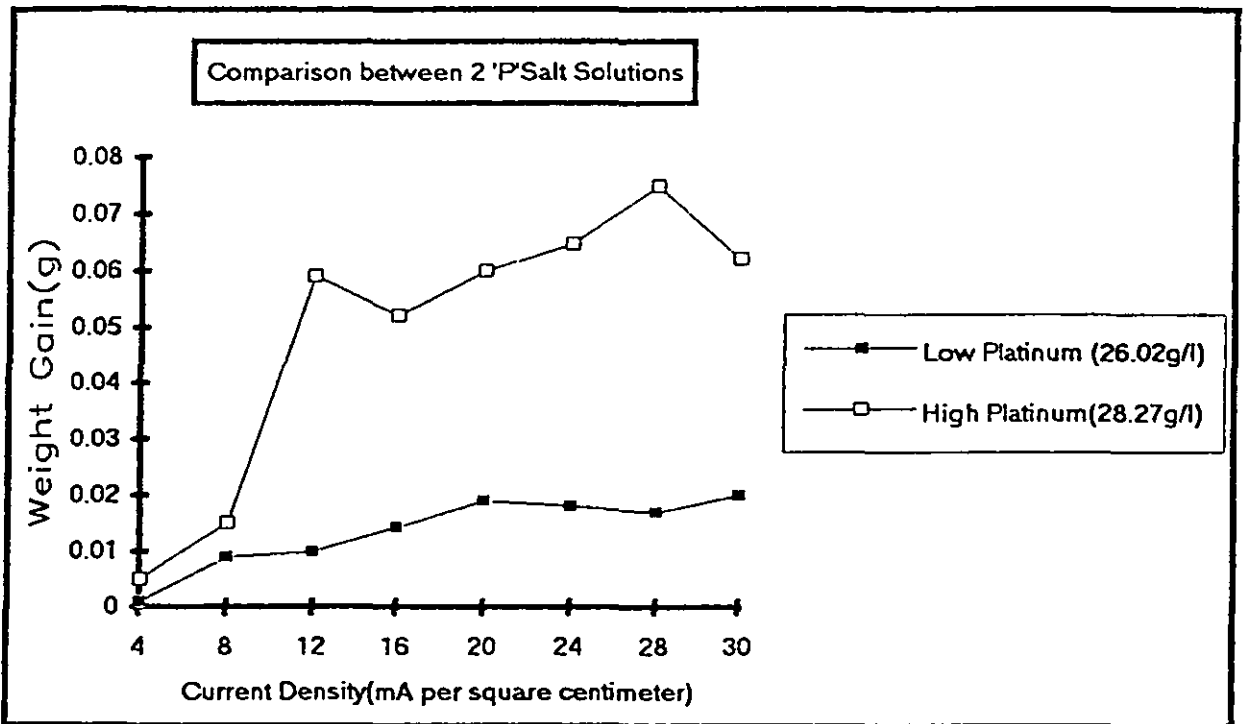


Figure 58

Effect of various current densities upon weight gain to compare the concentration of 2 'P' Salt solutions.

Amount of Disodium Hypophosphite and Phosphites upon 'P'Salt and Tank No.D

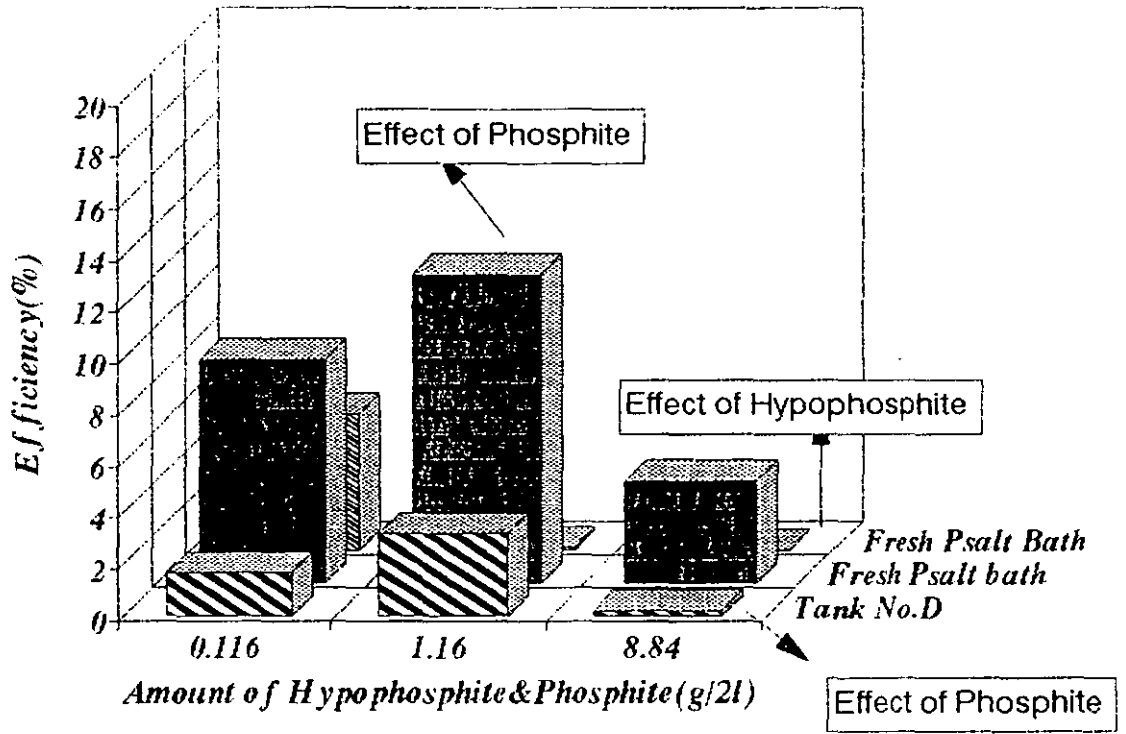


Figure 59

Effects of Disodium Hypophosphite and phosphites upon cell efficiency using 'P' Salt and Tank No.D.

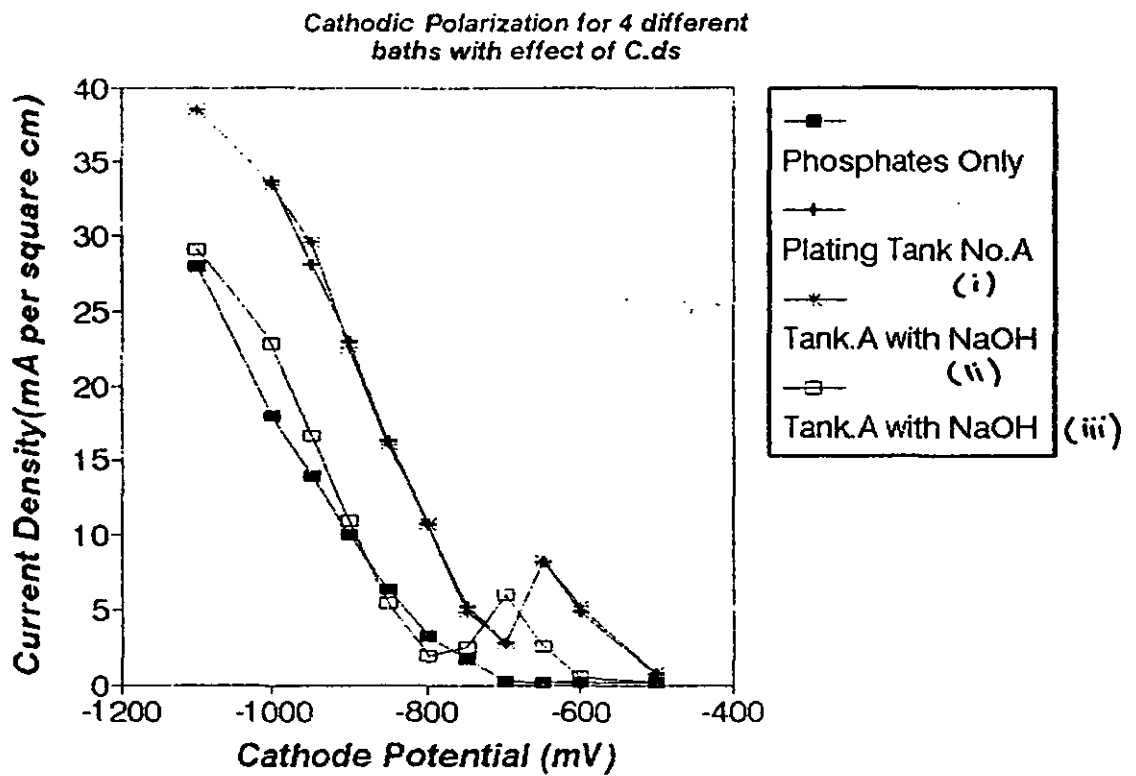


Figure 60

Cathodic polarization for four different solutions with effects of various current densities.

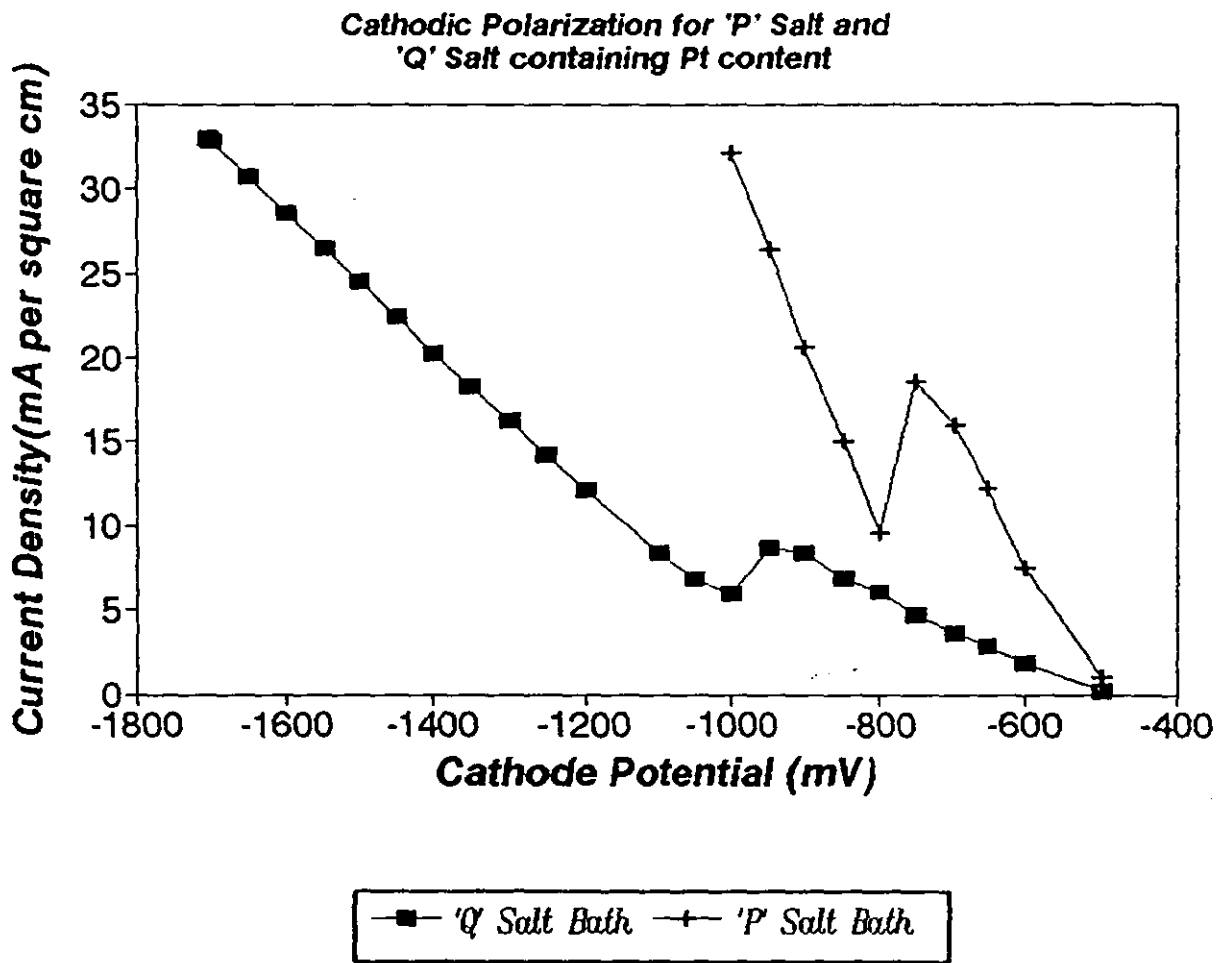


Figure 61

Cathodic polarization for 'P' and 'Q' salts solutions with effects of various current densities.

Comparison between different ratio of Phosphates in Pt Plating Baths

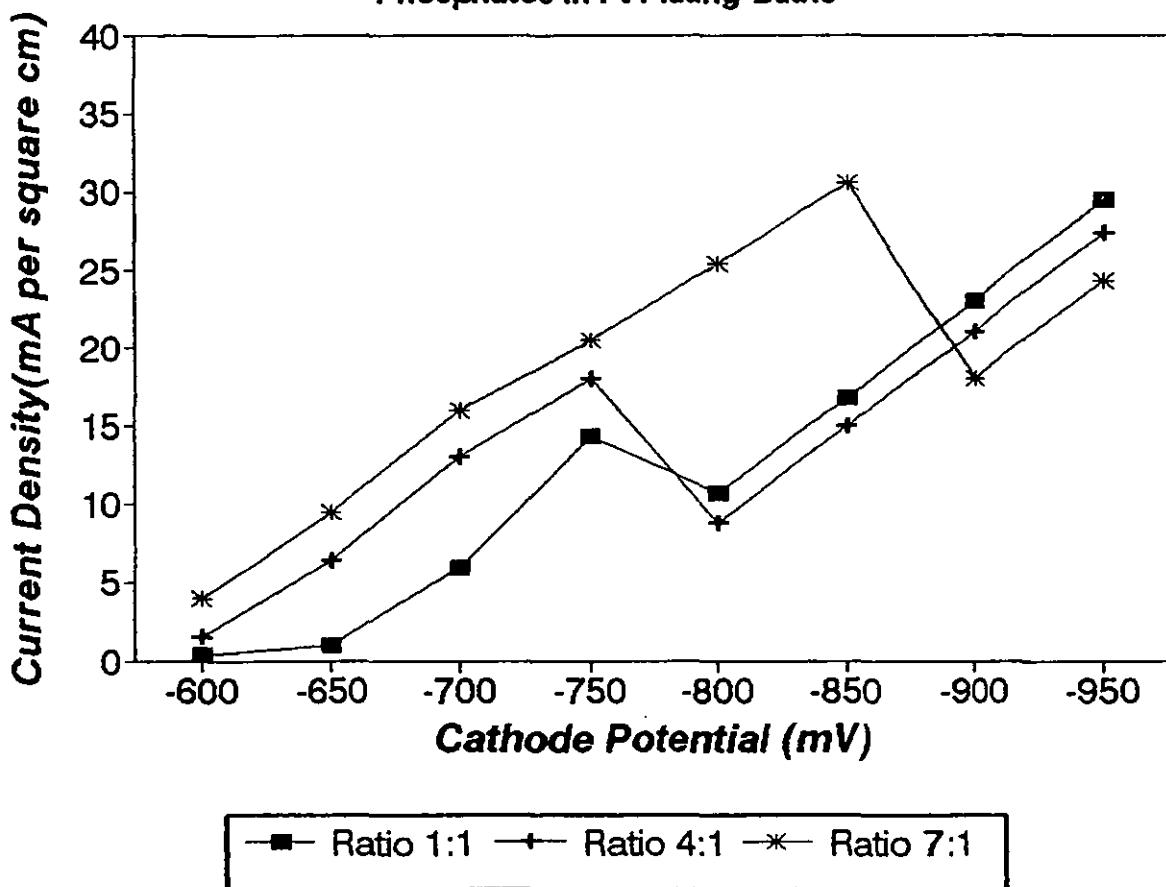


Figure 62

Cathodic polarization for different ratios of platinum solutions with effects of various current densities.

Comparison between different ratio of Phosphates in Pt Plating Baths

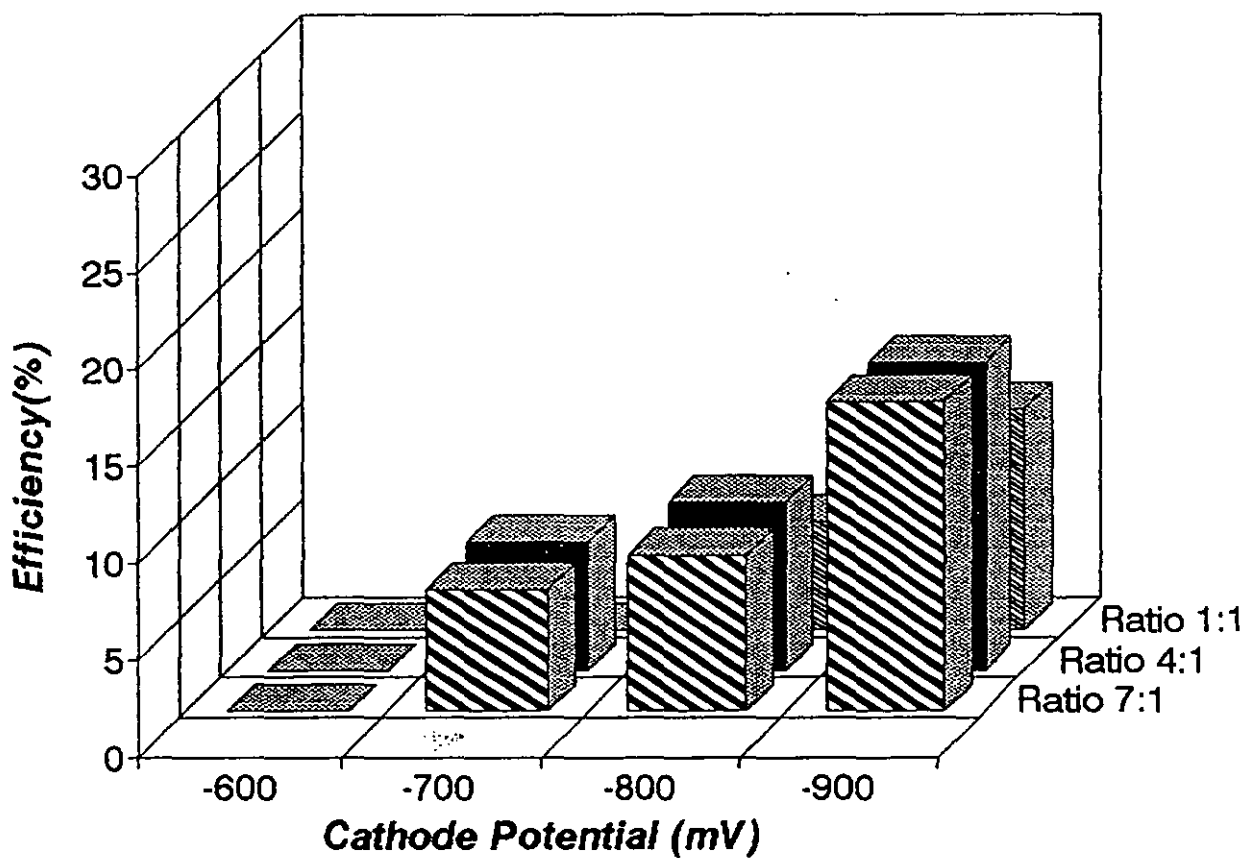


Figure 63

Cathodic polarization for different ratios of platinum solutions with effects of various cathode potentials upon cell efficiency.

*Cathodic Polarization for Phosphates
only and Pt with effect of C.ds*

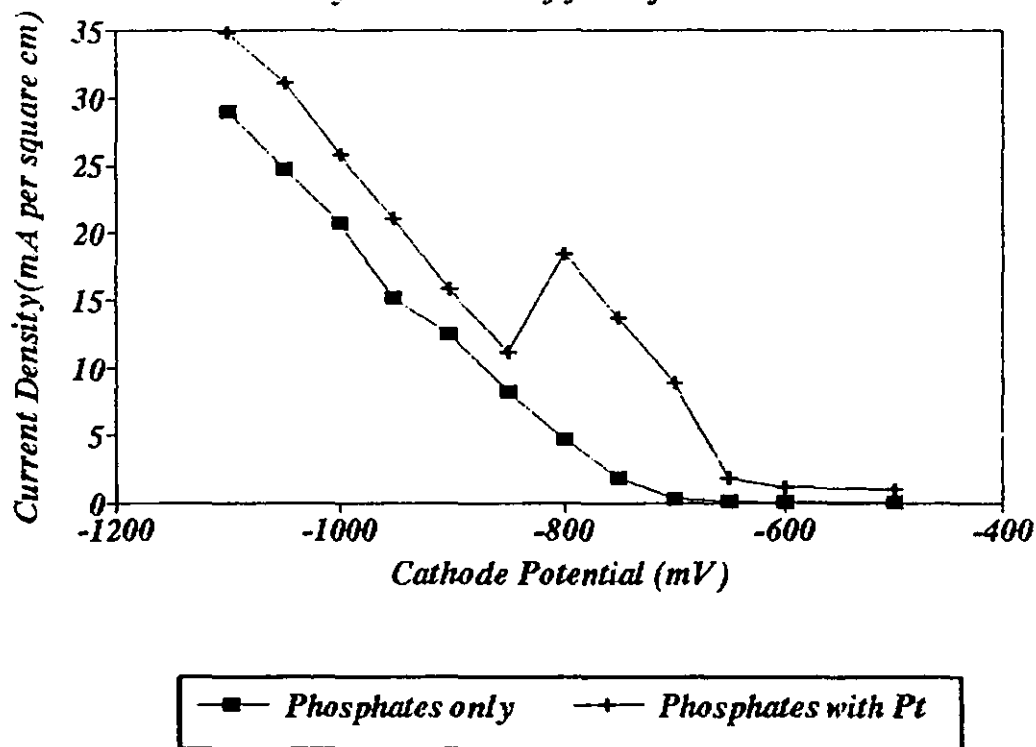


Figure 64

Cathodic polarization for phosphates and platinum solution with effects of various current densities.

*Cathodic Polarization for Phosphates
only and with Pt effect of C.ds*

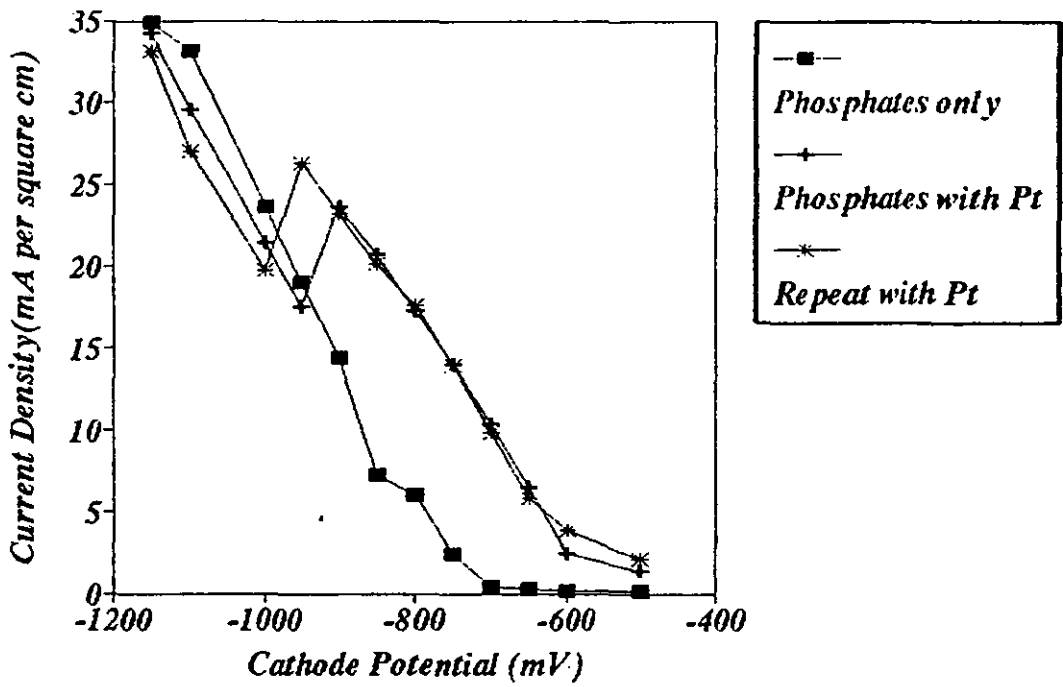


Figure 65

Cathodic polarization for phosphates and with repeated platinum solution with effects of various current densities.

*Comparison between Same Plating Tank No- A
with effect of high and low Temperature*

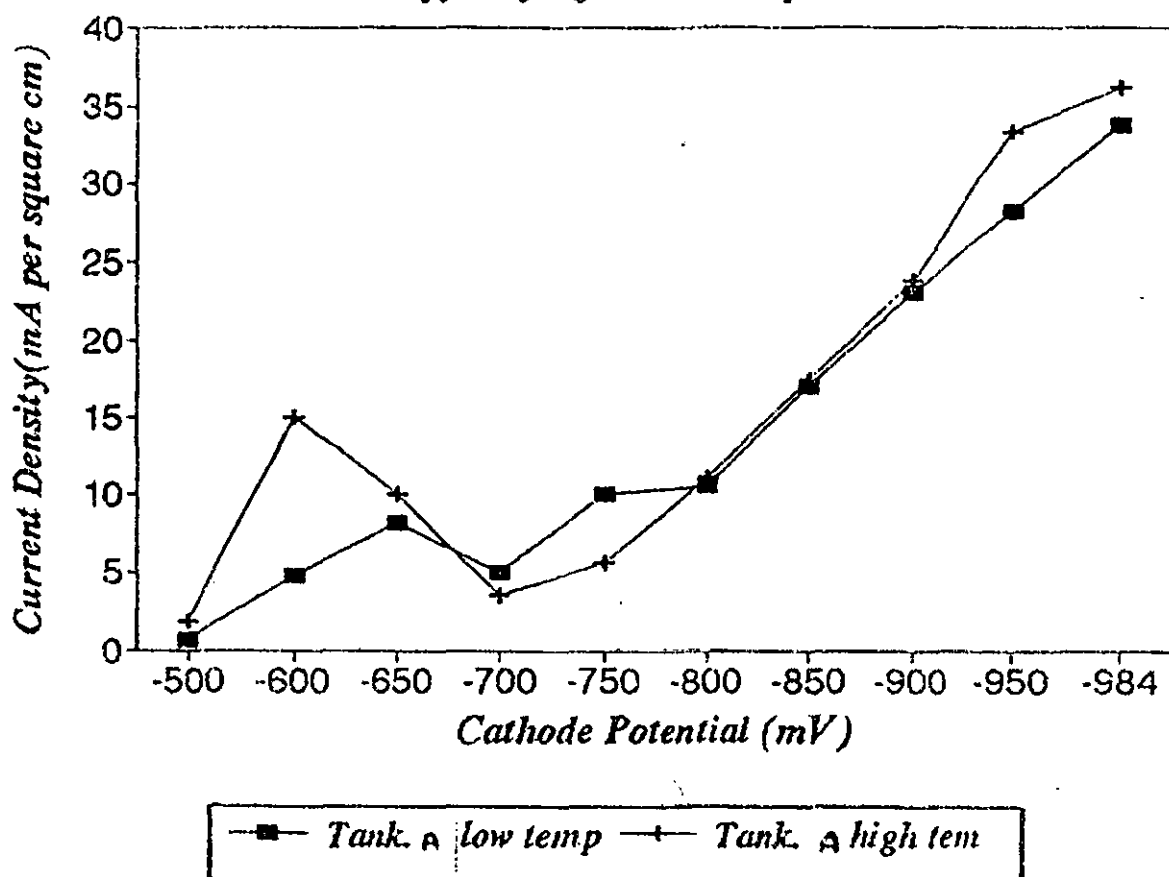
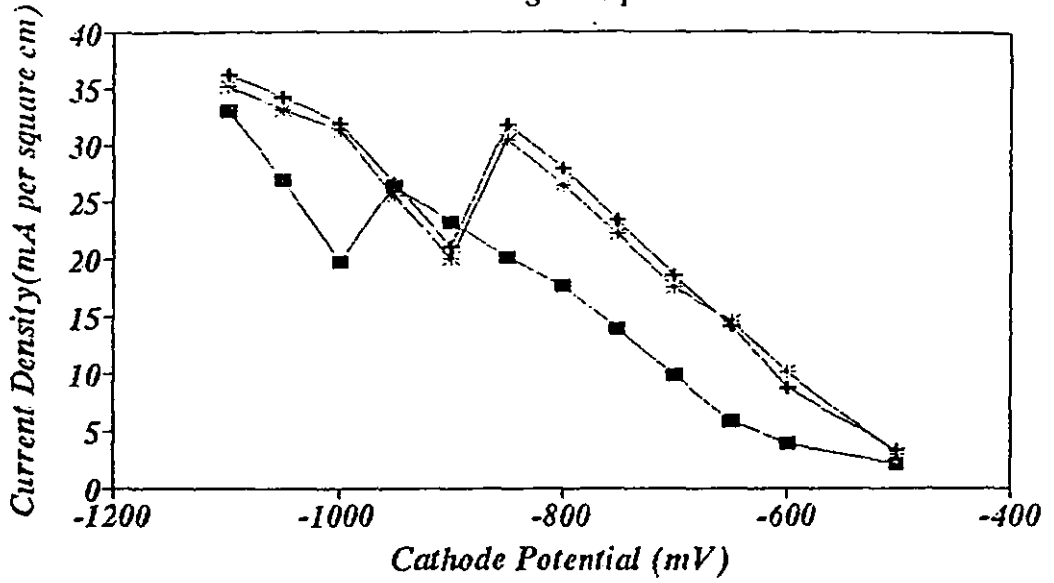


Figure 66

Cathodic polarization for tank No.A with low temperature and tank No.A with high temperature with effects of various current densities.

*Cathodic Polarization for Pt Baths
with low and high temperatures*



—■— Low temperature —+— High temperature —*— Repeat high temp

Figure 67

Cathodic polarization for platinum baths with high and low temperatures with effects of various current densities.

*Cathodic Polarization for Pt Baths
with low and high pH*

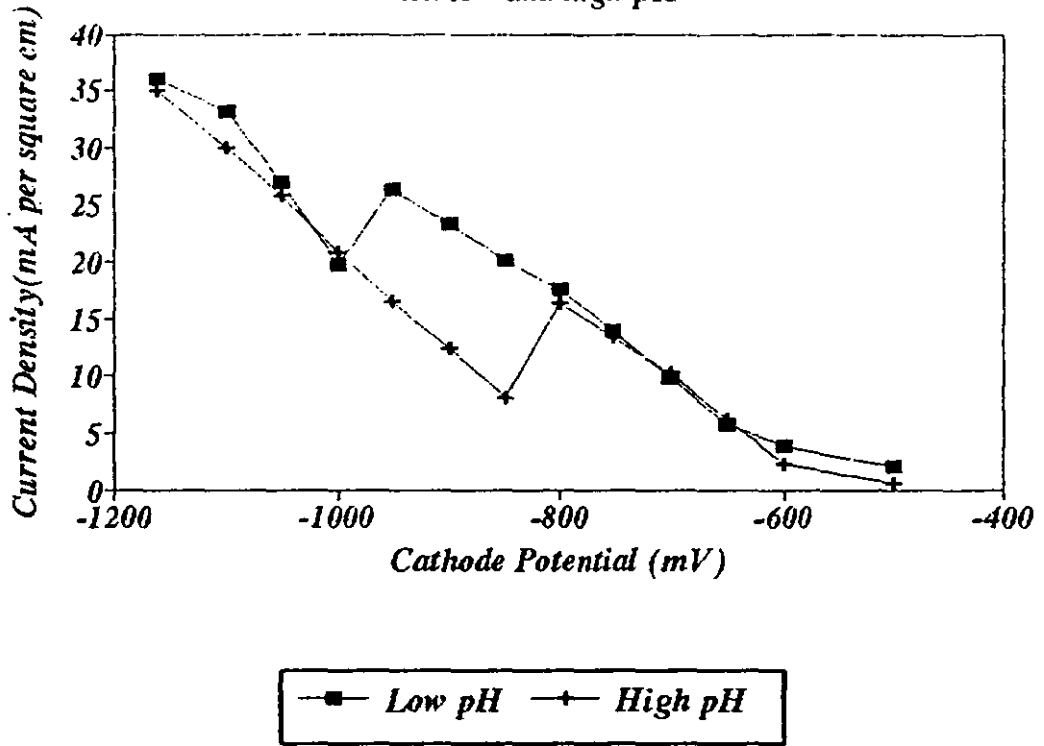


Figure 68

Cathodic polarization for platinum baths with high and low pH with effects of various current densities.

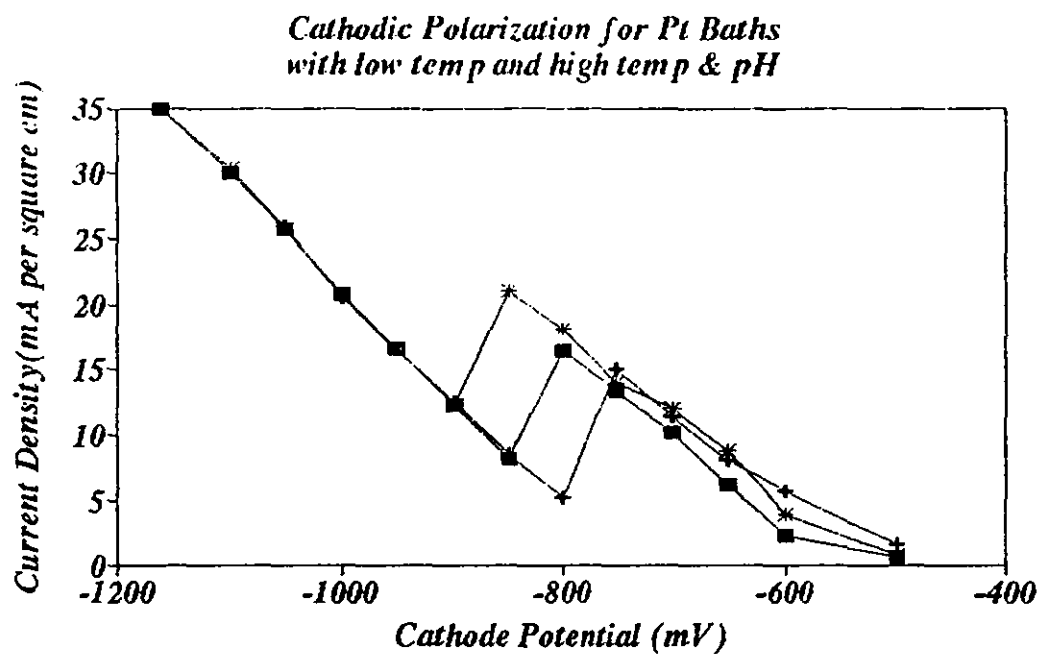


Figure 69

Cathodic polarization for platinum baths with high temperature and low pH and low temperature and high pH with effects of various current densities.

*Cathodic Polarization for Pt Baths
with high pH and Pt content*

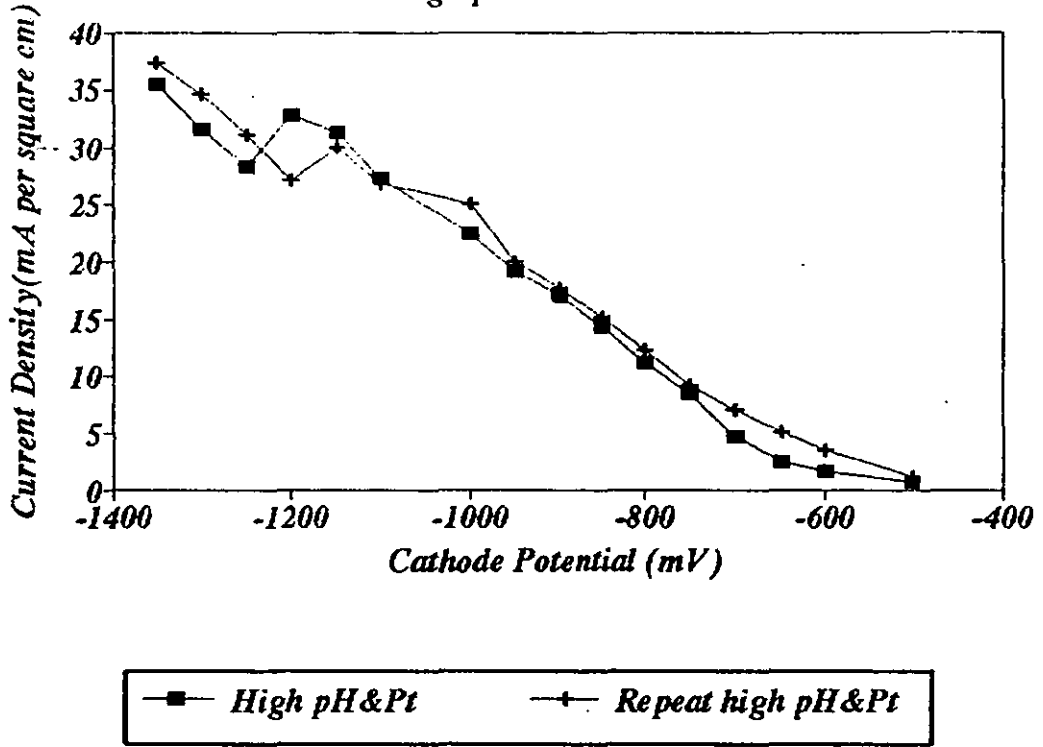


Figure 70

Cathodic polarization for platinum baths with high pH with high platinum content and low pH with low platinum content with effects of various current densities.

*Cathodic Polarization for Pt Baths
with high pH and Pt content*

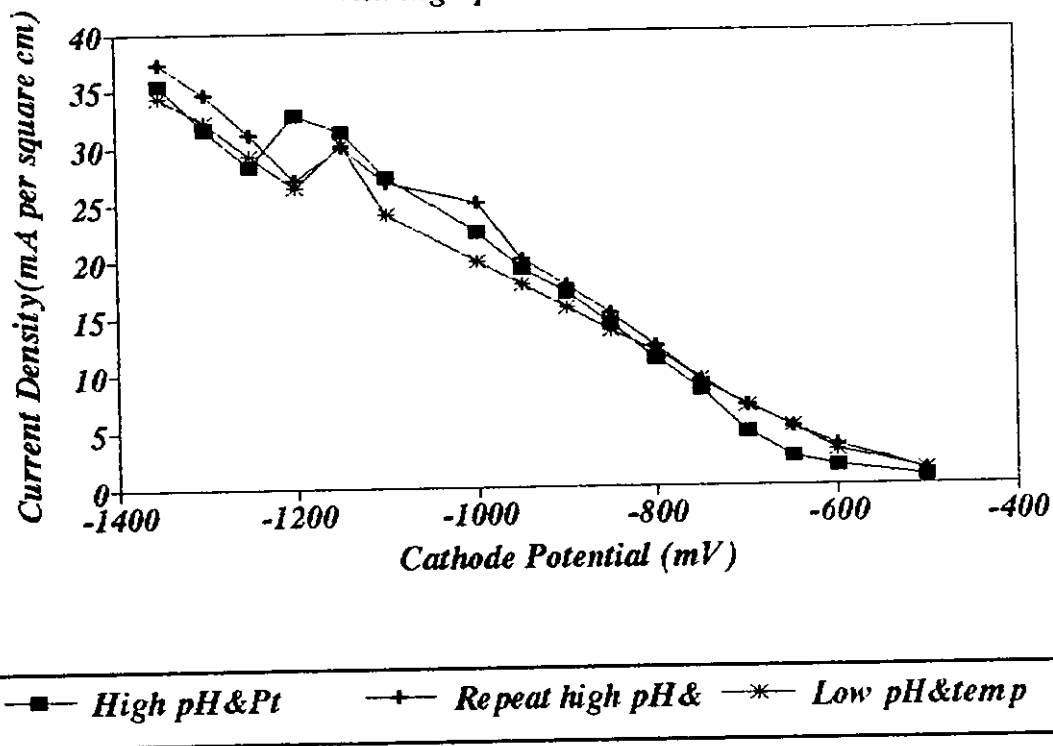


Figure 71

Cathodic polarization for platinum baths with high pH with high platinum content and low pH with low temperature with effects of various current densities.

*Cathodic Polarization for sodium baths
only and with Pt content*

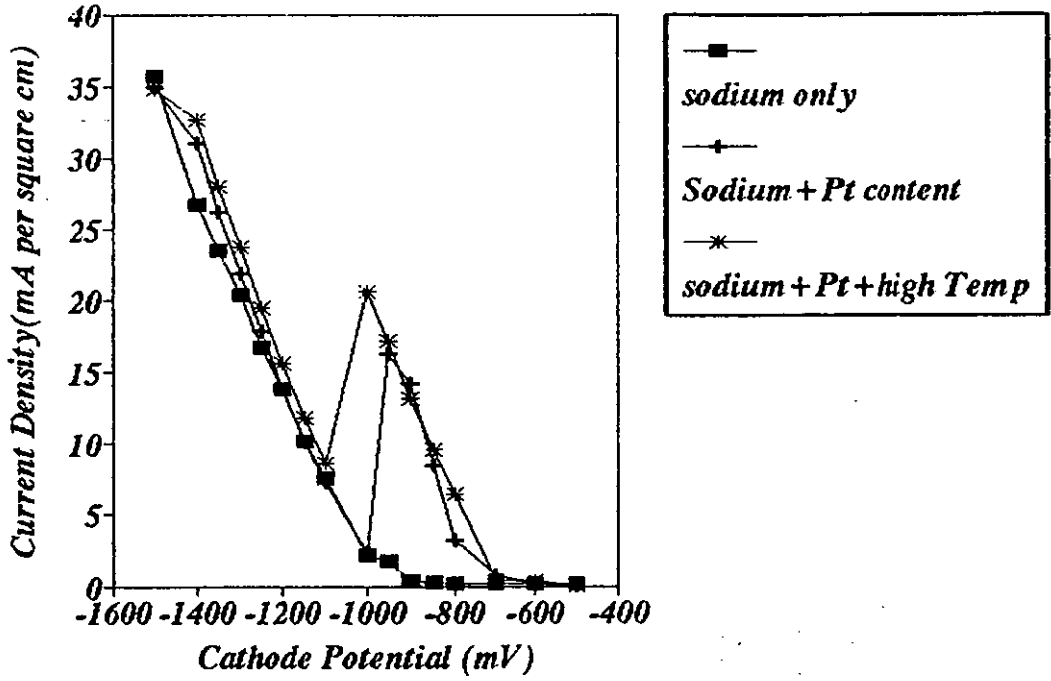


Figure 72

Cathodic polarization for sodium, sodium with platinum content and sodium with platinum content at high temperature with effects of various current densities.

*Cathodic Polarization for sodium baths
only and with Pt content*

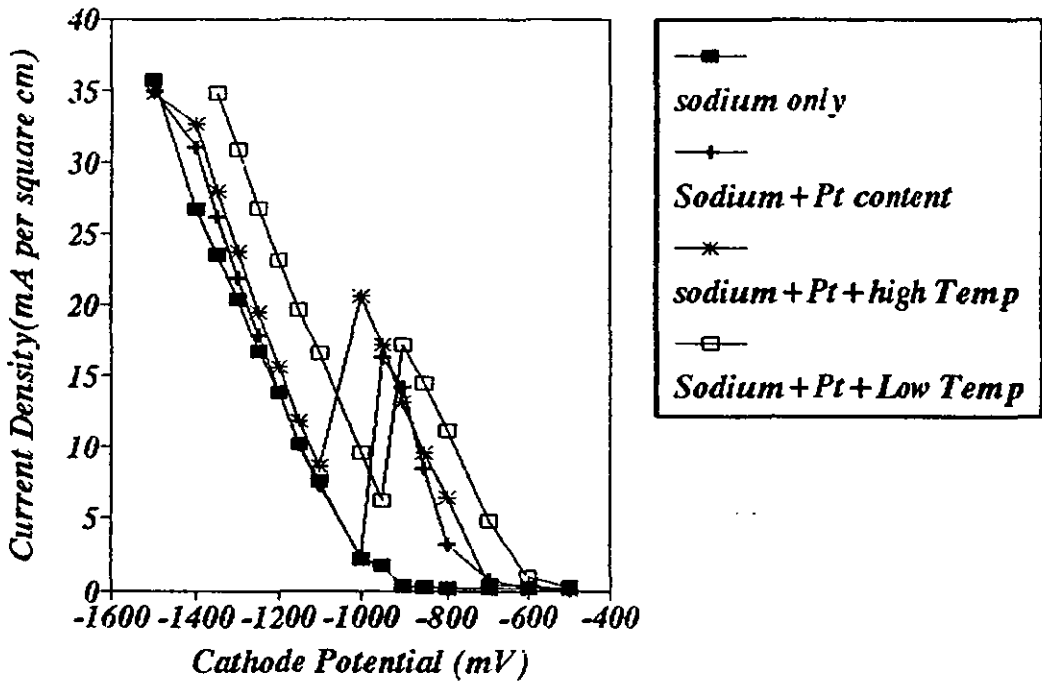


Figure 73

Cathodic polarization for sodium, sodium with platinum content and sodium with platinum content at high temperature and finally sodium with platinum at low temperature with effects of various current densities.

*Throwing power with effects of
Interelectrode Separation and C.d*

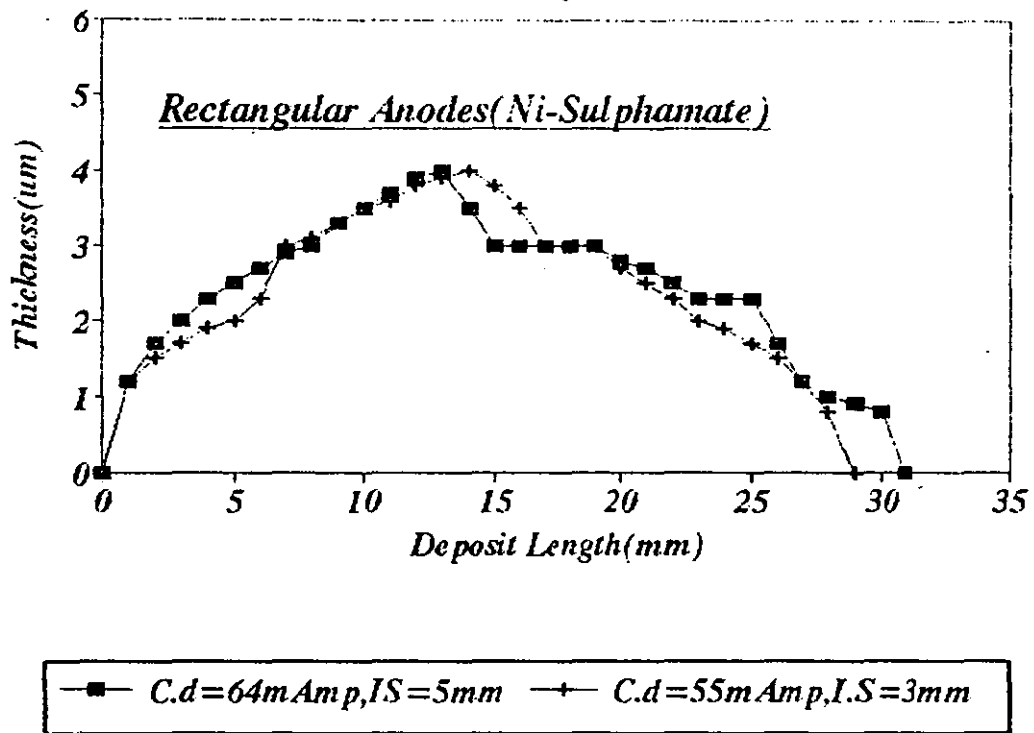


Figure 74

Throwing power with effects of interelectrode separation and current density upon deposit length and thickness.

*Throwing power with effects of
Interelectrode Separation and C.d*

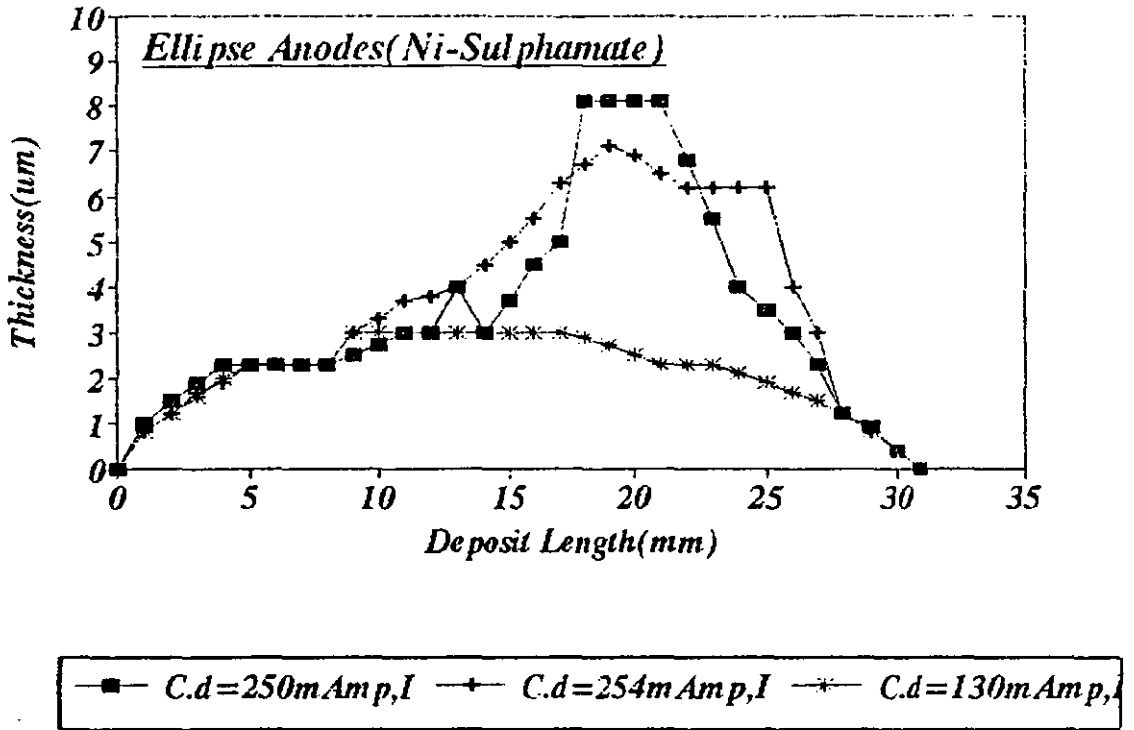
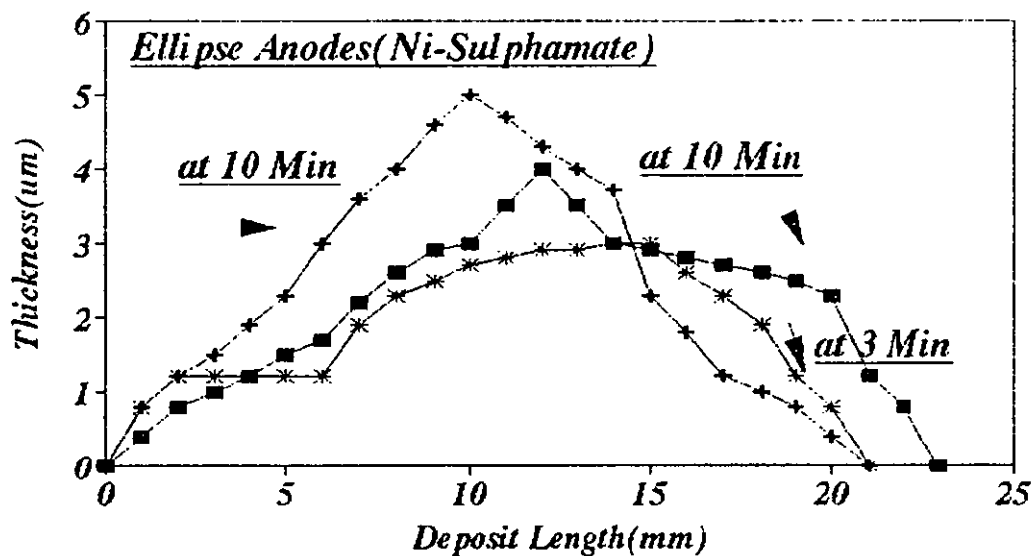


Figure 75

Throwing power with effects of interelectrode separation and current density upon deposit length and thickness, using ellipse anodes with Ni-sulphamate solution.

*Throwing power with effects of
Interelectrode Separation and C.d*



C.d=74mA/cm², 1S
 C.d=57mA/cm², 1.
 C.d=240mA/cm², 1

Figure 76

Throwing power with effects of interelectrode separation and current density upon deposit length and thickness, using ellipse anodes with Ni-sulphamate solution.

*Throwing power with effects of
Interelectrode Separation and C.d*

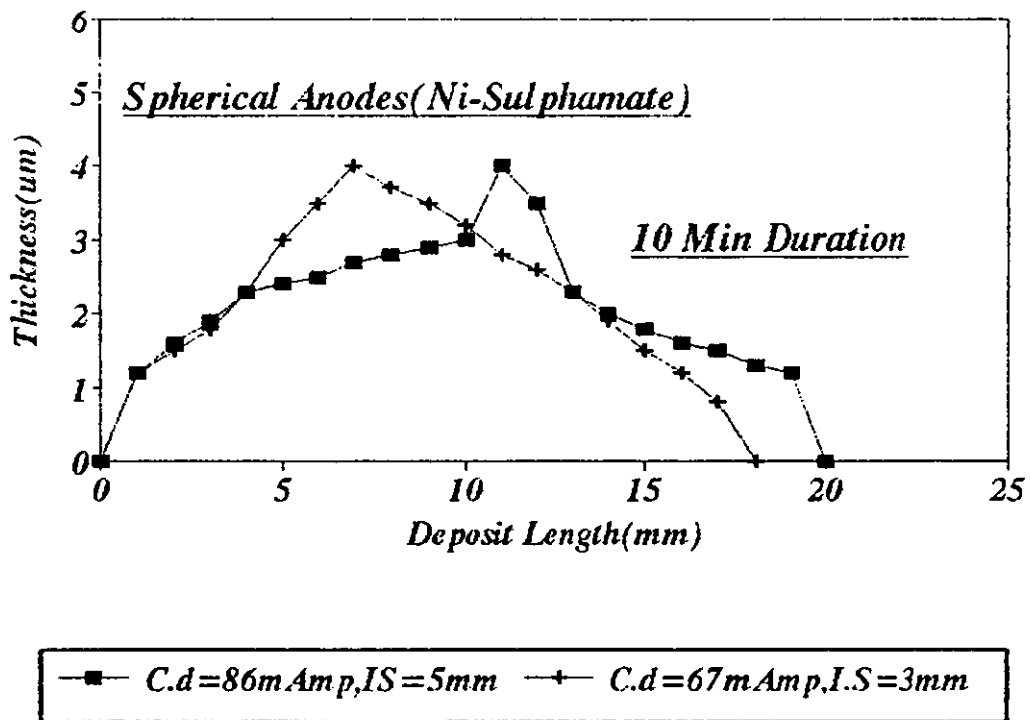


Figure 77

Throwing power with effects of interelectrode separation and current density upon deposit length and thickness, using Spherical anodes with Ni-sulphamate solution.

*Throwing power with effects of
Interelectrode Separation and C.d*

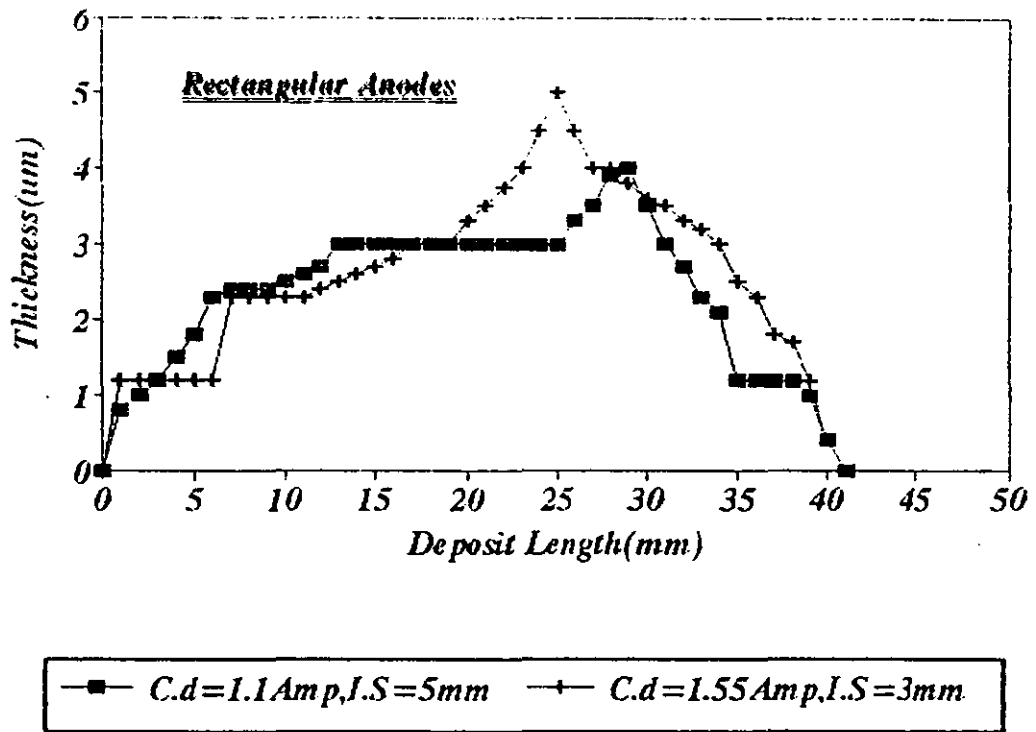


Figure 78

Throwing power with effects of interelectrode separation and current density upon deposit length and thickness, using rectangular anodes with Ni-strike solution.

*Throwing power with effects of
Interelectrode Separation and C.d*

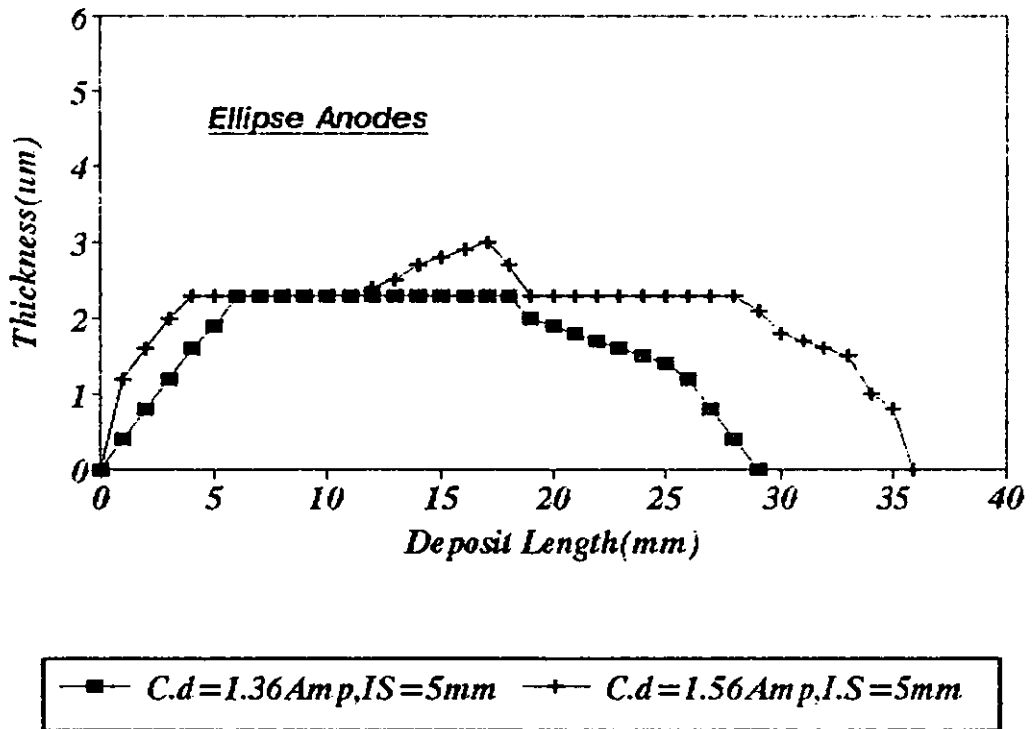


Figure 79

Throwing power with effects of interelectrode separation and current density upon deposit length and thickness, using ellipse anodes with Ni-strike solution.

*Throwing power with effects of
Interelectrode Separation and C.d*

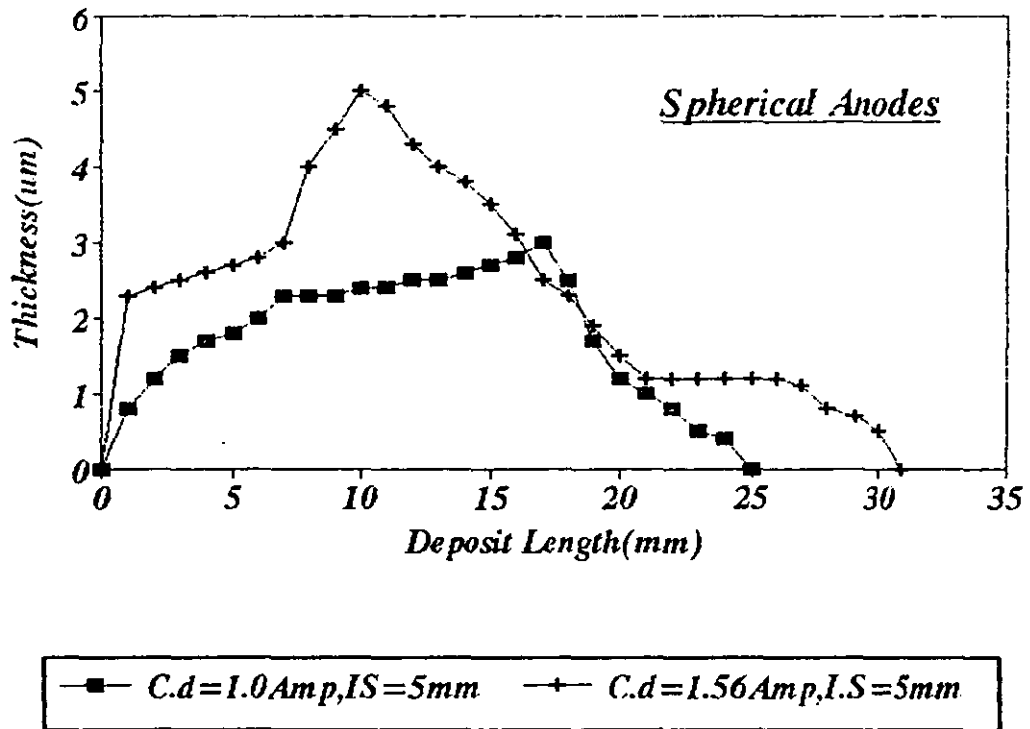


Figure 80

Throwing power with effects of interelectrode separation and current density upon deposit length and thickness, using spherical anodes with Ni-strike solution.

*Throwing power with effects of
Interelectrode Separation and C.d*

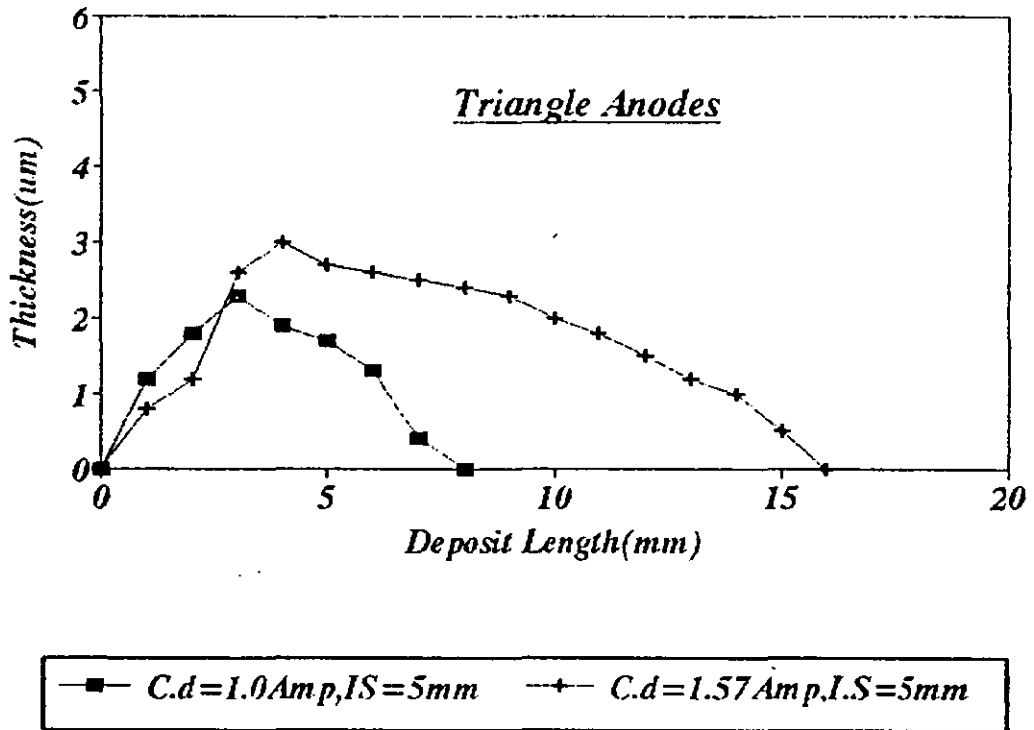


Figure 81

Throwing power with effects of interelectrode separation and current density upon deposit length and thickness, using triangle anodes with Ni-strike solution.

Figure 82

Effect of throwing power with effects of interelectrode separation, different shape of anodes, current density with Ni-sulphate solution.

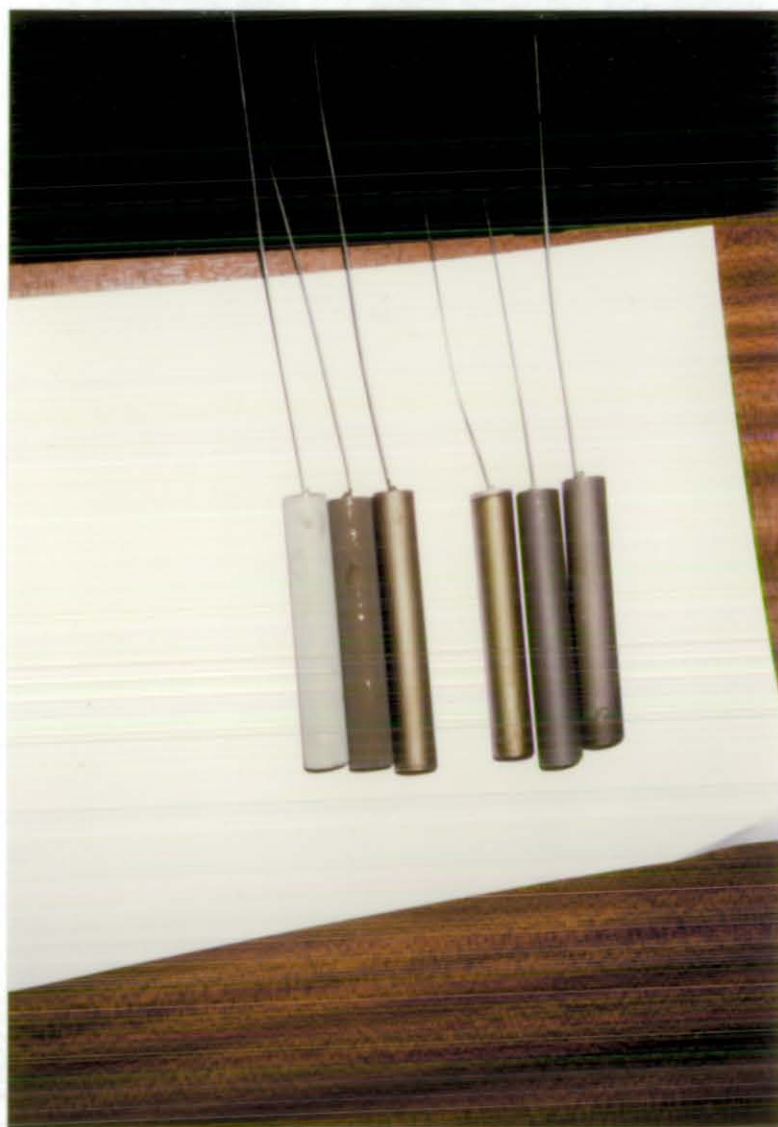
Figure 83

Effect of throwing power with effects of interelectrode separation, different shape of anodes, current density with Ni-sulphate solution.



Figure 84

Comparison between conventional plating and pulse plating. Pulse plated samples gave darker deposits than those produced by conventional plating.



*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.1*

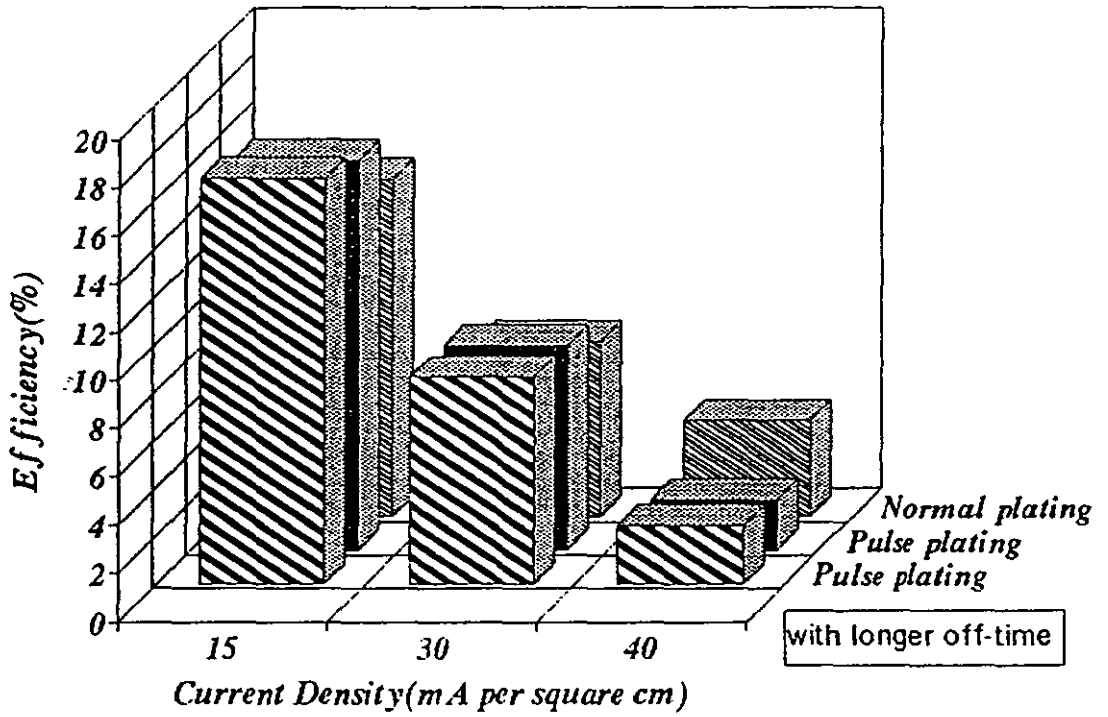


Figure 85

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.1.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.2*

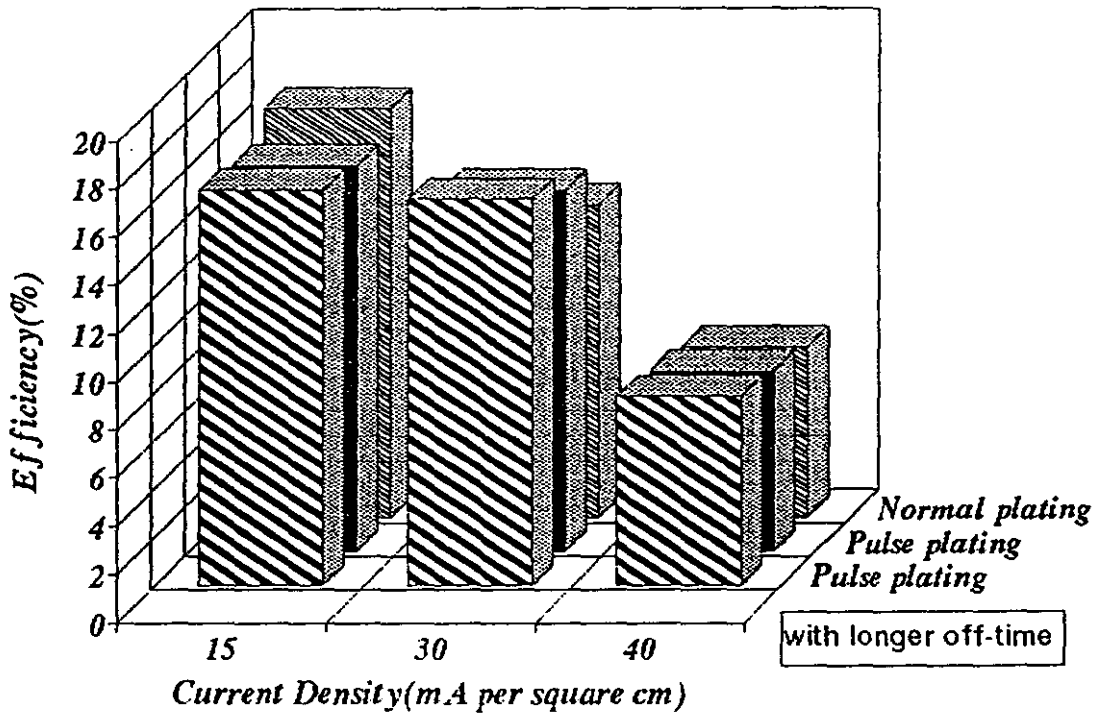


Figure 86

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.2.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.3*

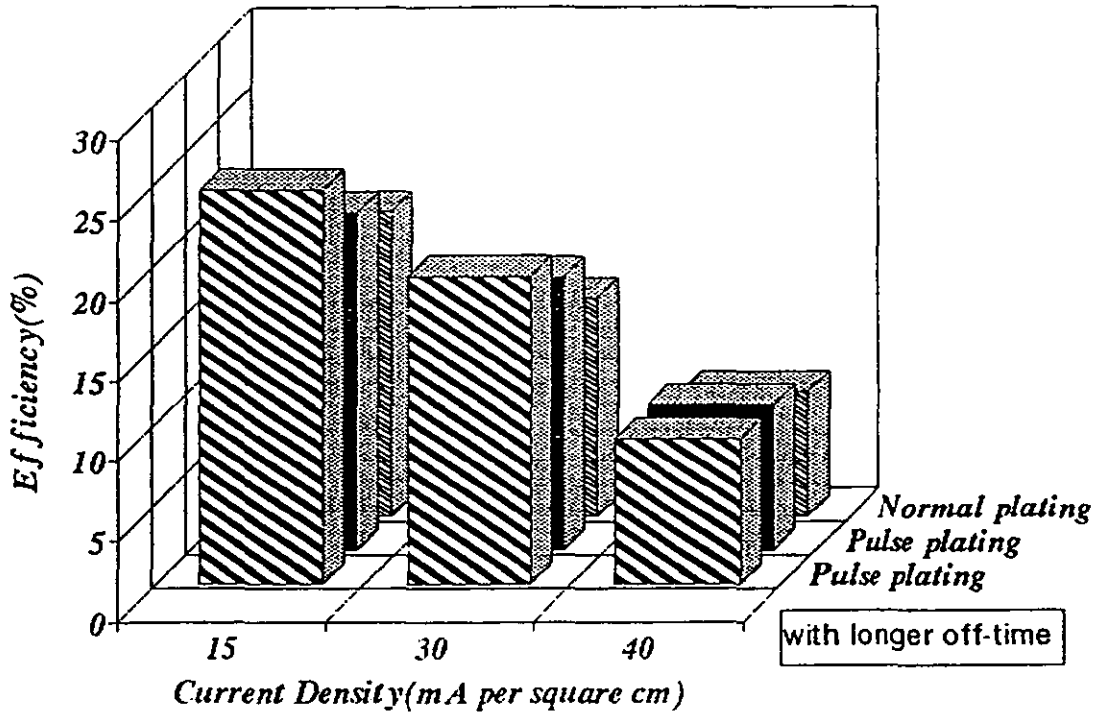


Figure 87

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.3.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.4*

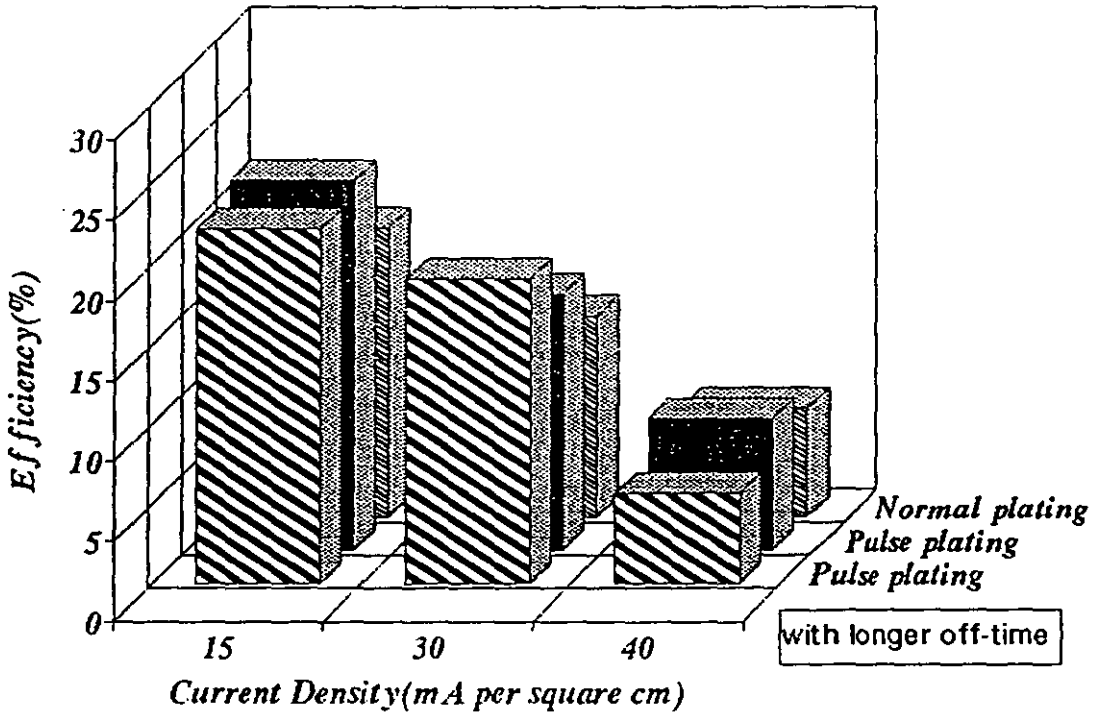


Figure 88

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.4.

Comparison between conventional & Pulse with effect of Efficiency of Bath No.5

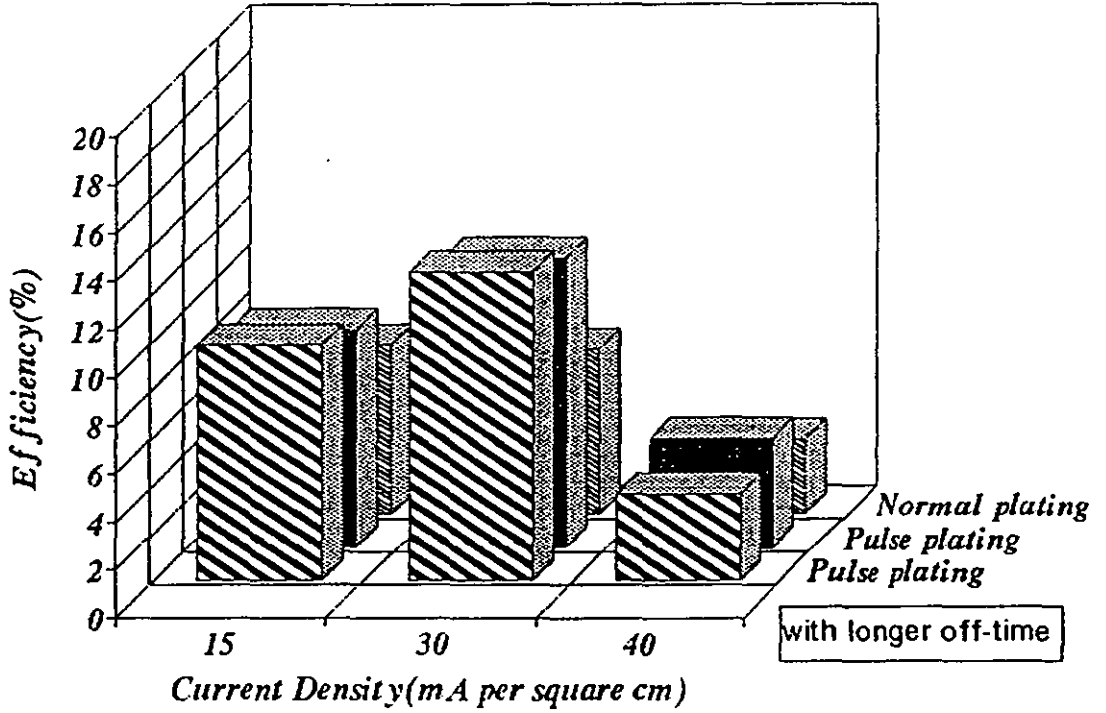


Figure 89

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.5.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.6*

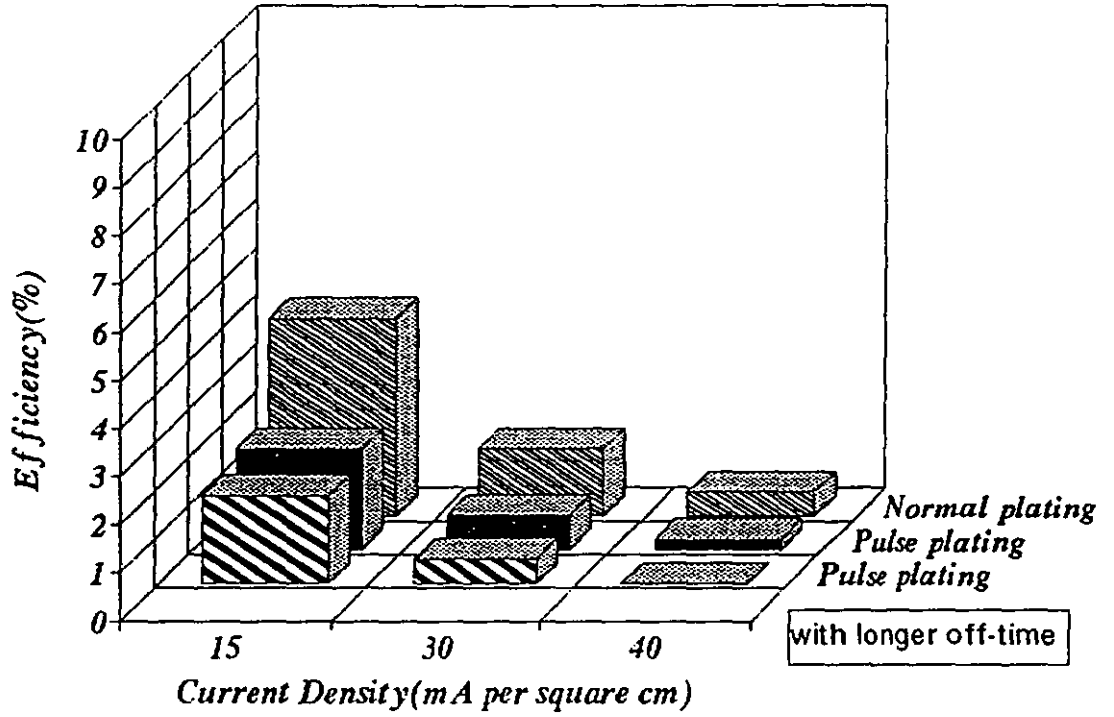


Figure 90

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.6.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.7*

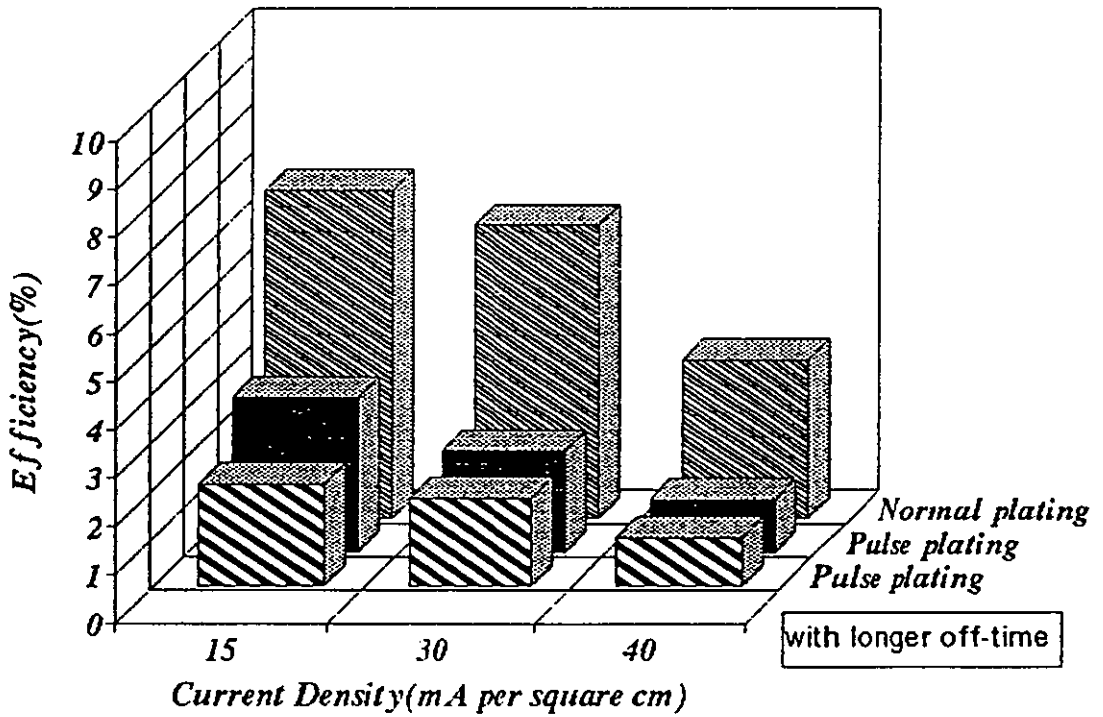


Figure 91

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.7.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.8*

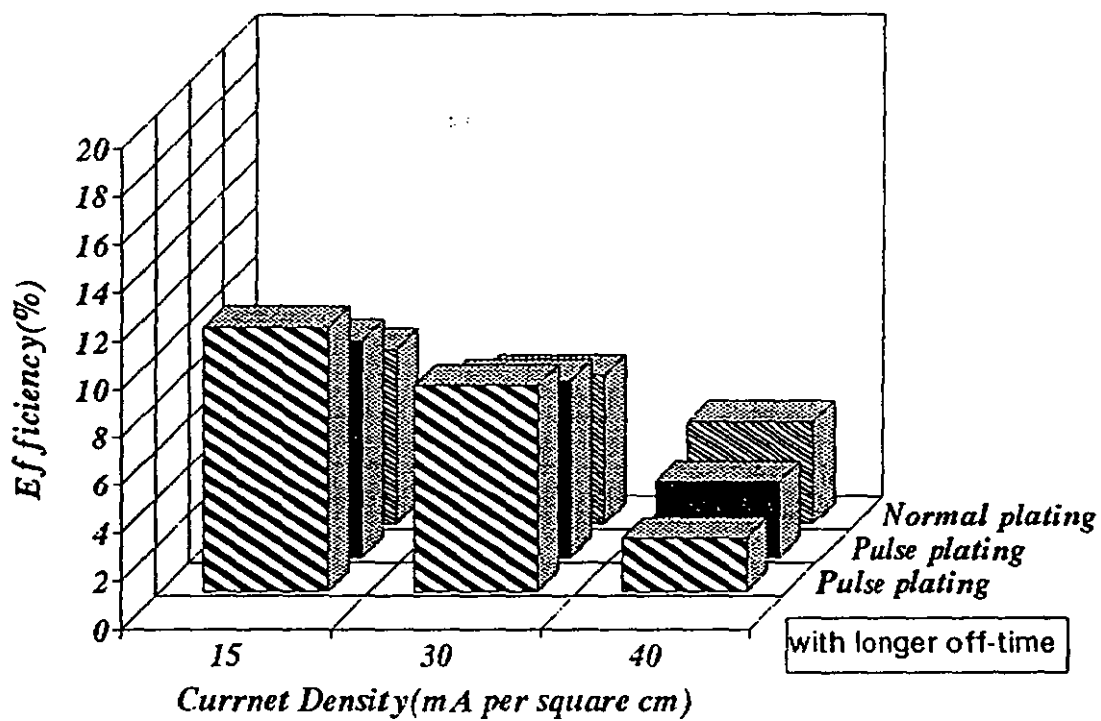


Figure 92

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.8.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.9*

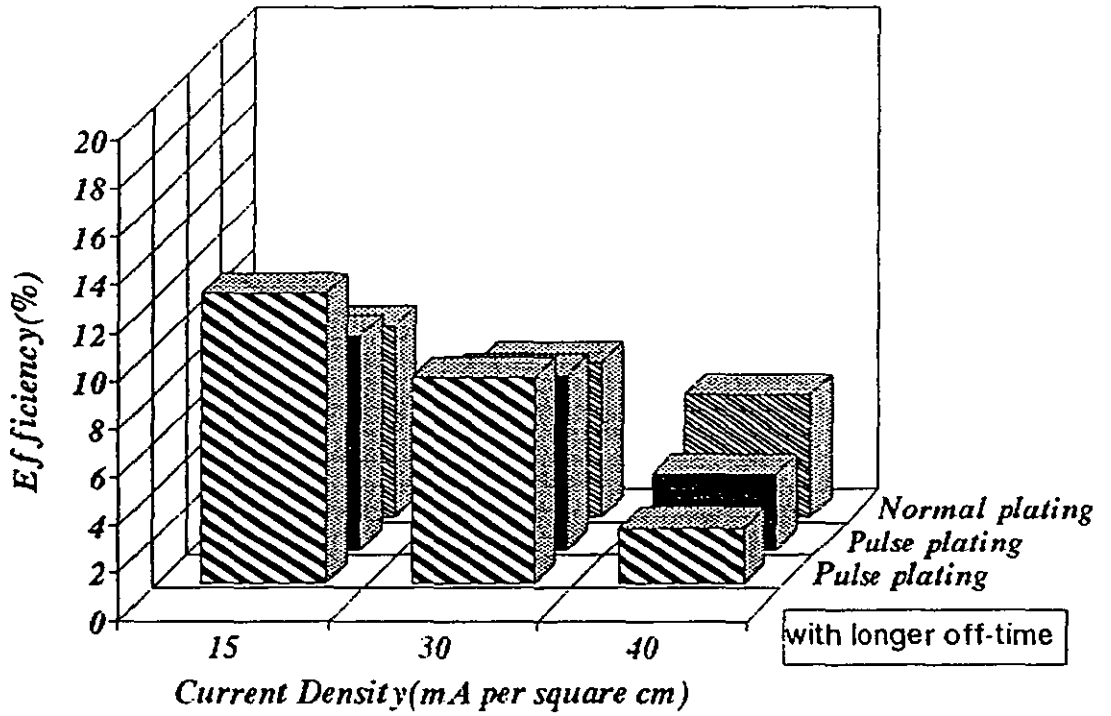


Figure 93

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.9.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.10*

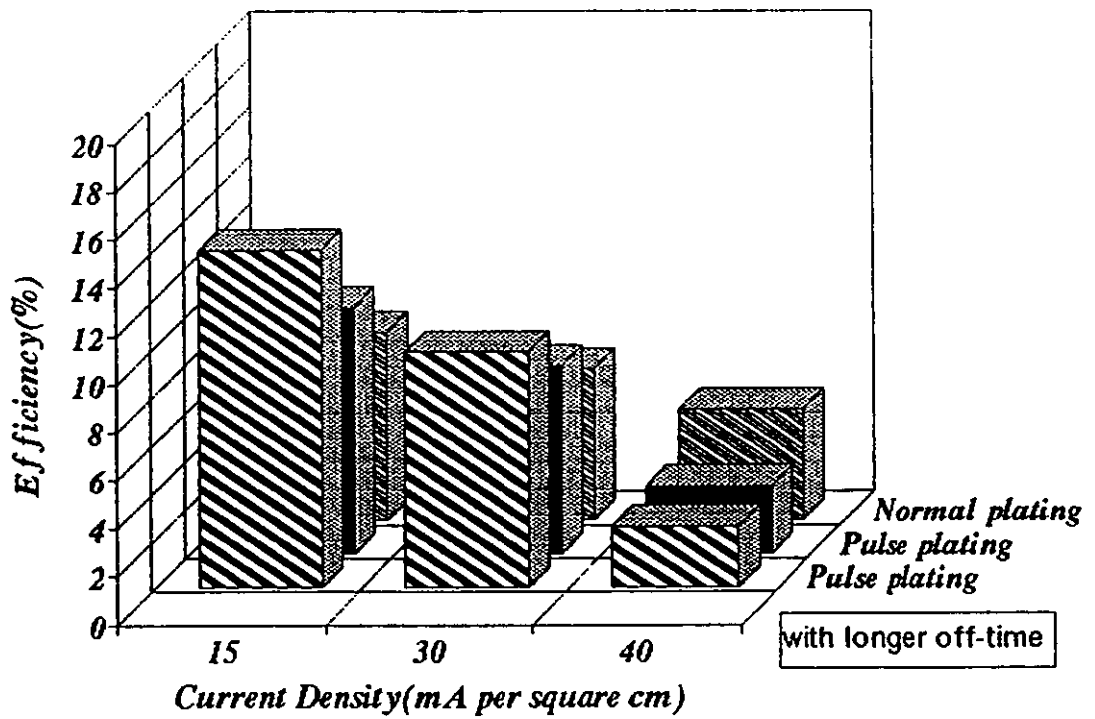


Figure 94

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.10.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.11*

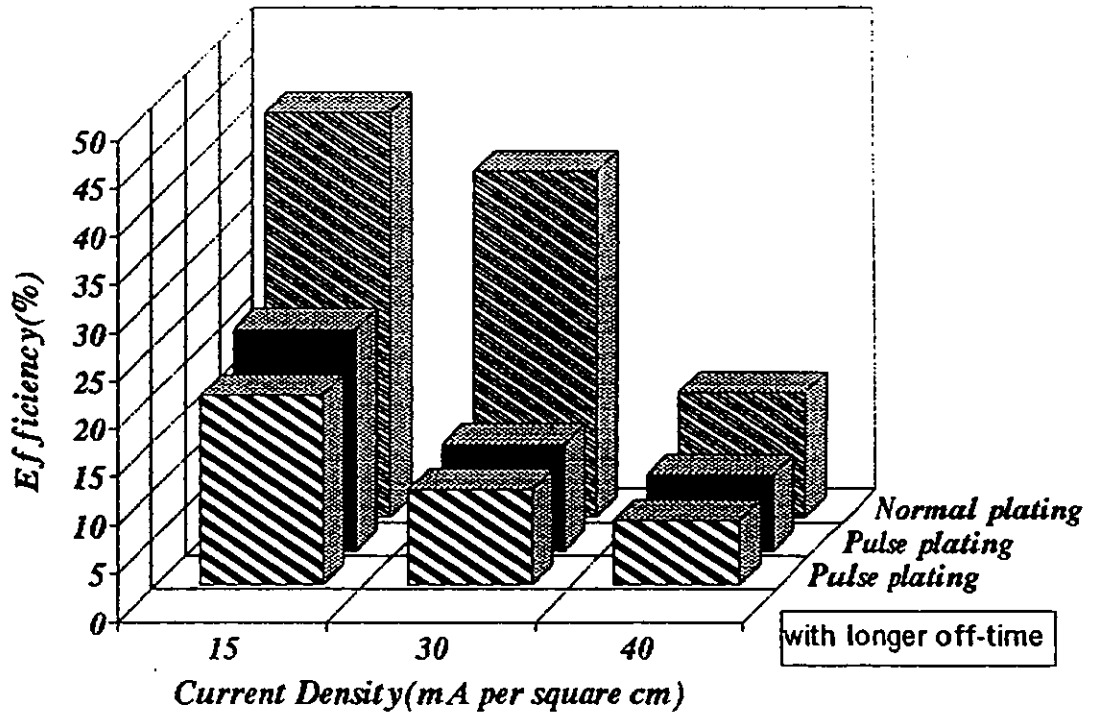


Figure 95

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.11.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.12*

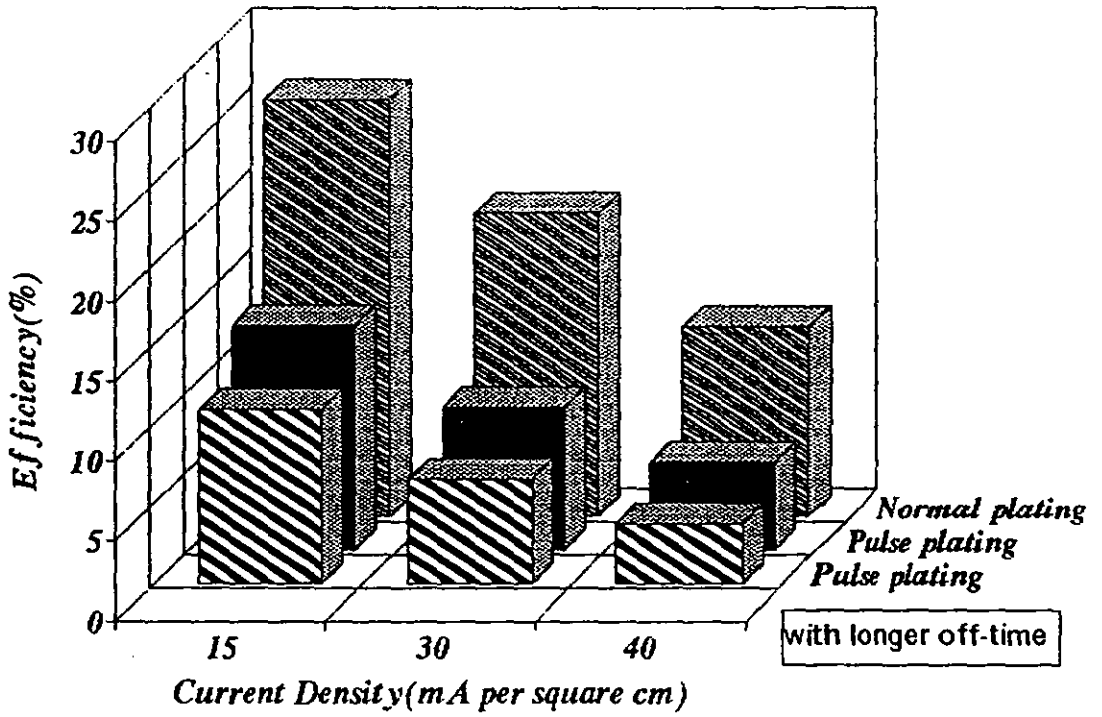


Figure 96

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.12.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.13*

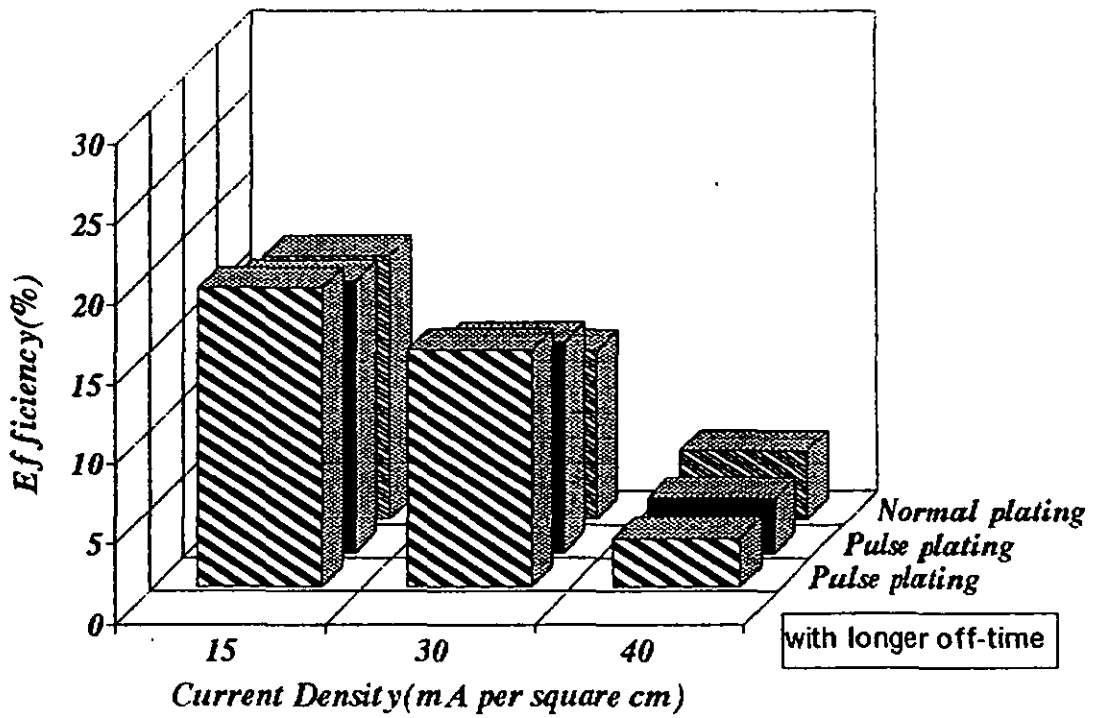


Figure 97

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.13.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.14*

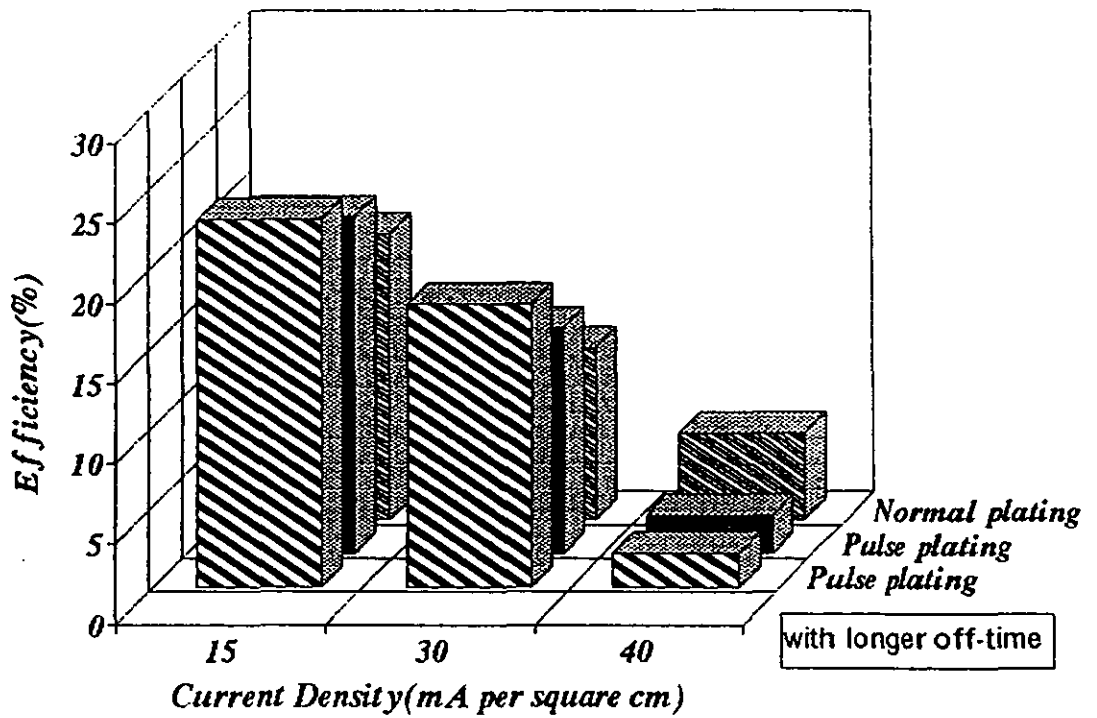


Figure 98

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.14.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.15*

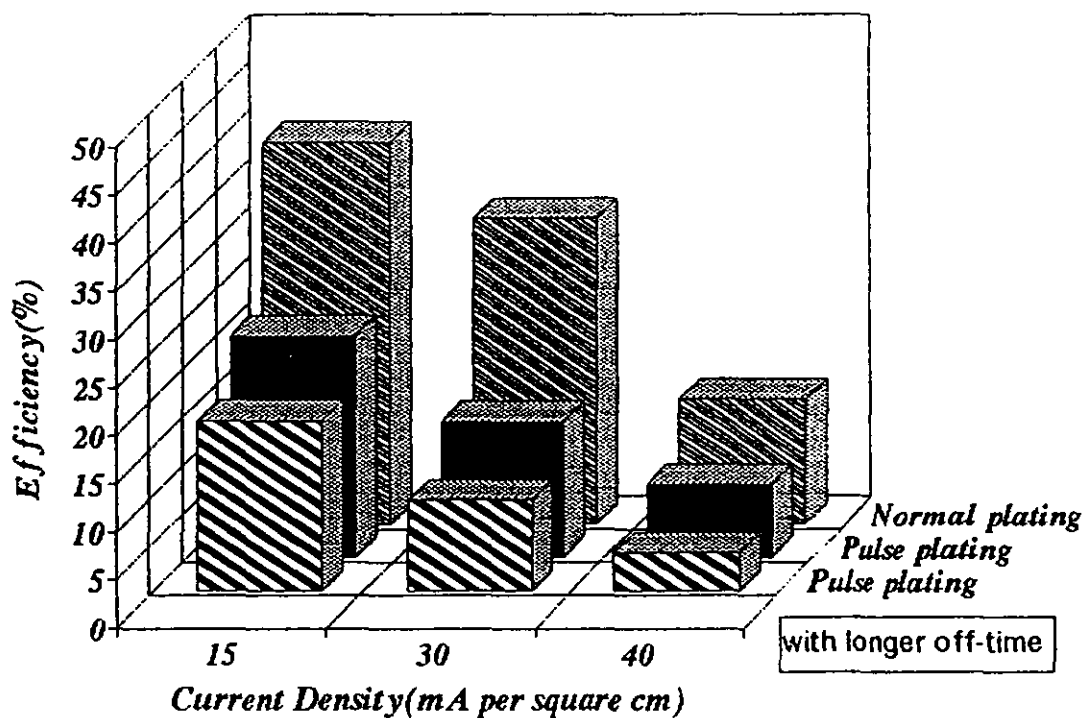


Figure 99

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.15.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.16*

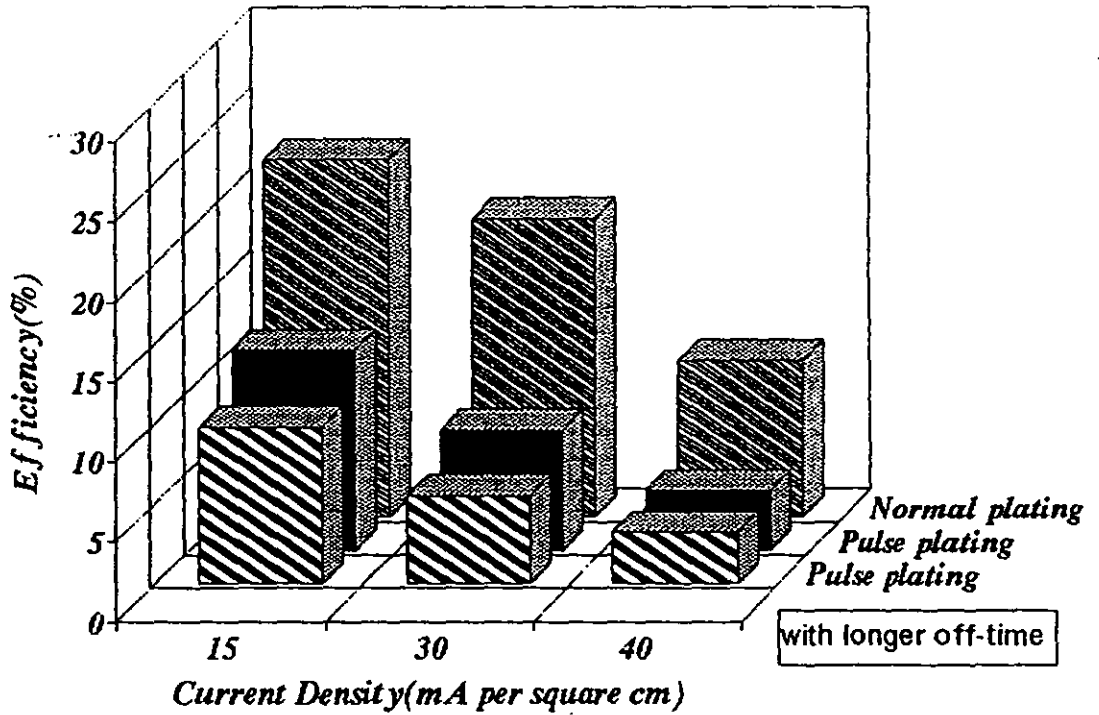


Figure 100

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.16.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.17*

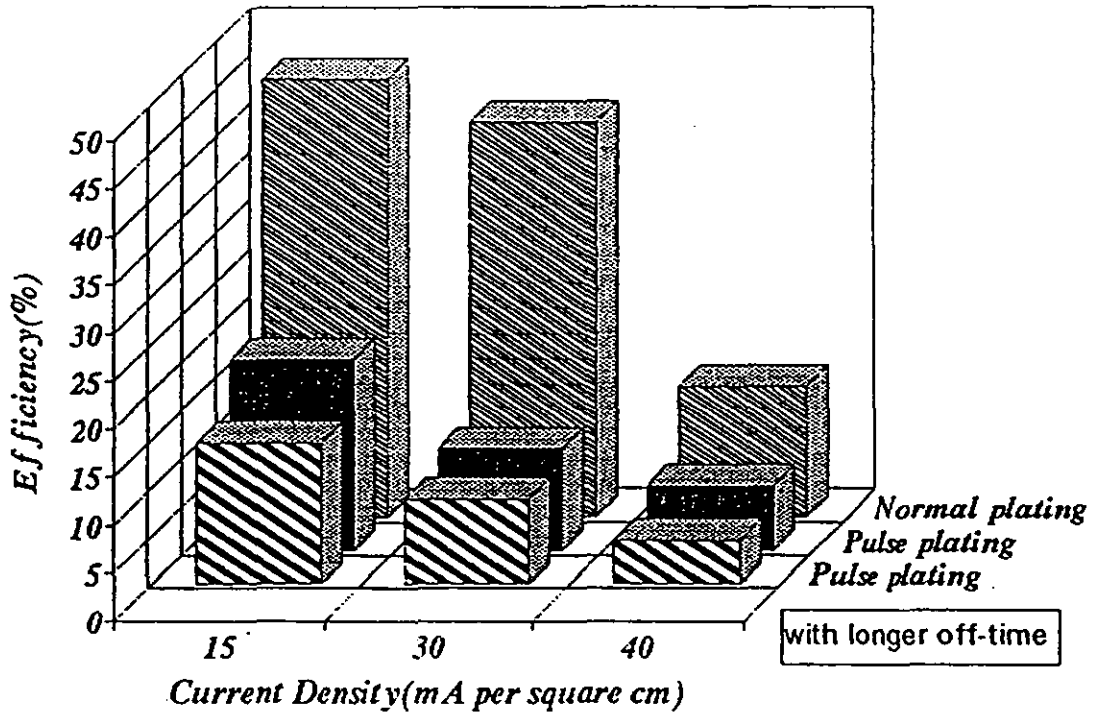


Figure 101

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.17.

*Comparison between conventional & Pulse
with effect of Efficiency of Bath No.18*

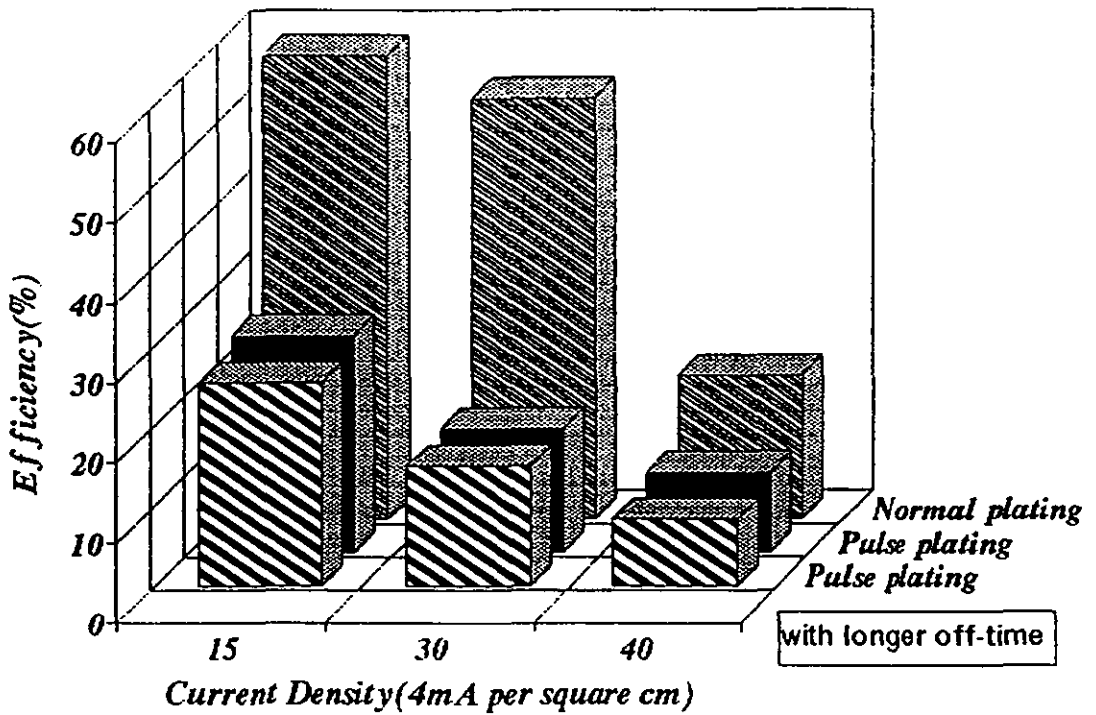


Figure 102

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.18.

Comparison between conventional & Pulse with effect of Efficiency of Bath No.19

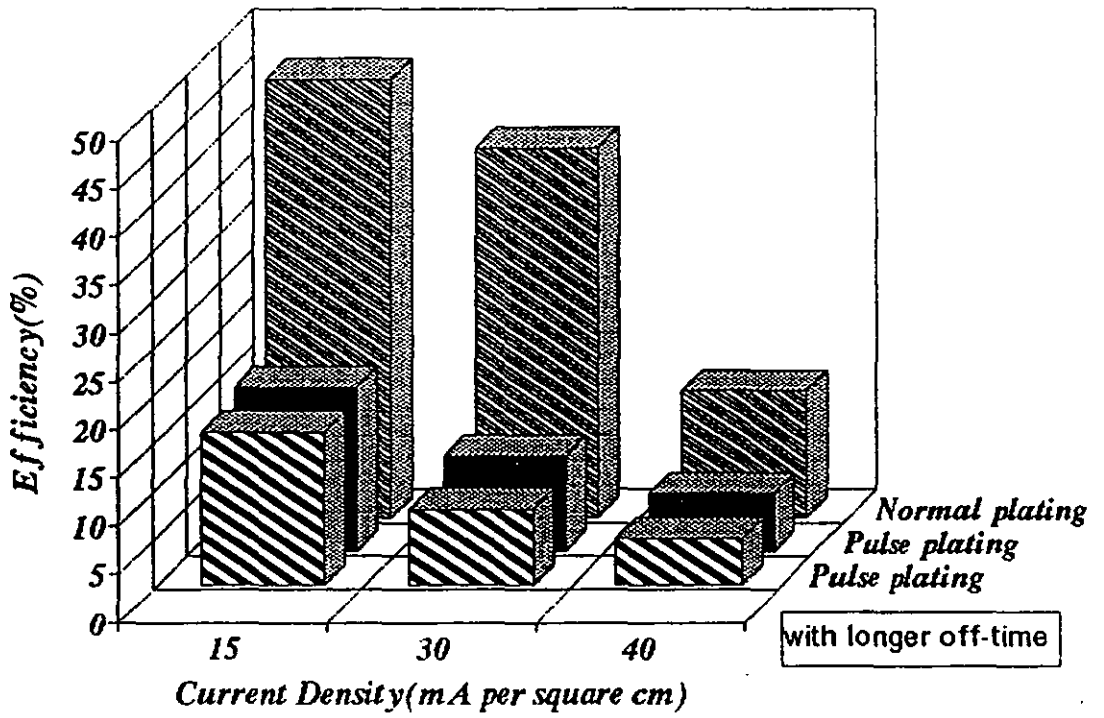


Figure 103

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum bath No.19.

*Comparison between conventional & Pulse
with effect of Efficiency of tank No.17*

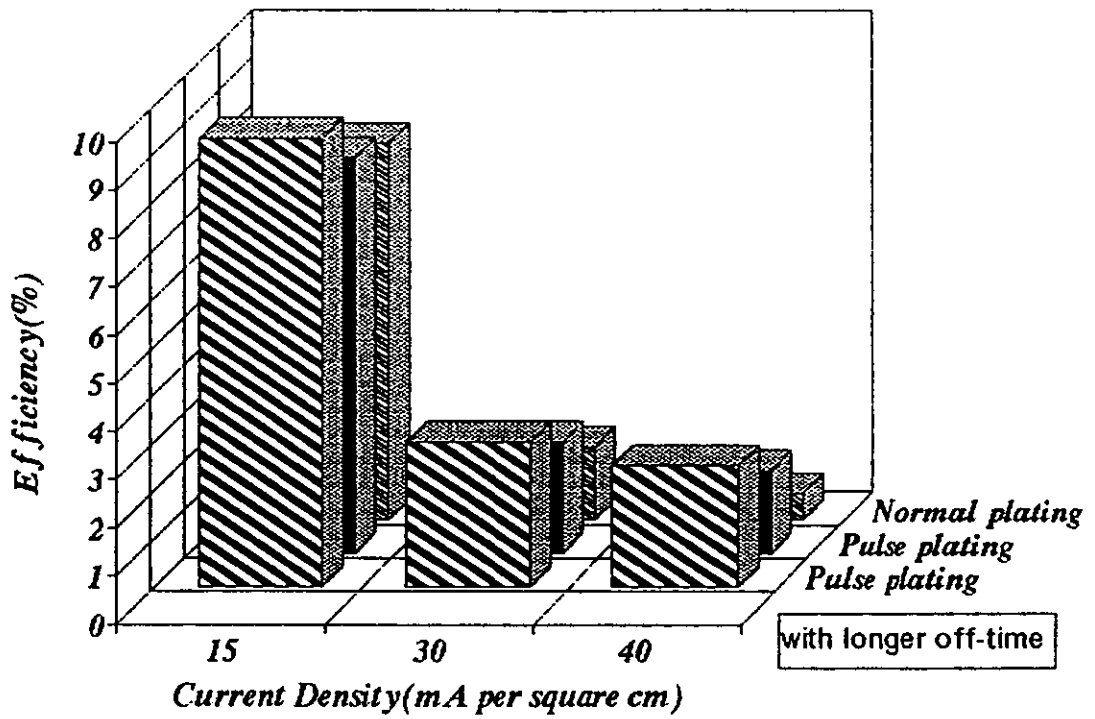


Figure 104

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum Tank No.17.

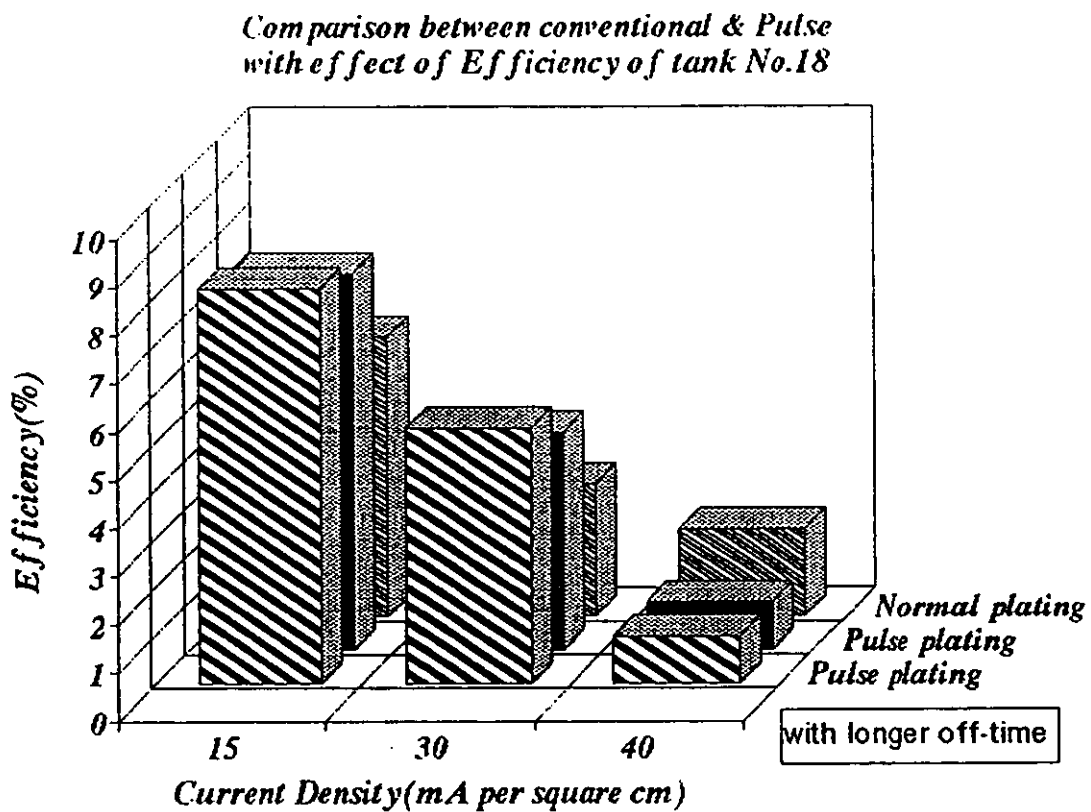


Figure 105

Comparison between conventional and pulse plating with effect of current density upon cell efficiency of platinum Tank No.18.

Figure 106

Shows the P.T.F.E material which was used in the laboratory before and after plating.

Figure 107

Shows the usual procedure for protection of fir-tree roots of blades during plating using H.V.R(High vulcanised rubber),



Figure 108

Flow diagram for pulse plating and features resulting from pulse plating method with aid of equipments used. The use of pulse generator, oscilloscope, power Mosfets distinguishes the pulse plating procedure from conventional plating arrangements.

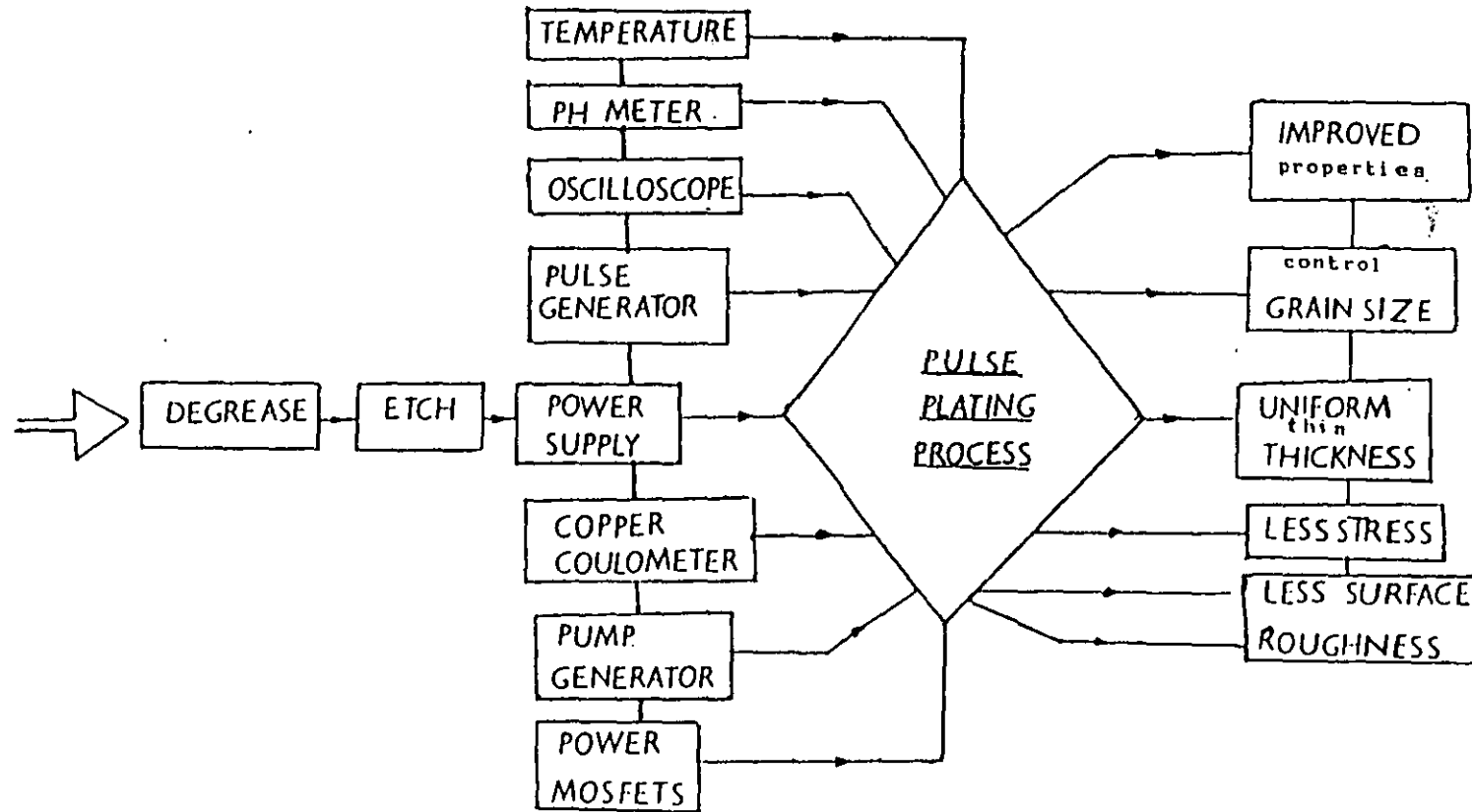
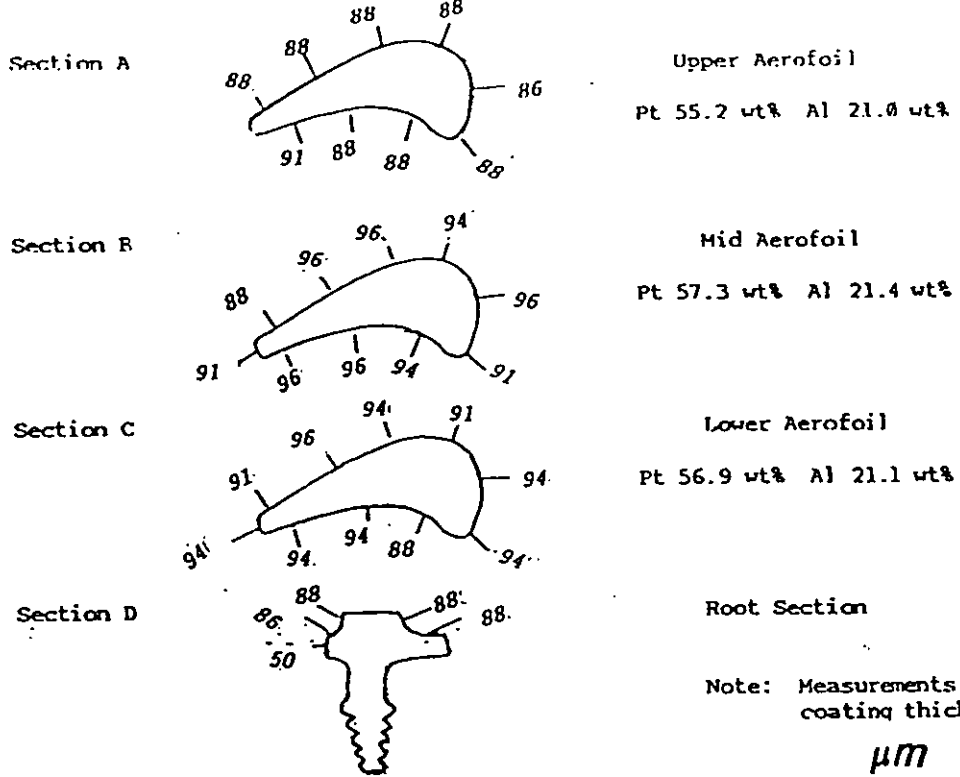


Figure 109

Westinghouse TG20 1st Stage Bucket Platinum Aluminised to RT22LT

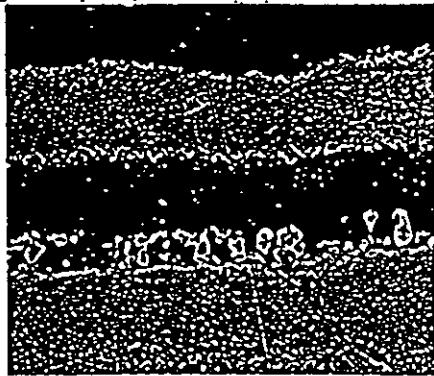
Serial No. OF 1011R



Note: Measurements of total coating thickness

μm

Coating Structure



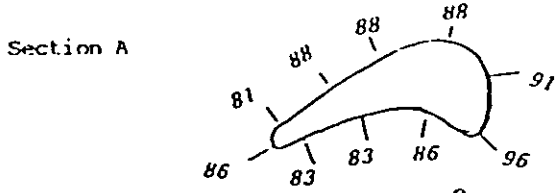
x400
etched
(marbles)

Typical RT22 platinum aluminide structure.
Pt rich outer layer (light etching), mid nickel aluminide (dark etching) and inner diffusion zone.

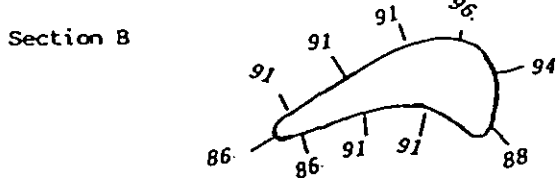
Figure 110

Westinghouse TG20 1st Stage Bucket Platinum Aluminised to RT22LT

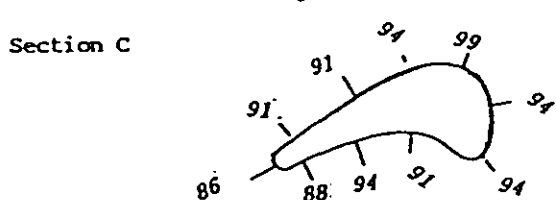
Serial No. FA 568R



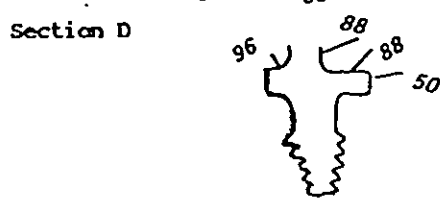
Upper Aerofoil
Pt 55.1 wt% Al 20.5 wt%



Mid Aerofoil
Pt 59.7 wt% Al 20.9 wt%



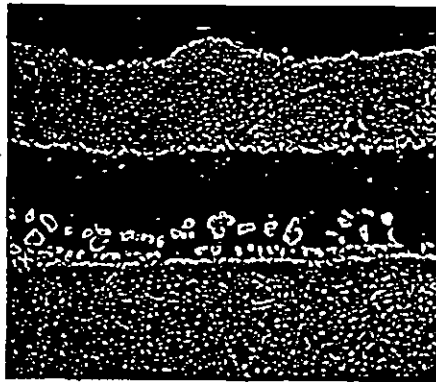
Lower Aerofoil
Pt 58.0 wt% Al 21.1 wt%



Root Section

Note: Measurements of total coating thickness
μm

Coating Structure



x400
etched
(marbles)

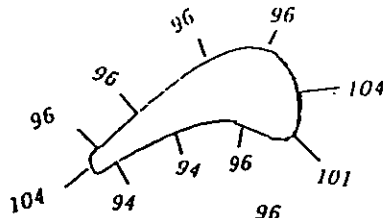
Typical RT22 platinum aluminide structure.
Pt rich outer layer (light etching), mid nickel aluminide (dark etching) and inner diffusion zone.

Figure 111

Westinghouse TG20 2ND stage Bucket Platinum Aluminised to RT22LT

Serial No. K01526

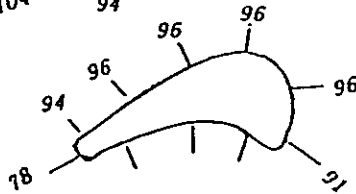
Section A



Upper Aerofoil

Pt 51.2 wt% Al 20.5 wt%

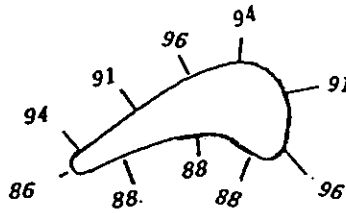
Section B



Mid Aerofoil

Pt 49.3 wt% Al 20.7 wt%

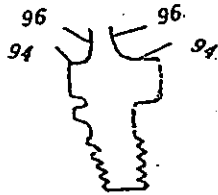
Section C



Lower Aerofoil

Pt 47.0 wt% Al 20.9 wt%

Section D

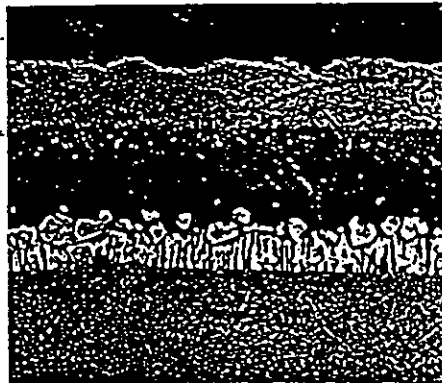


Root Section

Note: Measurements of total coating thickness

μm

Coating Structure



x400
etched
(marbles)

Typical RT22 platinum aluminide structure.

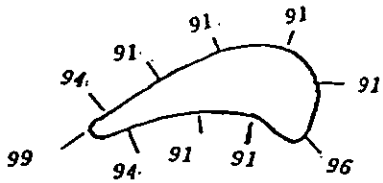
Pt rich outer layer (light etching), mid nickel aluminide (dark etching) and inner diffusion zone.

Figure 112

Westinghouse TG20 2ND Stage Bucket Platinum Aluminised to RT22LT

Serial No. K01664

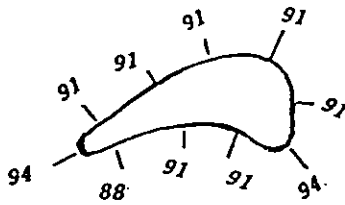
Section A



Upper Aerofoil

Pt 47.0 wt% Al 20.1 wt%

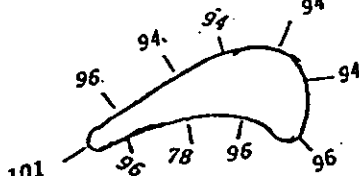
Section B



Mid Aerofoil

Pt 41.0 wt% Al 20.5 wt%

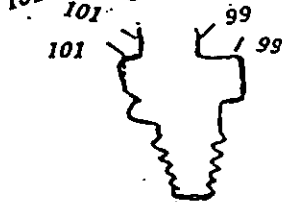
Section C



Lower Aerofoil

Pt 43.9 wt% Al 21.0 wt%

Section D

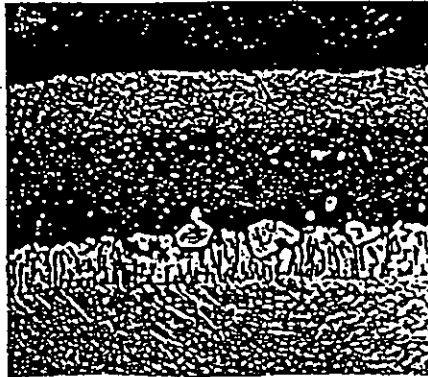


Root Section

Note: Measurements of total coating thickness

μm

Coating Structure



x400
etched
(marbles)

Typical RT22 platinum aluminide structure.
Pt rich outer layer (light etching), mid nickel aluminide (dark etching) and inner diffusion zone.

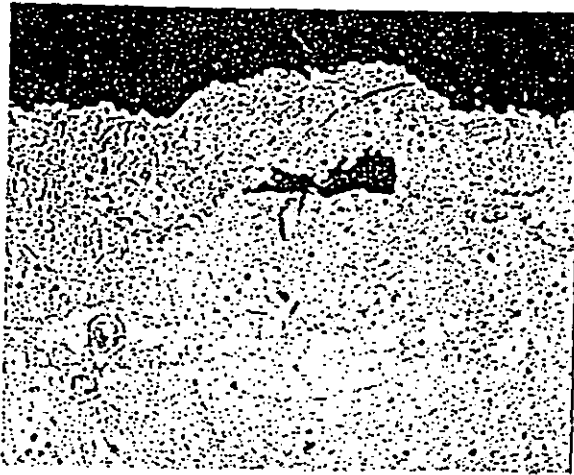
Figure 113

Illustrates coating thickness and chemical composition observed on U500 test tabs

	Test Piece ID	Thickness	Pt wt%	Al wt%
Retort 1	1	0.0040"	46.7	20.2
	2	0.0030"	45.9	20.8
Retort 2	1	0.0038"	43.4	20.1
	2	0.0032"	45.6	21.0

Figure 113. Continued

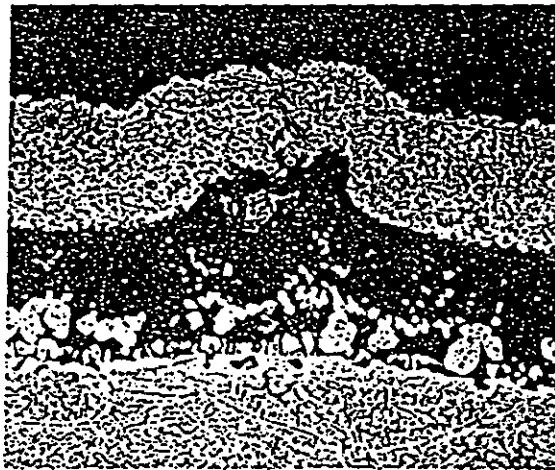
Photomicrograph 1.



x400
as polished

Typical Void Defect

Photomicrograph 2



x400
as polished

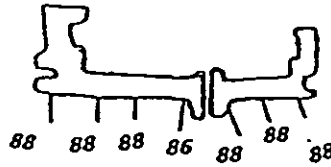
Typical Void Defect

Figure 114

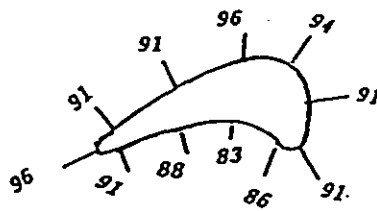
Westinghouse TG20 1st Stage Vane Rh and Pt Aluminized to RT44

Serial No. IH 981

Outer Platform

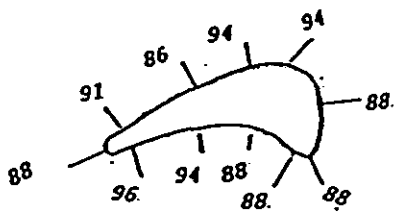


Upper Aerofoil



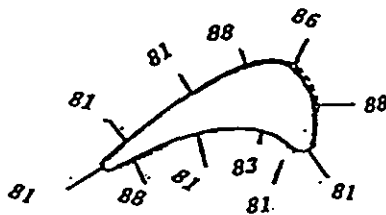
Pt 48.4 wt%
Al 28.4 wt%
Rh 3.6 wt%

Mid Aerofoil



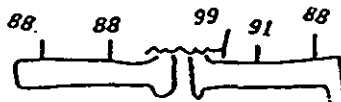
Pt 47.2 wt%
Al 30.0 wt%
Rh 3.4 wt%

Lower Aerofoil



Pt 45.0 wt%
Al 29.0 wt%
Rh 3.8 wt%

Inner Platform



Note: Measurement are of total coating thickness μm . All chemical compositions are measured at the mid chord concave position

Figure 114. Continued



x400
etched
(marbles)

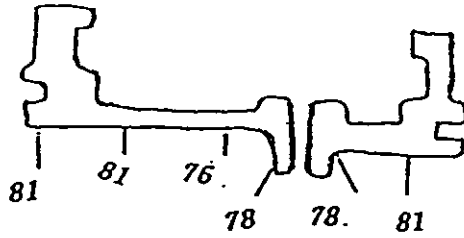
RT44 structure exhibiting outer precious metal rich layer (light etching)
transforming to nickel aluminide layer (dark etching)

Figure 115

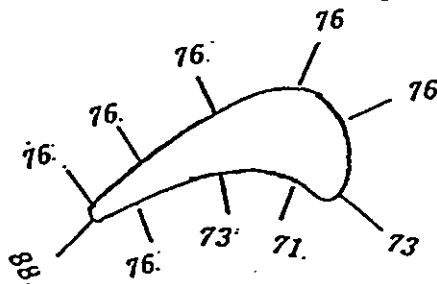
Westinghouse TG20 1st Stage Vane Rh and Pt Aluminised to RT44

Serial No. IH 5042

Outer Platform

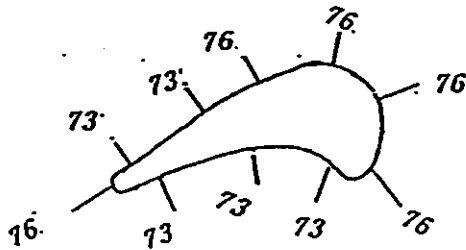


Upper Aerofoil



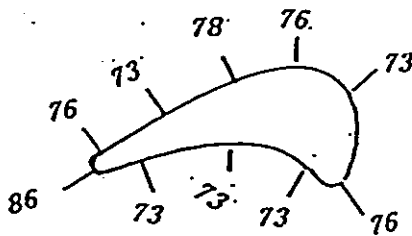
Pt 56.2 wt%
Al 25.3 wt%
Rh 4.0 wt%

Mid Aerofoil



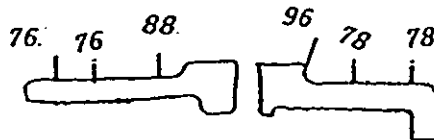
Pt 55.4 wt%
Al 27.2 wt%
Rh 4.4 wt%

Lower Aerofoil



Pt 53.7 wt%
Al 29.9 wt%
Rh 4.2 wt%

Inner Platform



Note: Measurement are of total coating thickness μm . All chemical compositions are measured at the mid chord concave position

Figure 115. Continued



x400
etched
(marbles)

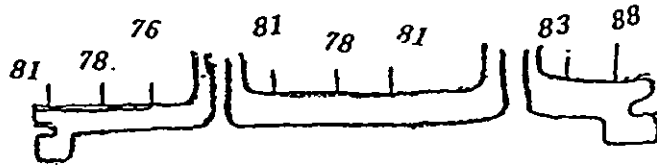
RT44 structure exhibiting outer precious metal rich layer (light etching)
transforming to nickel aluminide layer (dark etching)

Figure 116

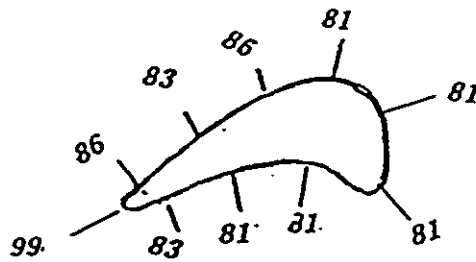
Westinghouse TG20 Stage Vane Rh and Pt Aluminised to RT44

Serial No. IHI KFS07

Outer Platform

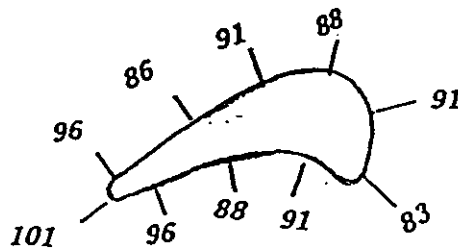


Upper Aerofoil
Vane 1



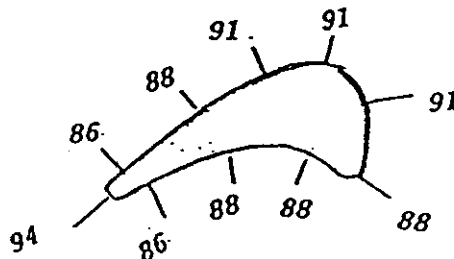
Pt 51.0 wt%
Al 27.0 wt%
Rh 3.5 wt%

Mid Aerofoil
Vane 1



Pt 54.5 wt%
Al 27.1 wt%
Rh 3.0 wt%

Lower Aerofoil
Vane 1



Pt 50.2 wt%
Al 28.0 wt%
Rh 3.1 wt%

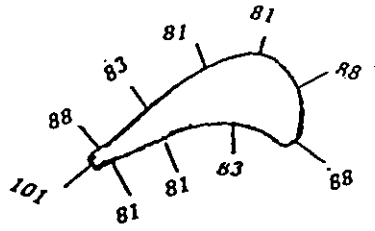
Note: Measurement are of total coating thickness μm .

For vane 1 concave aerofoil is inner surface

All chemical compositions are measured at the mid chord concave position

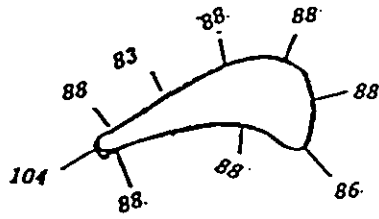
Figure 116. Continued

Upper Aerofoil
Vane 2



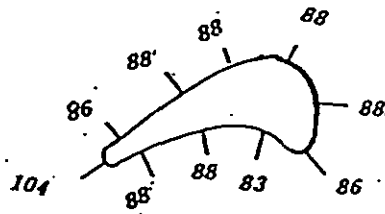
Pt 52.7 wt%
Al 28.7 wt%
Rh 3.1 wt%

Mid Aerofoil
Vane 2



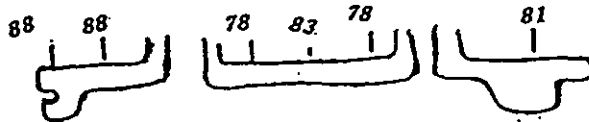
Pt 54.2 wt%
Al 27.8 wt%
Rh 3.5 wt%

Lower Aerofoil
Vane 2



Pt 49.2 wt%
Al 29.1 wt%
Rh 3.7 wt%

Inner Platform

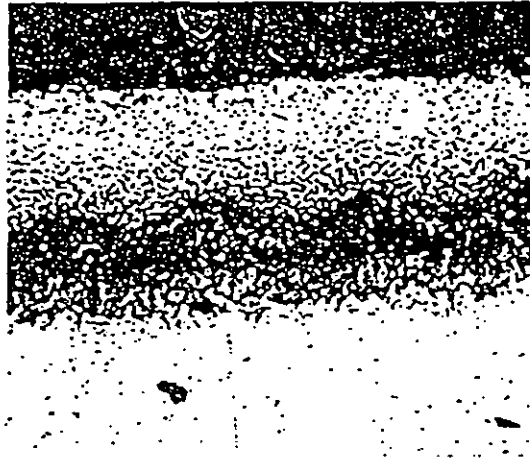


Note: All measurements are of total coating thickness μm .

For vane 2 convex aerofoil is inner surface

All chemical compositions are measured at the mid chord concave position

Figure 116



x400
etched
(marbles)

Vane 1. Mid chord concave position



x400
etched
(marbles)

Vane 2. Mid chord convex position

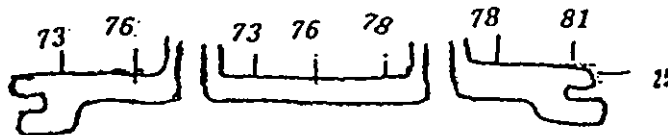
RT44 structure observed on vane 1 concave aerofoil, inner surface, and vane 2 convex aerofoil outer surface

Figure 117

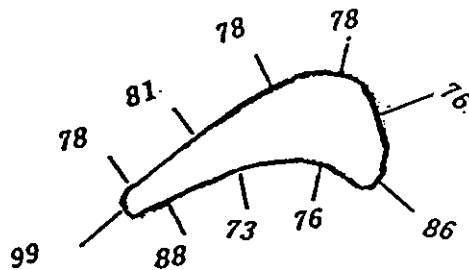
Westinghouse TG20 2ND Stage Vane Rh and Pt Aluminised to RT44

Serial No. SER 6278

Outer Platform

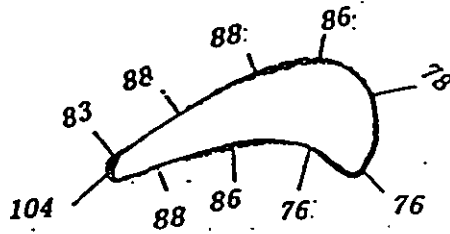


Upper Aerofoil
Vane 1



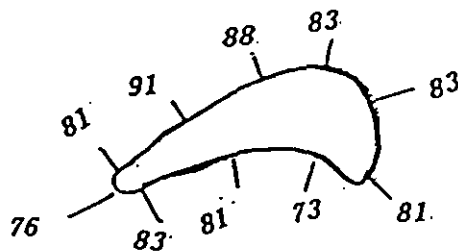
Pt 50.3 wt%
Al 26.1 wt%
Rh 3.0 wt%

Mid Aerofoil
Vane 1



Pt 46.0 wt%
Al 27.1 wt%
Rh 2.7 wt%

Lower Aerofoil
Vane 1



Pt 45.0 wt%
Al 28.0 wt%
Rh 3.4 wt%

Note: Measurement are of total coating thickness μm .

For vane 1 concave aerofoil is inner surface

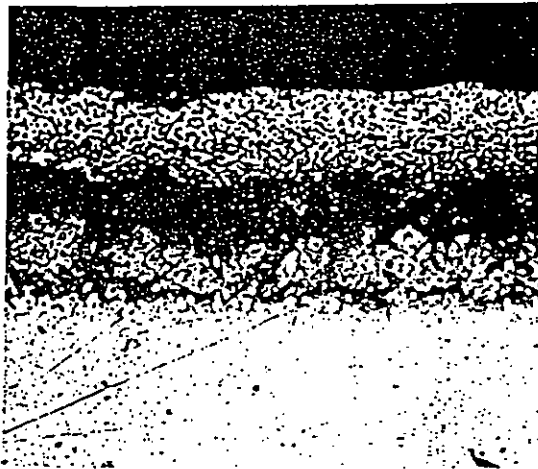
All chemical compositions are measured at the mid chord concave position

Figure 117



x400
etched
(marbles)

Vane 1. Mid chord concave position



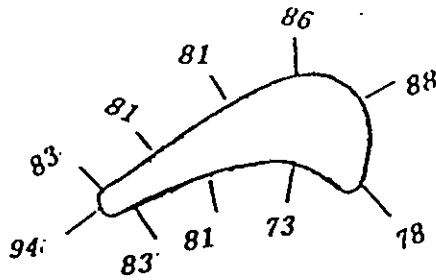
x400
etched
(marbles)

Vane 2. Mid chord convex position

RT44 structure observed on vane 1 concave aerofoil, inner surface, and vane 2 convex aerofoil outer surface

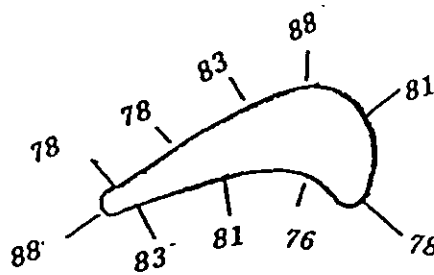
Figure 117. Continued

Upper Aerofoil
Vane 2



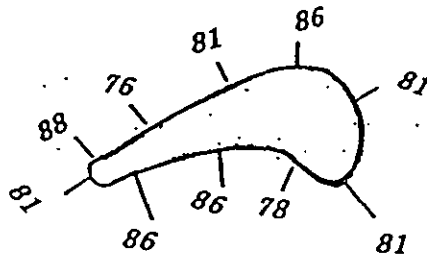
Pt 52.3 wt%
Al 31.0 wt%
Rh 3.5 wt%

Mid Aerofoil
Vane 2



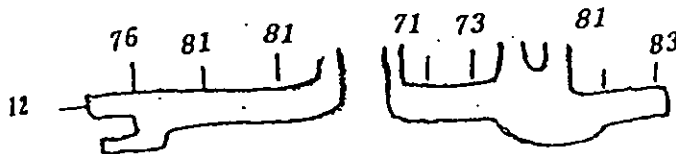
Pt 51.0 wt%
Al 29.2 wt%
Rh 3.1 wt%

Lower Aerofoil
Vane 2



Pt 49.9 wt%
Al 30.6 wt%
Rh 3.9 wt%

Inner Platform



Note: All measurements are of total coating thickness μm .

For vane 2 convex aerofoil is inner surface

All chemical compositions are measured at the mid chord concave position

Figure 118

Coating parameter observed on X45 test tabs

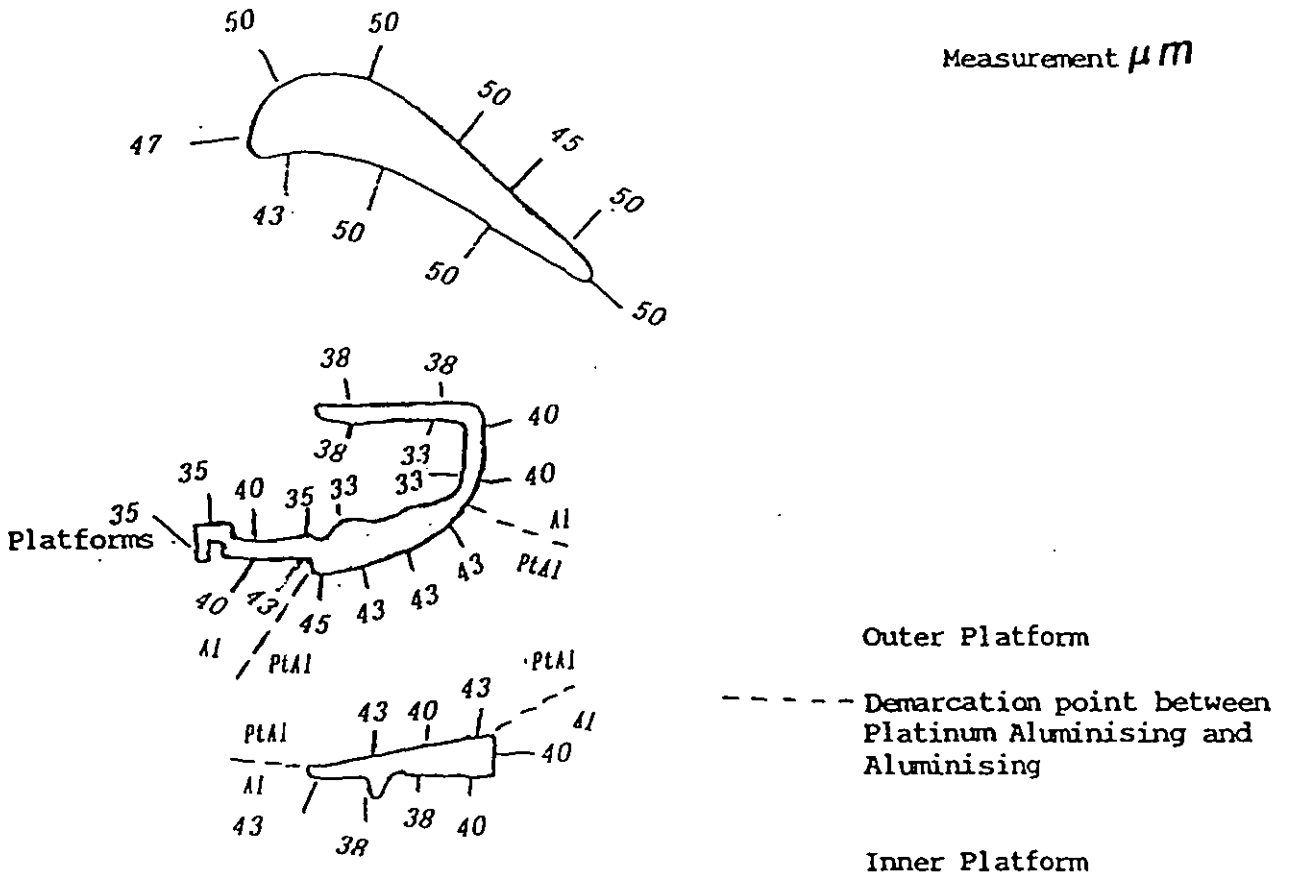
	Coating Thickness	Coating Chemistry		
		Pt wt%	Al wt%	Rh wt%
Retort A	0.0036"	52.5	29.7	6.5
Retort B	0.0035"	50.6	28.2	4.9
Retort C	0.0036"	54.2	27.4	5.6
Retort D	0.0036"	54.0	31.3	5.0

Figure 119

Metallographic Examination

Coating Thickness Profiles

Aerofoil



The observed Platinum Aluminide thickness, range of 40 to 53 μm is below the desired 50 to 75 μm range. The short fall in coating thickness is felt due to a powder problem and that moving to a more high controlled specialist powder will overcome this problem.

Figure 120

