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AGITATION FOR THE ELECTRODEPOSITION OF PRINTED CIRCUIT BOARDS

by

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This thesis is submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy of the Loughborough University of Technology

September 1990

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And above all, I am thankful to God for all his mercy.
DEDICATION

"There is no greater investment than that on human beings".

This has been Mum and Dad's priority.

Today this noble course is advanced by my brother, J.E. Amadi, to whom I dedicate this piece of work.

* * * * *
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**NOMENCLATURE**

- $A_c$: effective area of the cathode electrode (cm$^2$)
- $A_r^*$: Archimedes number (=$d^3g\Delta \rho/\nu L^2\infty$)
- $A_r^{**}$: Archimedes number (=$db^3g/\nu L^2(1-\varepsilon)$)
- $\overline{AR}$: average bubble size (cm)
- $a$: amplitude of vibration (mm)
- $C$: constant for all distributors
- $c'$: concentration of suspended particles
- $C_0$: concentration of copper sulphate solution (mol cm$^{-3}$)
- $C_x$: concentration of ions at the interface (mol cm$^{-3}$)
- $c_E$: concentration in the immediate vicinity of electrode surface (mol cm$^{-3}$)
- $c_0$: bulk concentration (mol cm$^{-3}$)
- $D$: diffusion coefficient of metal ion (cm$^2$s$^{-1}$)
- $D$: dielectric constant of the medium
- $D_b = db$: bubble diameter (cm)
- $D_0$: orifice diameter (cm)
- $d_1$: electroplating tank diameter (cm)
- $d = d_2$: agitator disc diameter (cm)
- $d_{bc}$: bubble critical diameter (cm)
- $de = deq$: volumetric - equivalent diameter (cm)
- $dc/dx$: concentration gradient diameter (cm)
E  applied potential

\( E_L \)  limiting potential

EF  enhancement factor

\( E_0 \)  Eotvos number \((= \frac{\rho_{Ldeq} g}{\delta i})\)

F  Faraday constant

f  frequency of bubble formation

g  acceleration due to gravity \((\text{cms}^{-2})\)

\( I_L \)  limiting current \((\text{mA cm}^{-2})\)

iL  limiting current density \((\text{mA cm}^{-2})\)

id  diffusion flux \((\text{cm}^2 \text{s}^{-1})\)

i0, A  constants related to metal deposition

K  distance between the far cathode and anode \((\text{cm})\)

K'  adsorption constant

\( K_L \)  mass transfer coefficient

M  mass of metal deposited \((\text{gr.})\)

\( N_b \)  number of bubbles per 648 cm\(^3\)

n  valency change, number of electrons

Q  volumetric rate of gas (air) flow \((\text{cms}^{-2})\)

r  radius of curvature \((\text{cm})\)

Re  Reynolds number \((=100ad/\nu_L)\)

\( Re_b \)  bubble Reynolds number \((=\rho_{L}U_{Bdeq}/\nu_L))\)

Sc  Schmidt number \((= \nu/D)\)
Sh \quad \text{Sherwood number (} = \frac{u_d}{nF\rho_d})

U_b \quad \text{rise velocity of bubble (cm/s)}

U_T \quad \text{terminal velocity (cm/s)}

V \quad \text{bubble volume size (cm$^3$)}

V_b \quad \text{total bubble volume (cm$^3$)}

V_o, B \quad \text{constants related to particle deposition}

W \quad \text{atmospheric weight of particles in deposit}

X \quad \text{denominator used in calculation (648 cm$^3$)}

Z \quad \text{zeta potential}

\varepsilon \quad \text{gas (air) voidage fraction}

\alpha \quad \text{volume fraction of particles in deposit}

\eta \quad \text{overpotential}

\sigma \quad \text{effective diffusion layer thickness}

\sigma_N \quad \text{Nernst diffusion layer thickness}

\sigma_s \quad \text{surface tension}

\sigma_i \quad \text{interfacial tension for the gas-liquid film}

\rho_L \quad \text{density of liquid (g cm$^{-3}$)}

\rho_g \quad \text{density of gas (air) (g cm$^{-3}$)}

\Delta \rho \quad \text{density difference (}=\rho_L-\rho_g\text{)} (g cm$^{-3}$)

\rho_\infty \quad \text{average density of the two-phase system (g cm$^{-3}$)}

\nu_L \quad \text{liquid kinematic viscosity (cm$^2$s$^{-1}$)}

\nu_g \quad \text{gas (air) viscosity (cm$^2$s$^{-1}$)}
\( \mu \) \hspace{1cm} \text{coefficient of viscosity of the medium}

\( \theta_\omega \) \hspace{1cm} \text{wake angle (in degree)}
A detailed study of the characteristics of vibratory and air agitation including cathode reciprocation methods for electrodeposition processes and their application for plating of composites and printed circuit boards has been carried out.

A study has been carried out employing a vibratory motor, offering amplitudes of 0-4 mm at 50 Hz, in acid copper sulphate as a model electrolyte in which α-Al₂O₃ particles are suspended for co-deposition yielding a composite electrodeposit. Using a horizontal disc vibrator at the bottom of the container, perforated discs have been shown to give superior agitation and a laminar/turbulent transition has been identified. Incorporation of particles is a maximum at the transition. In the laminar regime $Sh \sim Re^{0.037}$ and in the turbulent regime $Sh \sim Re^{0.82}$. Mass transport enhancement was measured for a variety of disc and tank diameters and enhancement factors for electrodeposition of 3-40 times for vibratory agitation were obtained, as against 1-2 times for air agitation.

In tanks agitated by air bubbles, it was found that the enhancing effect of air bubbles on the mass transfer coefficient is a function of the gas voidage fraction, irrespective of the absolute values of the liquid flow velocity, the gas flow rate and the gas distributor employed.

A sensor based on limiting current density characteristics of a wire tip electrode has been shown to be capable of measuring local variations of agitation and its effect on coating thickness variations during electrodeposition. The effectiveness of agitation is expressed as an enhancement factor.
CHAPTER 1
INTRODUCTION

Electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties or dimensions different from those of the basis metal is of vital importance in modern technology. The need for materials having an ever increasing wear resistance or corrosion resistance is a challenge in the field of materials science, engineering, design and development. There are many engineering applications for electrodeposited coatings, one of which is the use of copper coatings as overlays for printed circuit boards (PCB).

Copper is an excellent conductor of electricity and is therefore basic to such items as printed circuits and communications equipment including conductors and connectors.

This work is concerned with effects of agitation (vibratory and air) during electrodeposition processes especially those related to electronic component production. In this study emphasis is on optimisation of turbulent motion (flow) to maximise and enhance mass transfer rates. It is an electroplating process operated on a conducting substrate or medium. This is done taking cognizance of the agitation plates' size and its geometric dimension in relation to the bath (tank) size.

Agitation is by far the most effective way of increasing rates of electrodeposition as well as general mass transfer. Typically, agitative flow can reduce the diffusion layer thickness by over 100 times, for example, from 0.5 mm to 0.005 mm and consequently increase
rates by approximately that amount. However, the effectiveness of agitation depends not only on the rate of agitation but on the flow regime generated. From the analyses of the data obtained, laminar/turbulent transition regions are clearly perceptible. Turbulent regime (flow) being more effective than laminar regime (flow). The onset of turbulence occurs at a critical velocity or Reynolds number which is influenced primarily by geometrical considerations of the fluid motion, tank diameter, agitator disc and volume of electrolyte in the tank.

Vibratory agitation is applied through a vertical cylindrical shaft and horizontal agitator disc at the bottom of the tank which are electrochemically inert and the agitative effectiveness studied using mass transfer techniques just above the vibratory agitation disc. Agitation is achieved by the use of a vibromixer motor operating at mains frequency (50 Hz). Copper is being used as the electrodeposit metal, for modelling reasons and as a printed circuit board constituent.

Mass transfer analyses are generally valid because commercial processes are usually operated at fixed fractions of the limiting current densities for any given metal/solution combination, for example, $0.25 < \frac{I}{I_{L}} < 0.65$ for acid copper deposition [1]. However, other reasons for agitation do exist and must always be considered:

1. To avoid stagnation, disperse products and transport reactions.
2. To increase electrodeposition rates for stirring of the electrode diffusion layer.
3. To promote heat transfer between the agitated liquid and a heat-exchange surface and thereby equilibrate the deposit produced.
4. To incorporate particles in the deposit, promote mass transfer, produce uniformity, or to initiate and assist chemical reaction and thereby yield composite coating.

5. To modify the deposit characteristics, typically grain size hardness and strength.

Practically, agitation can be achieved in several ways in either the liquid phase or the solid phase. These include solution agitation by air sparging, mechanical movement work, solution pumping or jetting and the cathode can be moved by slow mechanical oscillation, barrelling, rotation or vibratory.

A characteristic study of air agitation was carried out for comparative purposes with vibratory agitation, so as to establish the validity of vibratory agitation methods in an electrodeposition process. Air agitation is often used in industrial processes such as steelmaking, ferroalloy production, electrodeposition, etc. This mode of agitation has been proposed for the enhancement of mass transfer and as a means of improving the yield of electrochemical cells [1-3]. The effectiveness of these operations - in promoting gas-electrolyte reactions and/or enhancing bath stirring is linked to the degree of dispersion of the air in the bath, the residence time or velocity of the air bubble as well as its size. A considerable body of work, primarily concerned with bottom-centred upward injection, has been undertaken on the fundamentals of these phenomena [4-17].

The ultimate objective of the investigation is to obtain a general correlation of gas dispersion, degree of mass transfer by way of enhancement factor (EF) and deposit thickness distribution profile on printed circuit boards in the electrodeposition process.
CHAPTER 2
SOLUTIONS FOR ELECTRODEPOSITION OF COPPER

2.1 COPPER SULPHATE PLATING BATH

Acid copper plating solution is probably the simplest of all commercial electrolytes and consists of copper sulphate and sulphuric acid. Copper sulphate (\(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\)) for copper plating should contain, according to British Standards BS 2867: 1957, at least 24.9 per cent copper, and must be free of impurities, such as chromates, nitrates as well as organic compounds. Maximum impurity limits of other radicals such as nickel, iron, chloride, etc should be as low as 0.3, 0.075, 0.02, per cent respectively. While the copper sulphate is the source of cupric ions (\(\text{Cu}^{++}\)), deposits from a neutral solution of copper sulphate alone are spongy and contain basic salts. Formation of cuprous oxide on the cathode, reduces cathode efficiency [30] and free acid is necessary to improve the conductivity and to produce coherent deposits.

2.2 FLUOBORATE COPPER PLATING BATH

The solubility of copper in the fluoborate bath is almost twice that in the sulphate bath which can thus be operated at extremely high current densities. Its applications are more particularly for electroforming and the production of gramophone records matrices, electrolytes and photogravure printing cylinders.

The British Standard - BS 2657: 1956 stipulates the percentage composition of copper fluorate solution to be at least 12.5 per cent (wt) of copper and maxima of 1.0 per cent silica (calculated as \(\text{SiO}_2\)).
2.5 per cent sulphate (as SO₄) and 0.2 per cent iron (as Fe). The amount of free acid in the solution of copper fluorate should not exceed 2 per cent by weight (as HBF₄) while the boric acid concentration (as H₃BO₃) should be between 0.75 and 3.75 per cent by weight.

Typical solution compositions are given in Table 1, in which Baths I and II are respectively "low" and "high" concentration electrolytes specified by Safranek and Winkler [31], while Bath III has been described by Struyk [32]. The function of the boric acid being that of a buffer, helping to keep the pH stable. The acidity is important for, if the pH is above 1.7, the deposit tends to be brittle and may be dark in colour.

The fluoborate plating bath produces finer-grained and smoother deposits than the sulphate electrolyte and in most cases addition agents are not essential.

2.3 **THE CYANIDE COPPER PLATING BATH**

The cyanide bath is the most widely used solution for general copper plating. This is because of some of its advantages over other copper plating solutions which include the following:

a) simplicity of operation  
b) relatively low cost  
c) excellent throwing power.

However, cyanide has some disadvantages which tend to be outweighed by the above advantages; these are:
i) limited maximum current density
ii) health hazards and effluent disposal problems.

The main constituents of the cyanide copper plating bath are copper cyanide (CuCN) and sodium cyanide (NaCN). These form a series of soluble complex salts in the following manner:

\[
\text{CuCN} + \text{NaCN} \rightarrow \text{NaCu(CN)}_2
\]

\[
\text{NaCu(CN)}_2 + \text{NaCN} \rightarrow \text{Na}_2\text{Cu(CN)}_3
\]

\[
\text{Na}_2\text{Cu(CN)}_3 + \text{NaCN} \rightarrow \text{Na}_3\text{Cu(CN)}_4
\]

According to the British Standard BS 2884: 1957, copper cyanide for electroplating should contain at least 69.0 per cent copper and 27.5 per cent cyanide (as CN). The impurity content limits are 0.05, 0.15 and 0.4 per cent for iron, insoluble matters and chloride respectively.

Copper cyanide plating baths operate at relatively high current density with agitation, but at higher current densities the cathode efficiency is greatly diminished and the risk of burning is increased. Similarly, the cathode efficiency decreases with increasing free-cyanide concentration but increases as the copper content concentration is raised. Temperatures vary with solution composition but usually lie between 49° and 77°C. The higher the temperature, the higher the permissible current density and, within limits, the cathode efficiency.
In Table 2 are some important characteristics of copper plating solutions, while Tables 3 and 4 show the compositions, process conditions of solutions for electrodeposition of copper and its alloys respectively. Comparative representation of copper sulphate and copper fluoborate plating solutions and acid copper sulphate with alkaline copper cyanide are shown in Tables 5-8.

2.4 **PYROPHOSPHATE COPPER PLATING BATH**

Pyrophosphate is well established as an important commercial process. It is widely used for plating on zinc-based die castings, on steel and on aluminium alloys, both for decorative applications and as a stop-off in the hardening of steel. It is also suitable for plating printed circuit boards [33,34] and has been used for plating copper on steel wire [35]. In recent years, the pyrophosphate bath has come into extensive use for electroforming and is an intermediate between the cyanide and acid copper baths although, in practice, differences in plating speed are not great. Deposits are of fine grain size, semi-bright and particularly easy to polish. By means of addition agents, fully bright deposits can be plated. Pyrophosphate baths have the advantages of avoiding the problems associated with the disposal of cyanide waste and the anodes need not be bagged. Its main disadvantage is that it is necessary to apply a preliminary cyanide copper strike deposit on zinc alloys, though on steel a more dilute pyrophosphate strike bath is satisfactory. It is expensive compared to the cyanide bath and cannot compete in cost with the acid bath.

The most commonly used bath contains potassium copper pyrophosphate, a highly soluble complex which is formed by reaction between copper and potassium pyrophosphates and which has been isolated as the hexahydrate, K_6Cu(P_2O_7)_2·6H_2O. In solution, the copper is present as
the complex \( \text{Cu}(\text{P}_2\text{O}_7)_2^{-6} \) ion. The ratio of pyrophosphate to copper \( (\text{P}_2\text{O}_7: \text{Cu} \text{ ratio } = 5.48:1) \) is essential and is considered as free phosphate. Practically, a ratio of pyrophosphate to copper of 7 or 8 to 1 is recommended. In some baths \([36, 37]\) which are operated at pH 9.3 and about 1-10 A/dm\(^2\) disodium orthophosphate is added and this helps to maintain good anode corrosion. A formulation for a patented addition agent used is:

\[
\begin{array}{c}
\text{N - N} \\
\text{S - C - C} \\
\text{S}
\end{array}
\]

in which \( R \) is either hydrogen or a metal atom \([38]\). Other addition agents, which have been proposed include trioxyglutaric acid and with sodium selenite (up to 7 g/l and 0.002-0.004 g/l) \([39]\) respectively, and also ammonia and tertiary amines \([40]\).

The hydrolysis of orthophosphates is a danger if its concentration exceeds 95-100 g/l. This is minimised by operating at a higher pH, for example, between 8.5 and 9.0 \([41]\).

The pyrophosphate copper bath is very suitable for plating of printed circuits and steel wire at high current density. This has been found to improve the adhesion and reduce the grain size of a subsequent copper deposit from an acid bath \([35]\).
2.5 COPPER ELECTRODEPOSITION

2.5.1 Electrodeposition of Copper From Acidic Electrolytes
The electrodeposition of copper from acidic electrolytes has wide commercial applications in the electroforming and electroplating industries and also has applications in the production of copper powders and in the electorefining industry.

Some examples of copper electroforms include electrotypes, gramophone records, heat exchangers and, more recently, the production of waveguides for microwave applications. A major application for electroplated copper was that it was often used as an undercoat underneath nickel/chromium layers on some car parts. Acid copper solutions containing organic brightening and levelling agents have very good levelling properties and acid copper deposits are frequently used as an undercoat in order to eliminate polishing or buffing, however the development of very high levelling nickel electrolytes has reduced the use of acid copper in this area.

Acid copper electrolytes became very important with the advent of the microelectronics revolution and the developing need for more complicated printed circuit boards as component packing densities increased. It was no longer possible to produce printed circuit boards with all of the interconnects printed on one side of the board so double sided boards were developed where the patterns on both sides of the board were connected by plating copper through the holes. This was achieved by activating the laminate in the holes using a palladium colloid catalyst, plating a thin layer of electroless copper on the activated surface and building up the thickness of copper in the hole using electrodeposited copper. In order to deposit an even thickness of copper in the holes, a solution with high throwing power was
necessary. This resulted in the use of cyanide copper electrolyte as it has a good throwing power but is not suitable for printed circuit board production because the highly alkaline solution causes degradation of the epoxy laminate. Then the pyrophosphate electrolyte rapidly became an alternative as the electrolyte to use for these purposes because the sulphate based copper electrolytes had very poor throwing power.

As the demands of the electronics technology became greater and multilayer boards were produced, the limitation of the pyrophosphate electrolyte became evident. This is because the electrolyte was very sensitive to very small amounts of organic impurities which caused "skip" plating and brittle deposits which subsequently cracked when components were soldered to the board. To overcome these problems, supply houses developed highly throwing power sulphate based acid copper electrolytes with a high acid/low metal formulation. Also, stable organic additives were developed which could withstand the high acidity levels of the electrolytes and gave the required deposit structure and ductility to withstand the thermal shock imposed on the deposits when the boards were soldered. These sulphate-based electrolytes rapidly replaced the pyrophosphate electrolytes and this became standard in the industry for circuit board production.

The need to use mounted components in the electronics industry in order to further increase component packing density became the order of the day. With this technology, the holes in the boards are only to connect the circuit and are no longer required for component leads. Thus, holes are produced which are very small and this causes even copper thickness distribution problems. The throwing power of the acid copper electrolytes available at the present are not sufficient to
plate these through-holes satisfactorily. The one solution to this problem is to use electroless copper to deposit the entire thickness of copper required (20-25 μm). Electroless copper solutions which are capable of achieving this have to be very stable and produce a copper deposit which can meet the stringent thermal shock requirements. In order to achieve this, the plating rate of these solutions is very slow and causes large scale production difficulties. Because of the impracticality of building the entire thickness of copper with an electroless solution (too slow and too expensive, usually producing low purity copper), ways are being sought to improve the throwing power of acid copper electroplating solutions. This constitutes one of the major aims of this thesis.

2.5.2 Initiation, Growth and Morphology of Electrodeposited Metal

Mechanisms of electrodeposition of metal by cathodic reduction of metal ions followed by crystallisation into a growing lattice have been investigated and proposed by many researchers [23, 24]. Hydrated metal ion, $M(H_2O)_x^{n+}$, is transported from the bulk solution to the outside of the double layer through the diffusion layer on the cathode surface. Water molecules may be moved sequentially and the ion discharges to deposit an adatom, $M_{ad}$, at the active site on the cathode surface.

The morphology of electrodeposited metal depends greatly on the operating conditions and can be classified into various types. Some types of deposit differ greatly from those obtained by non-electrochemical processes, due to different mechanisms for initiation and growth of the metal crystal. The adatom moves on the cathode surface or step towards special sites such as edges and kinks according to Bockris [23]. It is considered that the formation of a nucleus on the step is somewhat difficult until most of the edges.
and/or kinks are filled up. Spiral growth may appear when the crystal growth proceeds along a screw dislocation. This type of crystal growth occurs frequently.

Examples of many types of crystal growth of electrodeposition of metals are as follows:

1. Pyramids
2. Layers
3. Blocks
4. Ridges
5. Cubic layers
6. Spiral
7. Whiskers
8. Dendrites

According to Bockris, types 3 through to 8 are considered to be modifications of types 1 and 2 [23]. If a polycrystal grows with systematic orientation, a macroscopic repetition of pattern, or texture, may appear on the cathode surface.

Morphology of electrodeposits is affected by several factors such as the solution composition including the pH and impurities, the operating temperature, the flow rate of the electrolyte, the cathode potential and overvoltage, the current density, and the substrate. In the case of copper deposition, for example pyramids are obtained at relatively low current densities, while at high current densities, layers or polycrystalline deposits are obtained [23].
Since the local current density at the peaks of a cathode with a rough surface is larger than the average current density, the rate of electrodeposition is large compared to the average rate. By the same token, the deposition rate in the valleys between peaks on the rough surface is minimum. Consequently, the surface roughness is increased by electroplating.

2.6 THE MECHANISM OF DEPOSITION FROM THE ACID COPPER ELECTROLYTE

Copper forms two series of compounds: monovalent and divalent, cuprous and cupric - or, in more modern terms, copper (I) and copper (II). Both series form many complexes. In aqueous solution the divalent state is much more stable, and copper (I) tends to disproportionate to copper metal and copper (II) ion:

$$2 \text{Cu}^+ \rightarrow \text{Cu} + \text{Cu}^{2+}$$

The sulphate based electrolyte will be considered as the mechanism for the deposition of copper from an acid electrolyte is relatively straightforward.

2.6.1 Electrolyte Reduction of the Cupric Ion

In acidic solutions the copper (II) ion is usually present as the aquo ion. However, solutions of copper sulphate are slightly acidic due to the polarising nature of the copper (II), this is due to the following reaction:

$$\text{Cu(H}_2\text{O)}_4^{2+} \rightarrow \text{Cu(H}_2\text{O)}_3^{+} (\text{OH})^{+} + \text{H}^+$$

From the standard electrochemical series viewpoint, copper is more noble than hydrogen and so would be expected to deposit with a cathode efficiency of 100 percent so far as the mass transport does not impose limitations.
As a result of the transfer of two electrons to the copper ion, reduction occurs at the cathode surface:

\[ \text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \]  (3)

\[ \text{Cu}^+ + e^- \rightarrow \text{Cu} \]  (4)

At low current densities copper can be deposited from solutions containing only copper sulphate. However, at higher current densities, reaction (2) will result in codeposition of basic salts and this gives rise to a spongy deposit. The addition of sulphuric acid to the electrolyte has been found to prevent this phenomenon and allows the deposition of smooth and acceptable deposits, improved conductivity and helps to prevent hydrolysis of the copper salts, precipitating copper hydroxide (or hydrated copper oxide). In the sulphate bath increased copper concentration leads to increased resistivity of the bath and cathode polarisation increases somewhat when the copper concentration is above 1M (65 g/l Cu or 250 g/l CuSO\(_4\).5H\(_2\)O). However, if the copper sulphate concentration is less than about 60 g/l, the deposit quality may deteriorate slightly. Sulphuric acid decreases the solubility of copper sulphate by the "common ion" effect. Because the copper (II) ion is so easily reduced, problems are encountered when plating active metals such as steel and zinc die castings, because an immersion deposit of copper is easily formed:

\[ \text{Fe} + \text{Cu}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cu} \]  (5)

This immersion deposit tends to have poor adhesion and causes the deposit to lift after plating. A "strike" deposit from a cyanide based electrolyte is required in these cases.
2.6.2 Anodic Reactions
Copper anodes in sulphate solutions may become coated with films containing finely divided copper and copper oxide particles. This generally occurs at high current densities. Disproportionation of Cu(I) to metal and Cu(II) ions may also lead to fine particles in the anode, causing intergranular corrosion and cathode roughness. Anodes can also dissolve very unevenly in acidic electrolytes.

Bagging of anodes is one method by which the transfer of such particles to the cathode surface can be avoided. Addition of phosphorus, in amounts from 0.02 to 0.04 per cent, is claimed to increase the tenacity of the anode film and prevent the dislodgement of particles into the electrolyte. A small amount of chloride in the electrolyte can promote even dissolution of anodes and is required in electrolytes containing addition agents especially for these to function efficiently. However, an excess of chloride ion may give rise to a film of sparingly soluble copper (I) chloride on the anode which can again cause passivation.

2.6.3 Conductivity, Cathodic Polarization and Throwing Power
The plating bath is practically always an aqueous solution containing a compound of the metal to be deposited. Every plating bath contains ingredients which serve one or more of the following functions:

1. To provide a source of the metal or metals being deposited.
2. To form complexes with ions of the depositing metal.
3. To provide conductivity.
4. To stabilise the solution, for example, against hydrolysis.
5. To act as a buffer, that is, to stabilise the pH.
6. To modify or regulate the physical form of the deposit.
7. To aid in dissolving the anodes.
8. To modify other properties, either of the solution or of the deposit, peculiar to the specific case.
This does not mean that all plating baths contain eight ingredients, since some compounds perform more than one of these functions, and in some instances not all the listed functions are necessary. When current is passed from an anode to a cathode through an electrolyte containing a depositable metal ion, the metal will deposit on the cathode, but frequently the deposit will be useless, consisting of trees and nodules, either non-adherent or non-coherent, unless additives are present to control its physical form. Because of the high acid content, acid copper electrolytes tend to have high conductivities. The copper ion is easily reduced. This means that the activation energy which needs to be supplied in order to reduce the ion is low, thus cathodic polarization tends to be very low in these electrolytes.

This in turn means that the throwing power of these electrolytes is very poor and generally closely approximates to a primary current density distribution [25]. As acid copper electrolytes were adapted for plating "through-holes" on printed circuit boards, ways had to be found to increase the throwing power of these electrolytes. This was achieved by using a high acid content to maximise the electrolyte conductivity and a low metal content in order to maximise cathodic polarization potential. Although these electrolytes gave good throwing power, the low metal content meant that agitation and current density and temperature control became critical and reduced the overall plating rate which could be used. The high acid content also presented problems for the supply houses because it was difficult to formulate brighteners which were stable in these electrolytes. In spite of these problems, these electrolytes have become standard for the production of printed circuit boards.
Modern acid copper electrolytes can be split into two types. The standard electrolyte is used for decorative and electroforming applications and the high throwing power electrolyte is most usually employed for the production of printed circuit boards, typical formulations are shown in Table 9.

2.6.4 Addition Agents

In the majority of electroplating processes for acid copper plating, addition agents are added to the electrolyte in order to modify the deposit properties. Addition agents may be used as grain refiners or brighteners, as levellers or to harden the deposits. Many commercial brightener systems are available for acid copper systems.

Early examples of addition agents used in acid copper electrolytes include gelatin and glycine. These agents were used as grain refiners. These molecules are adsorbed at the cathode surface and tend to increase cathode polarization because of this [26]. One of the first brightening agents used in acid copper electrolytes was thiourea [28]. However, this compound gives a limited bright range and its concentration is critical. Because of these problems, thiourea has been superseded by brighteners which are easier to control and which do not cause a deterioration in the properties of the electrodeposited copper.

Furthermore, an early example of an acid copper brightener was the use of the sulphonation products of aromatic compounds prepared by the reaction of toluene with thionyl chloride in the presence of anhydrous aluminium chloride and sulphuric acid [27,29], a version of this process was used commercially by W. Canning Ltd [42]. Many compounds have been patented as brighteners and it is not possible to give a comprehensive list here due to space limitations. The most modern
brightener systems usually consist of a polyether which acts as a grain refiner in synergistic combination with a sulphopropyl sulphide [43-47]. This combination of addition agents gives a stable brightener system with a few harmful breakdown products. In addition to these compounds, brightener systems may also contain levelling agents which act as diffusion controlled inhibitors. Typical examples of these levellers would be substituted thioureas or phenosafranine dyes.

The actual mechanism of brightening is little understood but levelling occurs because diffusion of the levelling agent to peaks on a microprofile is much faster than diffusion to the troughs. These organic molecules act as deposition inhibitors and so increase the activation energy (polarization overpotential) required to deposit metal at a given rate (current density). Thus, since the cathode is considered to be an equipotential surface, deposition rates are reduced on peaks because of the adsorption of the levelling agent which causes an enhanced deposition rate in troughs [48].

Edwards discussed possible mechanisms of addition agent incorporation [49-54] but the experimental work carried out by him was concentrated on the addition agents which are commonly used in nickel solutions. Some studies have been made of the incorporation of brighteners in copper deposits [55-57] but no systematic study has been undertaken. Thus, the mechanism of incorporation of modern copper brighteners has not been established. The effect of a number of addition agents on the cathode potential-current density curves for an acid copper bath is shown in Figure 1 [58].
2.7 THE STRUCTURE AND PROPERTIES OF ELECTRODEPOSITED COPPER

The physical, mechanical, and electrical properties of electrodeposited copper from acidic electrolytes have been comprehensively reviewed by Safranek [49]. By varying addition agent concentrations and formulations, copper deposits with various properties can be produced. Copper deposits usually have good ductility and elongation values of between 5 and 25 percent can be obtained. The tensile strength of the deposits usually varies between 200-400 N/mm² and hardness values of 50-200HV1 can be obtained.

2.7.1 Grain Structure of Electrodeposited Copper from Acidic Electrolytes

Deposits from the sulphate base electrolytes containing no addition agents are columnar in structure. Copper deposited from these electrolytes are randomly oriented f.c.c. crystals [50] unless deposited at current densities of less than 1.5 A/dm² when the basis metal can affect the orientation of the crystal structure [51].

Additions of gelatin, phenolsulphonic acid, and many other agents tend to produce a fibrous structure. This is essentially a modified columnar structure and usually is 15-20 percent harder than columnar copper produced from an additive free electrolyte. Modern additives produce fine-grained deposits. The production of copper deposits having this structure is particularly important for the production of printed circuit boards. This is because the deposit turns through 90° at the top of the hole in the board, and a columnar structure causes weakness at this point which can result in cracking of the deposit when components are soldered to the board, that is, when the board is subjected to thermal shock. Ductility is also of prime importance in printed circuit board production since the coefficient of thermal
expansion for epoxy/glass laminate is higher than that of copper. A ductile deposit of copper can elongate to accommodate this whereas a brittle deposit will crack. Thus, modern brightener systems developed for printed circuit board production are aimed at providing maximum ductility and an equiaxed grain structure.
CHAPTER 3
APPLICATION TO PRINTED CIRCUIT BOARD (PCB) TECHNOLOGY

3.1 PLATING INTO THROUGH-HOLES

During the past decade circuit board design and manufacturing has undergone a rapid evolution in the direction of higher circuit densities. A typical printed circuit board contains about 5 mils wide conducting lines and about 31 mils diameter through-holes spaced 100 mils apart [58-60]. Efforts are continuing towards narrower lines and spacing (~2 mils) and smaller holes (~15 mils in diameter) [61]. At the same time, more functional as well as non-functional inner copper layers are being incorporated into individual boards for increased circuit density and improved mechanical properties. It is common to see boards with more than 20, some even approaching 30, inner layers. This current trend towards multilayer design with narrow lines and spacings will inevitably lead to a significantly increased number of smaller through-holes and vias and will make reliability of copper plating processes one of the most critical factors governing the performance and cost of the advanced printed circuit boards. The consequence of this trend will be holes having a larger aspect ratio; defined as the ratio of board thickness to hole diameter. Then more stringent demands will be placed on the plating technology to assure satisfactory performance from the finished products.

Therefore, the purpose of this work is to improve upon the already existing copper plating method (technology) of through-holes and vias using the vibratory agitation method as innovation. However, no attempt will be made to differentiate between the two-sided and
multilayer printed circuit boards in this work, although multilayer boards are generally considered to pose a greater challenge in plating. Here, "through-holes" refers to holes drilled through the circuit board while the terms "vias" refers to blind holes; that is, holes that are connected to either the primary side or secondary side of a multilayer packaging and interconnecting structure but not to both sides.

In the economic evaluation of printed circuit boards, three process characteristics for copper electroplating of through-holes are considered important; they are:

1. deposit thickness distribution in through-holes, as it relates to the thickness on the board surface;
2. metallurgical structure of the copper deposits;
3. speed of the plating process.

However, the development of addition agents that are compatible with the high throwing power acid copper sulphate baths has greatly improved the metallurgical properties of the copper deposits, especially the ability to resist cracking in the plated through-holes during the solder float test. Generally, it is necessary that circuit boards especially plated through-holes have uniform copper thickness and that the surface-to-hole copper thickness ratio be as close as possible. Non-uniform thickness distribution inside the holes has detrimental effects, such as lowering of current-carrying ability, increased chances for cracking of copper deposits and difficulty during wire insertion through the holes.
Mass transport of electrolyte is a critical factor in any electroplating process. Efficient, uniform agitation is particularly important in circuit board plating for which organic additives, which operate under diffusion control [62] are usually used, and deposit properties are critical. Kessler and Alkire [63,64] and Engelmaier and Kessler [65] have shown that inadequate mass transport within through-holes leads to poor deposits from acid copper baths with or without additives. In both pyrophosphate [66,67] and acid copper [68] systems, deposit ductility can vary by as much as a factor of five or more with agitation rate at a constant additive concentration.

In spite of its importance, no reliable method has been available to measure electrolyte agitative mass transport in most production processes, so that development of bath agitation schemes has usually been based on intuition rather than scientific methods. For example, circuit board agitation schemes generally involve some combination of gas sparging and board motion, although based on the need to produce deposits of uniform thickness over the surface and in recesses. Mass transport provided by such schemes apparently varies by at least 50 percent over the board surfaces and considerably more within the through-holes. Consequently, printed circuit board quality is notoriously variable.

Sufficient agitation is a common requirement to all three scales of macroscale, miniscale and microscale. Plating at macroscale is dominated by the primary current distribution as long as sufficient electrolyte agitation at the cathode surface prevents the formation of significant gradients in the cupric ion concentration. For the
miniscale, characteristic of the region within and close to a plated
through-hole, current distribution, and thus the plating thickness
distribution is determined by the interaction of ohmic conduction,
charge transfer kinetics, and mass transfer conditions. On the
microscale, which encompasses effects on the scale of surface
roughness, deposit thickness and grain size, additives play a major
role. Additives affect the microlevelling capability of the plating
solution and determine the deposit morphology.

Therefore, the consequence of insufficient agitation is inadequate
mass transport which in turn results in large ion concentration
gradients at the cathodic surfaces. Mass transport limited plating
results in poor quality deposits and the conditions at which the
deposits occur at the cathode do not reflect the condition in the bulk
of the plating solution. For this reason agitation has always been an
important aspect in the electroplating of copper. Most commonly,
agitation is achieved by the discharging of air from sparging pipes
located beneath the cathodic workpieces near the bottom of the plating
tank. The rising bubbles impart velocity to the electrolyte close to
the cathodic surfaces. Thus, the surface boundary layer is reduced
and plating conditions are less likely to be mass transport limited.
For the plating of planar vertical surfaces, the agitation provided by
air sparging generally is good quality plating.

However, for multilayer circuit boards air sparging does not provide
sufficient agitation in the plated through-holes in many instances.
As a result, air sparging is sometimes supplemented by mechanical
agitation, and so the level of agitation in plated-through-holes
resulting from these modes of agitation is exceedingly difficult to
predict. Clearly, there is no doubt that mass transport in plated-
through-holes is enhanced by air sparging resulting from the random short duration pressure field variations creating localised pressure differences from one side of the multilayer board to the other as well as from mixing currents created by the bubble wake eddies, however, the equivalent plated-through-hole velocities are obviously small compared to the circuit board motion and even much smaller to vibratory agitation. Furthermore, the flow field or pattern generated by air sparging cannot be sufficiently described to determine the electrolyte velocities.

Vibratory agitation is developed to generate optimum electrolyte agitation. Hence, improved uniformity of mass transport and of course good quality deposits both on the surface and through-holes of a circuit board.

3.3 CHARACTERISTICS OF ACID COPPER SULPHATE DEPOSITS FOR PRINTED CIRCUIT BOARD APPLICATIONS

Acid copper plating solutions developed primarily for printed circuit boards exhibit high throwing power and produce 1:1 ratios for hole-to-surface thickness of deposits. Presently, these copper solutions are used to provide uniform thickness, levelling and good thermal shock resistance.

From the 1940s to the 1960s, copper pyrophosphate electroplating systems were used almost exclusively by the printed circuit board industry. The pyrophosphate bath was widely accepted because it had high throwing power [69] - the same thickness copper was deposited on the surface of the board and on the wall of a hole. Good throwing power is required for product performance and economic reasons. If
throwing power is inadequate, the minimum thickness requirement for
the hole will necessitate an increase in the surface thickness of
copper, thereby increasing cost. Additional costs will result from
increased use of copper etchants, difficulty in etching and subsequent
rejection of boards.

Uniformity of copper thickness in holes is important for acceptable
component insertion. Poor throwing power can result in non-uniform
thickness and unsatisfactory contact of components. Uniformity of
copper thickness across the surface of the board is also important.
Variation will cause preferential etching of copper and result in
undercutting of circuit lines.

Despite widespread early use, copper pyrophosphate systems pose
difficulty in operation due to the need for waste treatment, stringent
analytical maintenance and pyrophosphate hydrolysis to orthophosphate
requiring bailout. Should the orthophosphate concentration reach 100
g/l, the bath must either be diluted or discarded. Acid copper systems
exhibiting a 1:1 ratio of throwing power have been accepted by printed
circuit board manufacturers due to benefits that include elimination
of bailout, operation at room temperature, ease of control and ease of
waste treatment. Good throwing power, thickness distribution,
levelling stress and hardness, and resistance to thermal shock and
contamination are additional features responsible for the widespread
use of acid copper baths.

3.3.1 Throwing Power
Traditional acid copper baths used in decorative applications did not
meet the requirement of throwing power for printed circuit boards
[70]. Therefore, the concentrations of both copper sulphate and
sulphuric acid were modified. Table 10 compares traditional and high-throw acid copper electrolytes.

The key to good throwing power in acid sulphate systems is the ratio of acid to copper. A 10:1 ratio yields a 1:1 ratio for hole-surface thickness of the deposit. The recommended copper concentration in high-throw acid copper baths is above 15 to 23 g/l. Throwing power will decrease as the acid-to-copper ratio decreases. A minimum acceptable is 8:1. With less than 8:1 ratio, throwing power will suffer, and the effect will be proportional to the thickness of the board. The high acid to copper ratio solutions are very conductive so enabling recesses to be non-resistive in a polarisation sense. Figure 2 illustrates the comparative throwing power of traditional and high-throw acid copper systems [71].

3.3.2 Structure, Levelling and Thermal Shock
Additives are used in high-throw acid copper systems to impart certain desirable characteristics such as equiaxed grain structure, levelling and resistance to thermal shock. A widely used system consists of three additives: a carrying agent, levelling agent and ductility-promoting agent. Deposit structure is important because an equiaxed structure was found to be beneficial during thermal shock testing. Levelling is necessary to produce uniform thickness throughout the wall surface of the hole and to eliminate "foldover" in multilayer boards [72]. Poor levelling can also lead to thermal shock failures. Resistance to thermal shock is necessary to maintain copper continuity after reflow of tin in tin plating or solder plate on printed circuit boards. A "cracked" deposit can lead to a discontinuity (open) in electrical circuits.
All three additives contribute to equiaxed structure of copper [73]. The primary additive functions as a "carrier" to guide the other two components and create an equiaxed structure. The other components cannot function properly at an insufficient level of carrying agent, and striations can occur. Therefore the key to an efficient acid copper bath is the carrying agent. Original acid copper systems contained thiourea and related compounds as the carrying agents, but their stability in highly acidic media was poor. A major concern in synthesising a new carrying agent was to ensure its stability in the high-throw acid copper electrolyte.

The levelling agent helps the deposits smooth over bore surfaces and imperfections of drilled holes. This additive also increases copper coverage in deep drill tears. Figures 3 and 4 illustrate the role of the levelling agent, and Figures 5 and 6 show its ability to eliminate "foldover" in printed circuit boards [74].

Azo dyes have been used as levelling agents [75] but this may generate potentially harmful breakdown products or contaminate process solutions after dragout from plating racks. New levelling agents are polymers and do not stain the deposit or produce harmful breakdown products.

The third additive promotes ductility of the deposit and thereby enhances thermal performance. This additive will produce uniform corners and create a deposit with equiaxed grain structure that consistently passed thermal shock testing. Levelling, thermal shock resistance and equiaxed structure are maintained by proper replenishment of the additives. In general, all three additives are combined in an optimised blend to facilitate replenishment. In unusual
cases, special additive blends can be formulated. For example, with multilayer boards, a special blend is used to ensure acceptable thermal shock performance for boards with a 3.5:1 aspect ratio (depth to diameter) [73]. If drilling defects pose problems, the levelling agent can be favoured to increase copper coverage in deep drill tears. To accommodate bath temperatures exceeding 30°C (85°F), special additive blends have been formulated to compensate for increased conductivity.

3.3.3 Thermal Shock, Stress and Hardness
Because thermal shock has become a primary concern of manufacturers of printed circuit boards (PCB), the industry is looking for a means to predict acceptable performance. During a study to determine whether stress or hardness values can predict thermal shock performance four types of electrolytes were evaluated:

1. one without additives
2. one with a carrying agent and a levelling agent
3. one with a carrying agent and a ductility agent, and
4. one combined system with carrying, levelling and ductility agents.

Table 11 presents the results of this study. All measurements were made on samples with a copper deposit thickness of 37.5 µm [76].

Hardness values were similar in all four systems, but thermal shock performance could not be forecast by hardness testing. The systems that were formulated to withstand thermal shock exhibited stress values from -35.9 (compressive) to 34.5 MPa (tensile), but other systems that failed thermal shock tests produced a stress within these
limits. Therefore, thermal shock performance could not be predicted by measuring internal stress. Modified stress or hardness tests eventually may lead to a means of predicting thermal shock results, but failures from epoxy smears or voids [77] may not be detected from these measurements. A thermal shock test followed by microsectioning appears to be the most reliable method for evaluating a copper deposit.
4.1 AGITATION METHODS

A variety of process functions are carried out in vessels stirred by agitation methods, be it rotating impellers, air, vibratory, etc. Some examples are (i) blending miscible liquids, (ii) contacting or dispersing immiscible liquids, (iii) dispersing a gas in a liquid, (iv) promoting heat transfer between the agitated liquid and a heat exchange surface, (v) suspending or dispersing particulate solids in a liquid to produce uniformity, to promote mass transfer or to initiate and assist chemical reaction and (vi) reducing particle agglomerate size.

Agitation methods by which these functions can be accomplished are mostly the following:

1. Air sparging
2. Magnetic stirring
3. Mechanical work movement (cathode bar reciprocation)
4. Solution pumping
5. Ultrasonic agitation
6. Vibratory agitation.

4.1.1 Air Agitation (Gas Sparging)

The gas may be a vapour such as steam which is generated in place by boiling the liquid to be contacted or which may be admitted through spargers at the bottom of the vessel. Air for example, has been used
extensively for mixing of reagents such as sulphuric acid with all but the most volatile of petroleum liquids. It can provide the gentlest agitation as in the washing of nitro-glycerine with water as well as vigorous mixing as in the case of electrodeposition processes.

In practical production plating electrolytes, agitation by air sparging is the most obvious means employed to achieve electrolyte mixing. The rising air bubbles impart velocity to the electrolyte close to the cathodic surface. Thus, the surface boundary layer is reduced and plating conditions are less likely to be mass transport limited. For the planar vertical surfaces, the agitation provided by air sparging generally is sufficient for good quality plating. However, air agitation does not provide sufficient agitation in plated through-holes of multilayer printed circuit boards [53] and there is the danger of oxidation of product species with air.

4.1.2 Magnetic Stirring
This form of agitation method is equally effective for solution mixing. It induces a centrifugal force which acts on the fluid and raises its level at the wall of the vessel. The depth and shape of such a vortex depends on the magnet and vessel dimension as well as rotational speed.

This method which causes vortex swirling is good in laboratories but poor for big processing tanks.

4.1.3 Mechanical Work Movement (Cathode Bar Reciprocation)
As an alternative to air or other forms of agitation, reciprocating mechanical movement of the cathode can be employed. This can also be employed in combination with air sparging.
Cathode bar reciprocation (mechanical agitation) is used for solutions which contain wetting agents or easily oxidisable constituents which prevent the employment of air agitation. The movement of the cathode bar can be either vertical or horizontal, depending upon the rate of movement required. Mechanical work movement can also be employed on anodic processes such as in electropolishing, anodising and etching, in these cases the mechanical movement is applied to the anode bar instead of the cathode bar as in electroplating.

Inasmuch as cathode bar reciprocation is cheap and easy, it is not effective. It is normally only used where, for plant or process reasons, air agitation cannot be used.

4.1.4 Solution Pumping

Fluid pumping arises from the need to move fluids from one location to another through conduits or channels. The chief parameter characterising the motion of a continuous medium is the Reynolds number ($Re = \frac{\rho v l}{\mu}$) where $\rho$ is the density, $v$ the rate of flow, $\mu$ the viscosity and $l$ the characteristic length. If the Reynolds number does not exceed several units, the liquid flow is said to be laminar. As the Reynolds number increases laminar flow gradually changes into turbulent flow. Flow in an agitation solution, displays very similar characteristics under both laminar and turbulent conditions.

At sufficiently high Reynolds number the motion in the cell (tank) becomes turbulent. This process is assisted by the fact that in the cell there enter several currents coming from various directions, and having different velocities. Thus it may be assumed that within the cell a liquid is well mixed and that the concentration of the solution is uniform throughout the cell (tank).
At this point the solution can be said to be fluidised and the possible uses of fluidised beds are manifold. A number of applications have become commercial successes. Generally, the fluidised bed is used for gas-solids contacting, although in some instances the presence of the gas or solid is used only to provide a fluidised bed to accomplish the end result.

Solution pumping can be sometimes combined with continuous filtration.

4.1.5 Ultrasonic Agitation

In the electroplating process, ultrasonic amongst other forms of solution agitation is used to agitate solutions. It has been claimed that ultrasonic agitation reduces anode and cathode polarisation and permits a 4 to 5 times increase in the deposition rate over that obtained with intensive mechanical agitation [78].

This method of agitation displaced air or hydrogen gas from blind pockets from copper pyrophosphate solutions and resulted in more uniform deposits [79,80]. The operating current density range may be increased by ultrasonic agitation. Several researchers [81-84] have studied the effect of ultrasonic agitation on the microhardness, porosity and grain size of electrodeposits. The authors attribute the hardening effect of ultrasonic agitation, which was reported by Walker et al [85] to a change in the crystal orientation. Although results have shown some improvements, practical applications of ultrasonic agitation are still limited to surface cleaning processes.
4.2 AIR AGITATION VIA BUBBLE FORMATION

Gas stirring of liquids and suspensions is often used in industrial processes. This mode of agitation has been proposed for the enhancement of mass transfer and as a means of improving the yield of electrochemical cells [1-3].

Two types of electrolytic cell agitated by bubbles can be distinguished: (a) cells with gas evolving electrodes, and (b) cells with gas introduction from the outside.

A great number of studies deal with the problem of mass transfer in cells where the gas is generated by an electrochemical reaction on the electrodes [1,86-99]. On the other hand, scarce information is available on cells with gas sparging from the outside [2,100-104]. Although mass transfer rates are higher in cells with gas production at the electrodes than cells with gas introduced from the outside, it is recognised that the former type of cell presents some limitations. For instance in the electrodeposition of metals, spongy and porous deposits may be produced, this does not happen when an inert gas is introduced from the outside. The investigations carried out in this work are made with gas (air) introduced from the outside.

In earlier work, N. Ibl [100] showed the feasibility of the use of gas sparging as a suitable method for improving mass transfer in cells. Ibl et al [93] studied the effect of the superficial gas velocity on the mass transfer coefficient in rectangular cells with porous plates as gas distributors. They found that the gas velocity is the most important variable. However, the experimental results could not be correlated as a single function of the gas velocity independently of
the gas distributor employed. Similarly, Sigrist et al [103] investigated a rectangular cell with internal (gas lift) and external liquid circulation, in this case the gas was introduced through a vertical porous plate facing the test electrode. They showed that the mass transfer coefficient depends on the gas void fraction irrespective of the values of the liquid and gas flow rates.

Cavatorta and Bohm [104] studied the effect of gas velocity, gas distributor, gas hold-up and flow regime on the liquid to wall mass transfer in a circular cell. It was found that the gas velocity as well as the gas distributor affect the mass transfer coefficient. Also it was recognised that the gas hold-up plays an important role in gas sparging systems, the combined effect of both gas velocity and gas distributor could be taken into account in correlating the mass transfer coefficient as a function of the gas hold-up.

\[ K_L = Cc^{0.25} \]  

(6)

where \( C \) is a constant for all distributors. Dimensionless correlations for mass transfer in electrolytic cells with gas (air) agitation as it applies to this work is presented.

However, by using air agitation in electrodeposition processes, it may cause oxidation of species in solution and air bubbles may adhere to the workpieces especially in holes and recesses thereby providing localised insulation and obstruction to electrodeposit growth. For this reason other means of agitation have recently been studied [105,106].
4.3 EFFECT OF AIR AGITATION

The growth, detachment and uplift of bubbles implies a stirring effect in an electroplating cell, consequently an increase in the rate of mass transfer. Hence, bubbles contribute positively to the increase in the rate of the electrochemical process itself, but it may be undesirable when it produces an increase in the rate of side reactions.

Bubbles, for example, in electroplating cells may cause the appearance of a non-conducting phase which forces equiflux lines to follow a tortuous path, increasing the apparent resistance of the electrolyte solution. Under extreme circumstances bubbles adhere so strongly to the workpieces that the surface may become covered by a complete gas layer, which causes sudden potential increase and current drop; hence, poor quality electrodeposit. It is evident from the operational standpoint of the electrodeposition process that this disadvantage of air agitation is only overcome through combination with mechanical motion of the cathode.

4.4 BUBBLE THEORY

A bubble is a globule of gas or vapour surrounded by a mass or thin film of liquid. Bubbles in a liquid originate from one of the three general sources: (i) they may be formed by desupersaturation of a solution of the gas or by decomposition of a component in the liquid; (ii) they may be introduced directly into the liquid by a bubbler or sparger, or by mechanical entrainment; (iii) they may result from the disintegration of larger bubbles already in the liquid. The appearance of a bubble requires a gas nucleus as a void in the liquid.
The nucleus may be in the form of a small bubble or of a solid carrying adsorbed gas, examples of the latter being dust particles, boiling chips and a solid wall [107].

The theory permits the approximation of the maximum size of a bubble that can adhere to a submerged horizontal surface if the contact angle between bubble and solid (angle formed by solid-liquid and liquid-gas interfaces) is known [108,109]. Bubbles are produced one at a time, their size being determined primarily by the orifice diameter $D_o$, the interfacial tension of the gas-liquid film $\gamma$, the densities of the liquid $\rho_L$ and gas $\rho_g$ and the gravitational acceleration $g$ according to the relation:

$$\frac{D_b}{D_o} = \left[ \frac{6\gamma}{D^2 (\rho_L-\rho_g)} \right]^{1/3}$$  \hspace{1cm} (7)

where $D_b$ is the bubble diameter. The size is independent of the gas flow rate, the frequency, therefore, is directly proportional to the rate. Equation (7) leads to

$$f = Q \frac{\rho_L - \rho_g}{\pi D \gamma}$$  \hspace{1cm} (8)

where $f$ is the frequency of bubble formation and $Q$ is the volumetric rate of gas flow in consistent units. Equations (7) and (8) result from a balance of bubble buoyancy against interfacial tension. They recognise no inertia or viscosity effects. At low bubbling rates, they are quite satisfactory [110-111].

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For very thin liquids, equations (7) and (8) are expected to be valid up to a gas-flow Reynolds number of 200 [112]. For liquid viscosities up to 100 cP, it has been shown that liquid viscosity has very little effect on the bubble volume [107], but liquid viscosity can cause the bubble size to increase considerably over that predicted by equations (7) and (8) for liquid viscosities above 1000 cP [113-115]. This data is found to agree very well with a theoretical equation obtained by equating the buoyant force to drag based on Stokes' law and the velocity of the bubble equator at break-off:

\[ D_b^3 = \frac{6}{\pi} \left( \frac{4\pi}{3} \right)^{1/4} \left( \frac{15 \nu_L Q}{2g} \right)^{3/4} \]  

(9)

where \( \nu_L \) is the liquid kinematic viscosity and \( Q \) is the gas volumetric flow rate.

4.4.1 Bubbles in Fluidised Beds

Fluidised beds are beds of solid particles supported by upward flow of gas (air) or liquid. Because of their temperature uniformity, excellent heat transfer characteristics, and solid handling possibilities, fluidised beds have found wide application for physical and chemical processes. Gas fluidised beds are inherently unstable to the growth of voidage disturbances and this is believed to be the origin of bubbles in fluidised beds [116]. There is a strong analogy between bubbles in liquids and in fluidised beds [107].

In view of the negligible surface tension forces and the fact that bubbles are usually at least 1 mm in diameter, bubbles are generally in the spherical-cap regime. Reynolds numbers tend to be of the order of 10 to 100 with the result that bubbles have large values of Wake
angle $\theta_w$ and closed laminar wakes, Figure 7. The terminal velocity of bubbles in fluidised beds is usually estimated using the following equations:

$$ U_T = 0.7920.5 \sqrt{g \rho_v \Delta \rho L / \delta_i} \quad (Re > 150, E_o \gg 40) \quad (10) $$

$$ U_T = 0.711 \sqrt{gd_e \Delta \rho L / \delta_i} \quad (Re > 150, E_o \gg 40) \quad (11) $$

where $E_o$ is an Eotvos number, with $\Delta \rho L / \delta_i = 1$ [107] while the influence of bubble size on shape for bubbles from 1-16 cm in diameter has been represented [117] by the equation:

$$ V = (\pi/6) d_b^3 e^{-0.057 d_b} \quad (12) $$

where $d_b$ is the maximum bubble width in centimetres in a plane normal to the direction of motion. Internal circulation of bubbles in fluidised beds is an aspect in which the analogy between liquids and fluidised beds ceases to apply since the bubble particulate phase interface is permeable. There is a net upward gas flow through a bubble [109].

### 4.4.2 Theory of Bubble Formation

When air or other gas is blown or pumped steadily through an orifice into a liquid of small viscosity, a more or less regular train of bubbles is formed. At very low air rates, the frequency and size of the bubbles is governed mainly by a balance between surface tension and buoyancy forces. At higher air rates the inertia of the liquid moved by the rising bubbles becomes more important than the surface tension. At this stage, the liquid is said to be fluidised or agitated. Consequently, the surface tension at this regime is zero. At still higher air rates, the momentum of the air issuing from the orifice is sufficient to maintain it as a jet before break-up into separate bubbles.
The volume of bubble(s) formed could be calculated if the number of bubbles formed is known as well as the radius:

\[ V_b = N_b \frac{4}{3} \pi r^3 \]  

(13)

In the theoretical derivation it was assumed that each bubble is spherical during formation. A bubble forming in a liquid of zero surface tension must in fact distort as it accelerates upwards, for the same reason that a steadily rising bubble takes on the spherical-cap shape. This distortion is brought about by the fact that the pressure on the surface of the bubble is constant, because it is filled with gas and with the unseparated flow which necessarily occurs during the initial motion. These distortions have been studied both experimentally and theoretically for a "two-dimensional" bubble by Walkers and Davidson [118].

Soon after each bubble detaches from the orifice, a wake is formed below the bubble, and the bubble shape takes on the spherical cap mentioned earlier. The formation of the wake therefore means that liquid is carried up with each bubble, and this liquid contributes further to the circulating current near the orifice. However, it is not easy to estimate the effect of the circulating current, but results show that it does not have much influence on the bubble volume. A complication that arises, particularly at the higher flow-rates, is the coalescence of bubbles shortly after formation, leading to the so-called double or quadruple bubble formation reported by Davidson and Schuler [119]. This occurs because a bubble gets into the wake of the one above, and is the first step towards the formation of a continuous gas jet observed at very high flow rates.
4.4.3 Bubble Size and Shape

When air is injected into a liquid through an orifice or many orifices in a plate or coil rather than through a capillary tube, size still increases with the radius of the orifice(s) but the increase is less pronounced and less regular than in the instance of a capillary [110]. The effect may be complicated by coalescence of two or several bubbles originating from two or several neighbouring orifices. Just as in the instance of drops, the volume of a bubble depends on the speed of its formation, but drop volume exhibits a maximum when the rate of flow is gradually accelerated, while bubble volume seems to pass through a minimum. At least such was the behaviour of air bubbles rising from narrow glass capillaries in water [113,120].

The general shape of bubbles is well known from photographic studies of bubbles in liquids [121], and X-ray studies of bubbles in fluidised beds [122]. The upper surface of the bubble is approximately spherical and its radius of curvature denoted by \( r \). The base is typically slightly indented. Since the radius of curvature \( r \) is not readily determinable, it is usually more convenient to express the bubble size as its "volume-equivalent diameter", that is the diameter of the sphere whose volume is equal to that of the bubble:

\[
d_{eq} = (\frac{6}{\pi} \frac{V_b}{\pi})^{1/3}
\]

(14)

where \( V_b \) is the bubble volume. A bubble in a viscous liquid shows the form of a spherical-cap shape if it is sufficiently large for surface tension forces to be negligible [121], that is if:

\[
E_0 = \frac{\rho L d_{eq}^2 g}{\delta_i} > 40
\]

(15)
where \( \rho_L \) and \( \delta_i \) are the liquid density and interfacial tension, and the dimensionless group \( E_o \) is known as the Eotvos number.

Since fluidised or agitated beds lack a phenomenon equivalent to interfacial tensions \( \delta_i \) is effectively zero. Thus bubbles in agitated solutions satisfy equation (15) and the analogy is reasonable. The shape of such a bubble can conveniently be described by the wake angle \( \theta_w \). Grace [123] showed that \( \theta_w \) is a function of the bubble Reynolds number:

\[
Re_b = \frac{\rho_L U_b d_{eq}}{\nu_L} \tag{16}
\]

where \( U_b \) is the bubble rise velocity and \( \nu_L \) the liquid kinematic viscosity. Observed shapes of bubbles in liquids are represented by:

\[
\theta_w = 50 + 190 \exp (-0.62 Re_b^{0.4}) \quad (E_o > 40, Re_b > 1.2) \tag{17}
\]

The measurement of the distribution of bubble sizes in gas injection experiments involving water and liquid metals has been undertaken by several authors [5,7,14]. It is agreed that the distribution of bubble sizes in the buoyant region of the cell is the result of bubble break up and coalescence. The maximum stable bubble size due to the break up of ascending bubbles has been analysed by balancing the forces responsible for the bubble stability (surface tension) and for break up (dynamic pressure force) [13]. From this analysis, it was found that the critical bubble diameter \( d_{bc} \) is proportional to the surface tension \( \delta_s \) and density of the liquid \( \rho_L \):

\[
d_{bc} = (\delta_s / \rho_L)^n \tag{18}
\]

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However, this does not agree with the experimental findings of Tacke et al [5], nor with the results of the present investigation which show the opposite behaviour. The present study has been conducted to compare the behaviour and characteristics of air agitation, which is widely used commercially for electrodeposition processes with vibratory agitation as an innovation in electrodeposition processes.

4.5 FACTORS INFLUENCING BUBBLE SIZE

The factors influencing bubble size may be classified as equipment variables, system variables and operating variables. In the case of equipment variables, they are directly decided by the bubble forming device, whose major parts are the chamber, the nozzle or orifice and the liquid column. Therefore, the important factors are as follows:

a) diameter, geometry, orientation, nature and material of construction of the nozzle (orifice);
b) chamber volume, and
c) arrangement of slots for multiholed plate or coil systems.

Most of these factors remain unstudied, though the influence of the diameter of the orifice and chamber volume have been reported in the literature [113,124-127]. System variables as factors affecting bubble size are associated with the liquid-gas combination chosen for investigation, and therefore are not experimental variables in any way. The most important system variables are:

a) surface tension;
b) density of the liquid $\rho_L$ and its viscosity $\mu_L$;
c) density of the gas $\rho_g$ and viscosity $\mu_g$;
d) contact angle $\theta$, and
e) velocity of sound in the gas.
The other factors influencing bubble size are the operating variables. However, these can be varied by the investigator as desired, they include:

a) volumetric flow rate of the gas;
b) velocity of continuous phase;
c) volume of the electrolyte in the tank;
d) pressure drop across the orifice, and
e) temperature of the system.

Here it is important to note that the temperature of the system as indicated does not actually influence the bubble size directly, but does so indirectly by varying the physical properties of the gas-liquid system. Even the other variables are not entirely independent, for example, the pressure drop across the system is a function of the flow rate, chamber volume as well as the power of the pump. Indeed, the various factors do not influence the bubble size to the same extent over the entire range of the other variables. Hence, surface tension, which is one of the most important factors determining the bubble size at vanishingly small flow rates, assumes much less importance at higher flow rates. Similarly, the viscosity of the liquid is much more important at higher flow rates than at lower ones.

4.5.1 Effect of Orifice Characteristics

When the gas flow rates are low, the effect of orifice diameter is such that the volume of the bubble is directly proportional to it [110, 113, 124]. Apart from the size of the orifice, the nature of it is of considerable importance. The thickness of the orifice plate or tube may also affect the bubble size. This effect has been reported to become significant [128] if the thickness is equal to or greater than 100 times the value of orifice diameter. In any case, the major variable associated with the orifice is the geometry of the opening.
4.5.2 Effect of Chamber Volume

Hughes et al [126] in their work found that for small chamber volume and small flow rates, the bubble volume is virtually independent of the chamber volume. Similar is the case when the chamber volume is large and flow rates are normal. At very small flow rates and large chamber volumes, the bubbles normally form in doublets and triplets and their size cannot be definitely determined. These conclusions have been verified by Davidson and Amiek [125] who varied the chamber volume in their equipment from 4 cm$^3$ to 400 cm$^3$.

The influence of chamber volume is closely related to that of the pressure difference, $\Delta P$, across the orifice. This can however, be defined as the volume between the orifice and that point in the gas stream where the pressure drop is very large. When the pressure drop across the orifice is large and the pressure variations occurring during the formation of bubbles are small compared to the total pressure drop, the gas flow rate does not change during bubble formation and the bubbles are said to form under constant flow conditions. This is true also when the chamber volume is zero. Thus, under constant flow conditions, zero chamber volume corresponds to a high pressure drop across the orifice.

Similarly, conditions are such that on the air-supply side of the orifice, the pressure is maintained constant during bubble formation, as the bubble size increases, the pressure inside it decreases, resulting in a higher flow rate. Therefore, constant flow conditions are not maintained and the rate of bubble growth varies.
4.5.3 Effect of Surface Tension of the Liquid

The fact that surface tension influences the bubble volume and size is obvious. At flow rates tending to zero, the bubble volume is such that the upward force due to buoyancy is balanced by the downward force of surface tension. So an increase in surface tension should result in an increase in bubble volume. This fact was investigated by many authors, by studying bubble formation at low gas flow rates and under nearly constant flow conditions [113,124,126,129]. However, under conditions of constant flow, surface tension has no effect on the bubble volume [115].

Similar results are reported by Siemes and Kaufmann [114]. Kumar and Kuloor [130] predicted that the surface tension effects are large at low flow rates and continuously diminish as the flow rate is increased. The results obtained from two liquids of surface tension values 72 and 41 dynes per centimetre are shown in Figure 8. The values of bubble volume in the two liquids are seen to be different at low flow rates but merge with each other at higher flow rates, indicating that the contribution of surface tension to the bubble volume is negligible at higher flow rates.

In the study of Quigley, Johnson and Harris [131] in which they used water and carbon tetrachloride, they found that at constant pressure conditions for higher flow rates, the effect of surface tension on bubble volume is negligible. These authors however, may not have adequately accounted for the large difference in the densities of the two liquids. However Davidson and Schuler found that under constant pressure conditions, surface tension does appreciably affect the bubble volume. Furthermore, works carried out by Satyanarayan, Kumar and Kuloor [132] indicates that the effect of surface tension on
bubble volume cannot be neglected after all as shown in some of their
data in Figures 9 and 10. They found that at very small orifice
diameter, the influence is more pronounced at small flow rates, as is
evident from Figure 10. Generally speaking, for both constant flow and
constant pressure conditions, surface tension affects the bubble
volume at low flow rates and has negligible influence at high flow
rates.

4.5.4 Effect of Liquid Viscosity
While studying bubble formation in various liquids from porous
earthenware, Schurmann [133] concluded that viscosity is the principal
factor which determines the bubble volume. Davidson and Schuler [115]
drew a similar conclusion that an increase in viscosity causes a
marked increase in bubble size. However contradiction to the above
results was from the finding of Datta et al [113]. Results of the
works of Quigley et al [131] and Coppock and Maiklejohn [129] are in
between the above two extremities. The former authors report that the
bubble volume increases slowly with viscosity, whereas the latter
finds the viscosity to be ineffective. The results seem to be
contradictory and irreconcilable. This may not be so because the
effect of viscosity is associated with those of flow rate, surface
tension and orifice diameter.

However, the effect of viscosity is dependent on the liquid used
during the investigation.

4.5.5 Effect of Liquid Density
When the density of a liquid is increased, the buoyancy force
corresponding to a specific size of the bubble increases, whereas the
surface tension force may remain constant. Indeed, for a definite
amount of surface tension force, the bubble volume obtained is smaller. Workers such as Benzing and Myers [124], Coppock and Maiklejohn [129] and Davidson and Schuler [115] agree that the bubble volume decreases with increasing density of the liquid. However Quigley [131] and co-workers disagree with the above and observe that the liquid density has no effect on the bubble volume. From all indications however, the density of a liquid does increase the buoyancy at all levels of bubble formation but its effect is most pronounced for liquids of high viscosity and at low flow rates.

The bubbles move and carry on its way a certain amount of liquid and this created a downward force in addition to that of surface tension. The volume of the liquid being carried along is independent of the liquid density, but the downward force increases with increasing density. This net effect of the increase in the downward force is in direct opposition to what takes place at zero flow rates. Perhaps the first set of investigators mentioned above used either very small flow rates or very high viscosities, hence under these conditions, the increased downward force resulted in their observing a decrease in the bubble volume with increasing density. On the other hand Quigley et al [131] who employed high flow rates and low densities, were led to observe the non-influence of density on the bubble volume. Again, a possible answer to this disparity in results depends on the electrolyte used for the investigation.
4.6 GAS PROPERTIES

4.6.1 Effect of Gas Properties
There has been no systematic study of the influence of gas properties. The gas density appears in the analysis either in the virtual mass term or in the buoyancy term. This is generally omitted from the analysis on the assumption that it is negligible when compared with the liquid density, i.e.,

\[ \rho_L - \rho_g = \Delta \rho \quad (19) \]

and

\[ \rho_g + \frac{11}{16} \rho_L = \frac{11}{16} \Delta \rho \quad (20) \]

This is related only to two-phase systems - water solutions (liquid) - gas (equation 20).

The viscosity of the gas has again a negligible effect on the bubble volume, hence the gas properties can reasonably be considered to be ineffective.

4.6.2 Effect of Gas Flow Rates
In the study of bubble formation, frequency of the bubble formation was initially considered as an important parameter. Later on, the frequency was observed to be decided by the flow rate and bubble volume. The flow rate is controllable but the frequency could not be controlled. From experimental observations, it is important to note that when flow rate is increased continuously for a particular system, a stage is reached when the frequency of bubble formation remains essentially constant, whereas the bubble volume changes. Thus the
bubble volume can assume an infinite number of values for a constant frequency. The bubble volume, however, is a single valued function of the flow rate provided all other conditions are maintained constant. Therefore, for purposes of developing a correlation, it is more reasonable to employ the gas flow rate, which is an independent variable, rather than the frequency, which is a dependent variable.

Experiments have shown a general agreement on the pattern of bubble volume variation when flow rate is increased. As the flow rate is gradually increased from zero the bubble volume remains fairly independent of the flow rate, whereas the frequency increases and so the degree of agitation. On increasing the flow rate, at first both the bubble volume and the frequency increase, but later on a stage is reached when the frequency remains essentially constant while the bubble volume continues to increase.

In summary, it can be said that there exists a considerable amount of discrepancy in literature regarding the influence of various factors mentioned above on the bubble volume. Most of the above discrepancies have arisen because of the lack of appreciation by various investigators of the effects of chamber volume, the types of flow associated with it, and of the interaction of the several variables considered, such as the viscosity, surface tension and flow rate.

4.6.3 Rise Velocity of Bubble
A number of studies have been reported on the experimental study of bubble velocity [5,7,14] in physical models of gas-agitated reactors. It has been found that the discharge velocity of the gas decreases abruptly in the vicinity of the injector to form a buoyancy-dominated region which extends over most of the cell [7]. In this region, the
bubble velocity increases with increasing gas flow rate but is independent of the orifice gas velocity. Recently, Lai and Salcudean [11] presented a theoretical model of the fluid motion in gas-agitated ladles which considers the interaction of the gas and liquid phases, however, the calculated gas flow pattern was not reported.

Davies and Taylor [134] showed that the rise velocity $U_b$ of a spherical cap bubble is related to its radius of curvature by:

$$U_b = 2/3 \sqrt{(gr)}$$  \hspace{1cm} (21)

This equation is experimentally reliable for bubbles in liquids if bubble Reynolds number ($Re_b$) is greater than about 40; below this value, departures from the spherical-cap shape have a significant effect on the rise velocity $U_b$ [121]. Bubbles in fluidised beds typically have Reynolds numbers of the order of 10 or less, below the range for which equation (21) is strictly valid in liquids. Even so equation (21) has been widely used for fluidized beds, and inaccuracies are no doubt masked by the erratic velocity variations typically observed [135]. In terms of the volume-equivalent diameter equation (21) can be written:

$$U_b = \frac{2/3 \sqrt{(r/d_{eq})}}{\sqrt{(gd_{eq})}}$$  \hspace{1cm} (22)

where the braced term is a weak function of $Re_b > 100$, this term is constant at 0.71, and the resulting expression will be

$$U_b = 0.71 \sqrt{(gd_{eq})}$$  \hspace{1cm} (23)

and has been widely used to predict the rise velocity of isolated bubbles in fluidized beds [109].
4.6.4 Coalescence of Bubbles

Bubbles grow in size as they rise in an agitated or fluidized bed [138,139] and it is apparent that there are at least three possible explanations for this, namely:

i) the effective hydrostatic pressure acting on the bubbles decreases as they rise up the cell;

ii) bubbles may coalesce in a vertical line, that is, one bubble may catch up another;

iii) neighbouring bubbles in a similar horizontal plane, may combine when they are very close to each other.

Harrison and Leung [140] made an experimental study of bubble growth by mechanism (ii). Nothing of a quantitative nature is yet known of (iii) but for many systems the effect of (i) is small. The experimental method for the study of bubble coalescence in a vertical line was suggested by the visual observation of the coalescence of spherical-cap air bubbles in water, for then the influence of one bubble on another is clear, when the following bubble approaches the leading bubble closely enough, it appears to be accelerated and gather into the back of the leading bubble; bubble coalescence thus occurs. This mode of coalescence may be explained by supposing that the wake behind a spherical-cap bubble travels with the bubble, and that coalescence takes place when one bubble moves into the wake of another. In any case, coalescence of detached bubbles is affected by various factors, for example, bubble density, solution flow velocity, nature of gas and solution.
4.7 VIBRO-AGITATION

4.7.1 Theory

Vibration in electrodeposition processes as a means of agitation has received limited attention and is rarely in use at present in industrial processing largely because agitation by air (or gas sparging) is relatively cheap, easy to use and its general effects well-known. However, vibratory agitation unlike air agitation, can readily be described directly in a quantitative manner and its effects are not entirely dependent upon analysing the resultant process performance. Vibrational energy can be transmitted or generated either electromagnetically or mechanically and may be applied to either the electrode itself or to the solution. Most systematic studies have been concerned with vibrated electrodes either for rapid electro-analysis [19,20,144] or for enhanced mass transfer [141,142-149]. Alternative studies of vibration solutions have been concerned with ultrasonic vibrational agitation [150,151] which is really a special case having some specific advantages and other uses such as cleaning processes. Conventional vibrational energy when applied to the solution has tended to be used for processes other than electrodeposition, for example, liquid-liquid solvent extraction [152,153].

Vibratory agitation has a particular advantage in the context of electrodeposition of composite coatings where there is a need to maintain second phase particles in suspension so that they may be incorporated in the growing electrodeposit. Other methods of agitation have been employed but cannot offer such a wide range of incorporation behaviour. It is such a context that this detailed study of solution vibrational agitation has been made using a standard
commercial vibro-mixer as agitator. Detailed study of the flow patterns induced by the agitator discs has been made by a dye-tracer technique and methods of calibrating the vibrator explored as a means of measuring the degree of agitation quantitatively.

4.7.2 Characteristics of Vibro-Agitation

Vibratory agitation is achieved by use of a vibratory motor which develops longitudinal vibrations in its axis shaft at the frequency used in the primary power supply - conventional alternating current at 50 Hz. The vibrational amplitude was shown to be simply related to the input voltage or power and calibrations obtained by using several techniques including stroboscopic methods. Some fluid damping occurred such that the calibration held good only if the fluid density, viscosity, etc were constant.

Development of vibratory agitation in the solution was by means of a circular disc or plate attached to the end of the motor shaft; it is positioned near the bottom of the electroplating tank. The form of the plate was critical in two respects:

a) The agitator disc should not be allowed to act as an hydraulic piston or lift pump;

b) Turbulent eddies should be allowed to develop in the whole tank.

For these prerequisites to be achieved, it was shown that the agitator disc to tank diameter should be approximately 1:3, thus allowing eddies to circulate through the disc and tank wall gap and the disc itself should be perforated as experiments carried out using both perforated and unperforated discs show perforated discs to produce superior distribution of eddies than the unperforated discs. Each hole
acted as the source of a turbulent jet and by truncating the holes improved agitation was obtained, see Figure 11.

One of the main aims of this work is the optimisation of turbulent agitation in order to maximise mass transfer and deposition rates and the object being to fill the vessel (tank) with turbulent motion. This objective may not be achieved if:

a) the agitator disc is too small, and
b) the agitator disc is too big and eddies produced are constricted by the tank wall.

The pattern of agitation in the tank showing these behaviours as related to the geometric dimensions of the agitator disc are represented schematically in Figures 12 and 13. Although the vibrator disc motion is entirely vertical some rotation also developed in the solution but this is considered to be quite minor in relation to electroplating process enhancement.

Experiments have been carried out at various levels of scale-up, typically tank sizes of 2 litres, 10 litres and 25 litres, and the same general pattern of behaviour has been noted.

4.7.3 Process Enhancement
Investigation of mass transfer to vibrating flat plates is of practical and theoretical interest. As stated in the review by Al-Taweel et al [144], the application of vibrations to electrochemical processes often results in (i) reduction of concentration polarisation, and consequent acceleration of metal deposition; (ii) increase in metal deposition current efficiency, (iii) facilitation
of electrode passivation and liberation of gas, and (iv) production of brighter, harder, less porous, fine grain deposits.

For electrochemical processes where diffusion is a rate-determining step, an increase in the frequency or amplitude of vibration increases the mass transfer rate [144]. The enhancement of mass transfer due to electrode vibration has been explained via a quasi steady-state model, a stretch-film model, an analogy model, and a combined model [144-146]. None of these models have been strongly supported by experimental results.

In view of the great practical significance of vibration as a means of agitation to improve transfer rates, studies on the effect of vibration on heat and mass transfer problems have been attracting the attention of many investigators in recent years. In spite of this, the available information regarding the effects of variables associated with vibration on the rate of heat as well as mass transfer is meagre. Although in most of the cases, profound improvement in heat and mass transfer rates have been reported, there has been considerable disagreement among the results of these investigators with regard to the magnitude of the improvements in transfer coefficients and the intensity of vibration at which the transition takes place from low improvement to rapidly rising improvement region. The correlations proposed in the literature were also of a divergent nature and in most cases, they were developed based either on the concept that the film [142] surrounds the entire vibrating path or that the film is carried back and forth with the vibrating surface.
For vibratory agitation two main purposes were envisaged. Firstly, a means of enhancing deposition rates and most usefully in excess of that experienced in conventional air agitated processes. Secondly, a means of achieving improved electrodeposition of composite coatings in which second phase particles are suspended dynamically in solution until they are physically trapped in a growing cathodic electrodeposited surface. The effectiveness of vibratory agitation in single metal electrodeposition can be defined in terms of limiting current density and can be converted to a diffusion layer thickness. If an agitation enhancement factor is defined as the limiting current density value obtained with agitation related to that obtained in still solution values can be compared as in Table 20.

To measure enhancement satisfactorily a mass transport analysis of this type of agitation was taken. Initially, some concern is felt regarding the choice of characteristic length dimension in the vibrational Reynolds number. It is observed that the length of vibrating surface, in the case of cylindrical rods, has no effect on mass transfer coefficients and the characteristic dimension was reported to be the diameter of the cylinder [143]. The degree of agitation was expressed in a Reynolds number through the relative motion of the vibrator disc, and is assumed to be the length dimension in the Reynolds number. The definition of Reynolds number [105] was based on the conventional form $Re = \frac{ud}{\nu}$. Here $u$ is the relative motion velocity (cm s$^{-1}$), $d$ the critical dimension taken as the disc diameter (cm) and $\nu$ the kinematic viscosity (cm$^2$ s$^{-1}$). In this case of vibratory motion the velocity $u = \frac{s}{t}$ where $s$ is the distance for which the full frequency cycle is applied and is equal to $2a$ where $a$ is the amplitude of vibration. The time $t$ is derived from the frequency $f$ ($t = \frac{1}{f}$) which was 50 Hz in all the experiments. Consequently, Reynolds number was reformulated as:
Re = \frac{2\pi fd}{v} = \frac{100 a d}{v} \tag{24}

Later investigations suggested that the disc to tank wall gap was critical and that in this case a modified Reynolds number was preferable:

Re' = \frac{100 a d_2}{v} \left[ \frac{(d_1 - d_2)}{d_2} \right] \tag{25}

The mass transport rate was measured using a limiting current method for a model acid copper sulphate solution. Both potential sweep and potential step techniques were employed and good agreement was obtained. The Sherwood number, Sh, was used as a measure of mass transfer (equation 39). A mass transfer correlation of the usual form was anticipated.

Sh = \text{const} \, Re^a \, Sc^b \tag{26a}

or

Sh = \text{const}' \, Re^a \text{ for constant Sc} \tag{26b}

In this relationship modified Sherwood number as in Reynolds number was used to normalise the results obtained.

Sh = \frac{i_L d_2}{nFCD} \left[ \frac{(d_1 - d_2)}{d_2} \right] \tag{27}

where \(d_1\) is the diameter of the tank and \(d_2\) is the diameter of the vibrator disc. This study thus provides a set of fundamental data for better understanding of mass transfer for vibratory agitation and equations for predicting mass transfer coefficients.
4.7.4 Other Means for Exploiting Vibration

Different types of vibrating apparatus have been employed in different forms to study electrolytic reactions regarding ionic mass transfer. For example, oscillations and vibration of electrodes employed in electrochemistry particularly in polarography, either as a vibrating dropping mercury electrode [148,149] or as a platinum micro-electrode of different shapes [19,20,150,151]. These vibrating electrodes give reproducible polarograms under a certain range of frequency and amplitude. The ionic mass transfer rate under vibration improved by increases in either amplitude or frequency [152,153].

General correlations for mass transfer in vibrating systems have been obtained for the dissolution of benzoic acid cylinders under surface vibration [154], and in diffusion controlled electrolytic processes on cylindrical electrodes under horizontal longitudinal vibration [155]. The most significant study has been that of Eisenberg et al [156] on the rates of mass transfer at cylinders rotating about their axes in the centre of a stationary cylinder, employing the solid dissolutions and an electrolytic redox reaction.

Studies on ion transfer rates at rotating and vibrating electrodes in stirred vessels and forced convection flow of the electrolyte through cells of different configurations have been reported in literature [143,157,158] but earlier studies [159,160] on ionic mass transfer with flow normal to the electrode have been confined to either one electrode size or to the low Reynolds number region. The majority of the earlier studies [161,163] on mass transfer with crossflow deal with dissolution and sublimation rates. In such systems material transport may considerably alter the transfer surface.
CHAPTER 5

ELECTRODEPOSITION OF COMPOSITE COATINGS

5.1 INTRODUCTION

A composite material may be defined as the combination or fabrication of two or more materials acting in union, often being called upon to provide physical and mechanical properties unobtainable by the individual constituents acting alone. The key to successful production of electrodeposited composites is the mode of agitation, vibratory agitation being in particular very advantageous.

The improvement in the properties of materials by incorporating dispersed phases such as oxides, carbides, borides and nitrides is well known. A number of methods have been developed for the preparation of composite materials, these methods include metal spraying, internal oxidation, powder metallurgy, diecasting, slipcasting and electrodeposition.

Of the various processes of preparing composite alloys, the method of electrodeposition is most promising in that it offers the following advantages: first, the ease with which high purity electrodeposits can be prepared is an asset toward preserving the property of electrical conductivity; the second is that electrodeposited composites show exceptional uniformity, a quality essential to achieving optimum mechanical strength; and the third is the possibility of making intricate shape components directly by electroforming.
The historical foundations [163] of electrolytic codeposition lie in the fact that during conventional electroplating the irregular erosion of metal anodes and presence of impurities in materials used results in the build-up of finely divided contaminated particles in the electrolyte, unless preventative measures are taken. The effects of such contaminants are deleterious, giving rise to surface roughness, pitting and the formation of nodules. The electrolytic codeposition of contaminant particles suspended in electrolytes has been evident since the very beginning of the electroplating process. Present day electroplating processes eliminate the undesirable effects of contaminant codeposition by effecting their removal with the use of anode bags, high purity chemicals and periodic filtration of the electrolyte.

The previously damaging effect of electrolytic codeposition has been turned to advantage by a number of investigators. This has been achieved by adding particles, specially selected for their material properties, to the plating electrolyte and then codepositing under controlled conditions. The end product is a composite electroplate comprising a metal containing a random dispersion of the particles which have been added to the electrolyte.

The possibility of codepositing inert particles from electrolytic baths has long been known. One of the earliest references dates back to 1928 by Fink and Prince [164]; they produced self-lubricating copper coatings containing embedded graphite particles. The codeposition concept was again applied 20 years later by Aquesse [165], in a Belgian patent. He claims to have improved the life span of cutting tools manufactured using sintering techniques by codeposition of a hard phase. In 1959 Grazen [166] described an
electroplating process for producing coatings of Ni, Cu, Ag etc, containing finely divided particles of oxides and carbides, which were claimed to greatly improve the wear resistance of gauges and tools.

In the early 1960's several investigators recognised the need to further develop the technology of electrolytic codeposition. Withers [167] used electroplating with periodic reversal of the current to prepare Ni cermets containing dispersions of Al₂O₃, ZrO₂ etc. He suggested that particles of sizes up to 44 μm could be included in the deposit, but considered that those of 1-3 μm gave the best properties. At the same time Spencely [168] investigated the preparation of nickel-silicon carbide coatings whilst Fabian [169] was concentrating efforts on the production of chromium-thoria and nickel-thoria. Sautter [170] found that the Al₂O₃ content of a nickel coating was affected only slightly by temperature, pH and current density. Tensile strength measurements exhibited an increase in yield strength, Sautter suggested that this increase was attributable to dispersion strengthening similar to that observed in sintered or internally oxidised metal-oxide systems.

From the late 1960's the number of publications relating to the electrolytic codeposition of inert particles with metals has increased markedly. The increase has largely been due to the flexibility of the process and to its competitive position with respect to other production techniques for such composite materials.

5.2 PROCESS VARIABLES OF ELECTRODEPOSITED COMPOSITE COATINGS

Several variables exist which might be important in determining whether or not a dispersed phase is obtained.
5.2.1 Materials

Electroplating processes which are readily amenable to composite electrodeposition are those which operate at a high cathode efficiency. This includes processes for electrodepositing nickel, copper, silver and cobalt, whilst those metals such as chromium involve more elaborate techniques. Coatings can be formed on all substrates that can normally be electroplated. Any metal or alloy that can be obtained by electrolysis can be used as the metallic matrix of a composite coating.

A large variety of second phase particles, which can be powder or fibre, conducting or non-conducting, are available for codeposition. The second phase particles may be elements like Al, B, Ba, Cr, Fe, Mo, Ni, Si, Ta, Ti, W and Zr present as oxide, carbide, nitride, boride or sulphide; or they may be materials such as diamond, glass, graphite and synthetic materials (e.g. PTFE). The type of second phase particles used depends on the desired characteristics of the composite coating. The particles used need to be insoluble in the plating bath employed. Size of particles is limited to 40-50 μm by practical problems in keeping larger particles in suspension.

5.2.2 Apparatus

The process of electrolytic codeposition is operated by suspending particulate matter in conventional electroplating solutions and then depositing in the normal manner. To obtain coating with consistent properties it is necessary to achieve as regular a particle dispersion through the matrix as is practicable. It is therefore reasonable to assume that the more regular the dispersion of the additive in the plating bath the more regular the dispersion in the coatings.
Reported methods of agitation range from simply bubbling air through the solution via a manifold to mechanical agitation by means of an impeller. Air agitation is difficult to control and stirring, unless extremely vigorous, gives varying degrees of agitation. Similar problems are encountered with variable magnetic stirrers although they were used in investigations by Williams and Martin [171]. Two techniques have been developed [172] for the production of homogeneous deposits - liquid/air process and the plate pumping process.

The liquid/air process operates by drawing liquid from the plating solution through a tube, connected to a peristaltic pump (Figure 14), and circulating it through a closed loop. To supplement the agitation caused by recirculation of the plating solution air is added to the system. The drawbacks with this technique are that care is needed to avoid flotation of the suspended particles and the occurrence of dead corners has to be avoided, as otherwise particles will sediment and take no further part in the process.

A second method developed [172] is termed the plate pumping process. This process achieves the same conditions as the liquid/air process but without having to rely on an external pump. Suspension of the particles is achieved by vertical reciprocation of a perforated plate near the bottom of the electrolysis cell, Figure 15. The vibration of the plate causes liquid jets to be formed which agitate the electrolyte sufficiently well to suspend the particles. The plate pumping process is the more favourable of the two as in this process the particles are in a dynamic resting position due to their mutual collisions, and thus have a greater chance of being incorporated in the cathodic deposit.
All ancillary equipment required for electrolytic codeposition is of the conventional plating type. The production route adopted for codeposition is simply to set up the unit and then examine the readiness of the plating solution to codeposit the second phase particles.

5.2.3 Composition of the Plating Bath

The electrolytes used for codeposition are identical to conventional electrolytes for the electrodeposition of pure metals. The electrolyte should be able to deposit the matrix metal and the type of second phase material required. However, it appears that the pH of the plating solution plays an important part in ensuring that the particulate phase can be codeposited successfully with the matrix.

The effect of pH on incorporated alumina in the nickel-alumina system has been reported by several researchers [170,173,174,175]. The results of Sautter [170], Sinha et al [173], and Pushpavanam [174] are in close agreement as far as the nature of their data is concerned. The codeposition is negligible below pH 1-2, increasing sharply around pH 3.5 and further stabilises or decreases with increasing pH. No explanation for this behaviour is available in the literature. Hayashi et al [175] showed that in their experiments there was a decrease in incorporation at higher pH. The incorporated alumina content was also higher than that reported by the other workers. Thus it is seen that although research has been carried out on the effect of pH the correlation with incorporated particles is not yet clear. Ghouse et al [176] have reported that the codeposition of molybdenum sulphide and tungsten disulphide increases at decreasing pH from Watt's type baths.
Codeposition with copper as the metallic matrix from sulphate baths is generally less than that from cyanide baths [170]. The codeposition of alumina and copper from different copper baths has been investigated by Hoffman [177]. He found that no codeposition was obtained from sulphate and fluoborate baths, a small amount was obtained with a pyrophosphate bath and the highest incorporation was with a formate bath (copper sulphate bath to which ammonium formate is added until a pH of 3.5 is obtained). The sulphate bath has been investigated by other researchers. Chen et al [178] have pointed out the influence of the structure of the alumina particles on codeposition with copper from an acidified copper sulphate bath. He concluded that α-alumina with a hexagonal structure could be codeposited but that γ-alumina with a spinal-type cubic structure could not be codeposited. However, since then Roos et al [179] have reported the possibility of codepositing γ-alumina as well as α-alumina from acidified copper sulphate plating solutions. They found that the relative effects of electrolysis conditions and addition agents on codeposition of α and γ alumina with copper were identical, although much smaller quantities of γ-alumina are codeposited as compared with α-alumina.

Kedward et al [180] studied the codeposition of carbides of Cr, Si, Ta and W with a cobalt matrix. They found that over the normal electrolytic operating conditions, i.e. pH 3.25-5.5, very little difference in volume contents is obtained. Particles of materials such as borides, carbides and sulphides have been codeposited with chromium [163,181]. Early attempts to codeposit alumina with chromium from hexavalent and trivalent baths were unsuccessful [163,180,182]. However, Addison and Kedward [180] reported that codeposition of alumina was possible only from trivalent chromium baths. Raj Narayan
et al [183] found that it was possible to codeposit alumina with chromium from a hexavalent bath if the alumina particles were either nickel-coated or dry ground before mixing in the bath.

5.2.4 Type and Concentration of Second Phase Particles

The influence of particle size and concentration has been researched by many workers. Results generally indicate that codeposition increases with increasing concentration of second phase particles suspended in the electrolyte until a maximum is reached. The amount of particles incorporated depends not only on the composition of the plating bath but also on the type of second phase particle.

Chen et al [178] studied the effectiveness of oxide incorporation by electroforming composites from suspensions of alumina and titania of a given size in copper sulphate solutions. Analysis showed that larger sized, 1 and 3 μm, α-alumina particles were readily codeposited while the smaller, 0.05 and 0.02 μm, γ-alumina particles did not codeposit. For titania on the other hand, the smaller 0.03 μm (rutile) particles are codeposited while the 1.5 μm (anatase) particles are not. These results indicate that particle size does not determine whether oxide incorporation will take place, but that incorporation is selectively dependent on the nature of the oxide crystalline form i.e. α-Al₂O₃ and rutile TiO₂ are more easily codeposited.

The quantity of oxide particles added to plating electrolytes has a considerable influence on the amount incorporated in the deposit. In the plating of Ni-Al₂O₃ alloys, Sautter [170] found that increasing the concentration of alumina in the nickel sulphate electrolyte increases proportionally the amount of alumina in the deposit. Similar results have been reported by Celis and Roos for copper-alumina and gold-alumina systems [184,185].
Nwoko and Shrier [186] concluded that for Ni-\(\text{Al}_2\text{O}_3\) maximum particle incorporation was attained with a bath concentration of 60 g/l alumina, at higher concentrations there was a decrease in particle content; the latter is predominantly due to the inability to maintain all the solid particles in suspension and to the greater degree of agglomeration in the bath which may be due to the agitation being insufficient to hold the heavy load of particles in solution.

Conductivity of the particles also influences codeposition. Investigators [179,187,188,189] have found that large amounts of conducting particles (e.g. Cr and WC) can be embedded even at low concentrations of particles suspended in the plating solution. For non-conducting particles, such as alumina, a much lower incorporation is obtained for similar bath loads. Zahari and Kerbel [190] found that the structure of nickel composites varied with electrical conductivity of codeposited particles. Uniform coatings were obtained with non-conductive particles (alumina) but porous and non-uniform deposits were obtained with highly conductive particles (Cr carbide). Conductive particles were found to have a greater tendency towards agglomeration than non-conductive particles.

5.2.5 **Effect of Addition Agents**

The addition of small amounts of certain substances, organic or inorganic, are often used to influence the form or structure of deposits from normal electrolytic processes. Certain substances have the ability to produce smoother deposits, levelling deposits, or bright deposits, or to affect the internal stress in the deposit.
The addition agents can influence the incorporation of second phase particles by either modifying the properties of the cathode film or by affecting the ion adsorption on the oxide surface thereby changing the discharge mechanism of the ion-oxide complex at the cathode. Very little data exists on the effects of organic addition agents. The addition of urea, a brightening agent, to a nickel Watt's bath has been found to be detrimental to the codeposition of alumina [182]. However, the addition of EDTA or amino acids has been successful in aiding the incorporation of alumina from a copper sulphate bath [191]. Much more data is available concerning the influence of inorganic addition agents. Work by Tomaszewski et al [191,192] supports an earlier theory that cation adsorption is the mechanism by which codeposition is accomplished. In this work they used an acid copper sulphate electrolyte which did not readily produce composite coatings. Soluble salts of monovalent cations, $\text{Cs}^+$, $\text{K}^+$, $\text{Na}^+$, $\text{Rb}^+$ and $\text{Ti}^+$, were found to promote the codeposition of fine, bath-insoluble, inorganic powder.

Lakshminarayan et al [193] studied the effect of chloride ions on the codeposition of alumina particles with copper. They found that when the chloride ion concentration was increased the amount of codeposited alumina decreased, this was due to the formation of a thick insulating film of cuprous chloride on the cathode during electrolysis. Tomaszewski [194] also studied the influence of anions on the codeposition of suspended particles. In nickel and copper baths, the adsorption by barium sulphate of copper and nickel ions, as well as the codeposition of this powder with electrodeposited nickel and copper, was found to be affected by the presence of anions in the electrolyte. Generally, the anions were found to produce poorer composite coatings of barium sulphate with copper than with nickel.
The presence of particles with negative charges on their surfaces were found to have an unfavourable effect on the adsorption of nickel ions. Tomaszewski concluded that the addition of specific multivalent cations to nickel electrolytes containing negatively charged particles dramatically increases the amount of codeposition. Monovalent cations previously used as promoters in acid copper sulphate electrolytes proved to be ineffective in promoting codeposition in these nickel solutions.

The beneficial effect of monovalent cations has also been reported by Roos et al [179,184]. From their study of electrolytic copper-alumina coatings they concluded that the use of addition agents such as aluminium sulphate, ammonium formate, and monovalent cations like Tl⁺ and Rb⁺ promote the amount of embedded alumina particles.

Chen et al [178] also obtained an enhancement in the codeposition of alumina-copper, but they believed that it was both unwise and unnecessary to increase the amount of oxide incorporation in the deposit by use of addition agents because of the possible deterioration of physical properties of the deposits; they stated that increased oxide content could be accomplished readily by other means such as increasing the oxide concentration of the suspension or by increasing the solution stirring speed. Other workers [179,195] have, however, proved that it is beneficial to use addition agents as there are limits to bath loads and stirring speeds.

5.2.6 Effects of Current Density and Temperature

The relationship between current density and particle incorporation seems to be dependent on the type of second phase particles. Generally, increasing current density results in decreasing
incorporation [176,196]. For instance, Toshima and Saito [197] showed that by increasing the current density the amount of ZrO$_2$ codeposited with copper and nickel decreased. For nickel-alumina the amount of embedded particles increases to a maximum then decreases with increasing current density [186]. Similar results were obtained for iron-silica codeposition [171].

In the nickel-silicon carbide system codeposition increases with increasing current density [198], but it seems that the opposite effect can be obtained if electrolysis conditions are varied. Metzer and Florian [198] have shown that the codeposition of SiC particles larger than 5 μm, decreases with increasing current densities in a nickel sulphamate bath, but the codeposition of finer SiC particles shows a maximum with increasing current densities.

The codeposition of alumina with copper from sulphate solutions has been shown to go through a maximum with increasing current densities [179,184].

It is generally reported that there is little or no effect on codeposition when temperature is varied. However, the temperature used must be within limits necessary to produce satisfactory deposits. Narayan and Narayana [199] have reported that for chromium-graphite composite coatings an increase in the temperature of the plating bath from 30°C to 50°C increases the amount of codeposited graphite. Beyond 50°C increasing temperature has practically no effect.
5.2.7 **Agitation of Plating Bath**

There seems to have been very little attention devoted to bath agitation until recently. Bath agitation is necessary to hold the inert particles in suspension throughout the volume of the electrolyte and to remove hydrogen bubbles from the surface of the workpiece. Williams and Martin [171] in 1963 realised the importance of agitation, they reported that the degree of agitation should be held between the limits set by a too violent agitation which swept the particles off the surface before they could be keyed into the deposit and by a too gentle agitation which failed to keep the particles in suspension.

One of the first papers dealing with the effect of the rotation of the substrate on the alumina content of electrodeposited nickel was published in 1978 [200]. It was observed that the alumina content of the deposit decreased with increasing rotating speed of the rotating cylindrical cathode. Well defined hydrodynamic conditions for the codeposition of alumina particles with copper were published in 1980 [201]. The amount of embedded alumina was seen to vary with rotation speed as shown in Figure 16. A constant amount of alumina was seen to be embedded under laminar flow conditions, but at the start of the transition zone a marked decrease in the alumina content was evident. With further increases in rotation speed an increase in the alumina content was observed, until the turbulent zone was reached when a decrease in the amount embedded occurred. It was shown that particle agglomeration occurred in non-laminar flow conditions, therefore it may be opportune to avoid such conditions in industrial electrolysis cells in order to optimise the mechanical and physical properties of composite coatings.
Further work by Masuoko and Mushiake [202] on alumina dispersed nickel plating baths (both Watts and sulphamate) has shown that in successive processes of embedding particles into the matrix that the detainment of particles on the growing surface of the deposit is directly affected by the revolution rate of the cathode. They concluded that the maximum size of the particles caught by the cathode is inversely proportional to the revolution rate of the cathode.

The strong dependence of particle code-position on the processing variables has been mentioned as observed by many authors. However, before a certain composite of a metallic matrix and second phase particle can be codeposited it is important to consider the mechanisms involved in the codeposition and also the final characteristics required of the end product.

The development of composite coatings has allowed modification of the physical and mechanical properties of metals made by electrolysis. Industrial applications already realised are mainly in the field of mechanical engineering, space and automobile industries and the electric and nuclear sectors.

5.3 INDUSTRIAL APPLICATIONS

5.3.1 Wear Resistant Coatings

It is necessary to consider the mechanism of wear before considering the type of composite coatings that may be used.

When a material is brought into rubbing contact under load with an electroplated composite, a very thin film of the composite is removed to expose a layer of matrix metal and particles. Due to the softness
of the metal matrix relative to that of the particle inclusions, wear of the composite will continue theoretically until the applied load is carried by the hard particle protrusions. When this point is reached, provided the applied load does not exceed the compression yield strength of the composite, its wear and frictional characteristics will be determined by the material properties of the occluded particle. Consequently, while the hard particle inclusion contributes most to the wear resistance of the system, it is basically essential that the matrix metal must possess good general wearing properties.

The actual wear performance of a plated composite is also dependent on the size, shape and volume content of the particle as well as its intrinsic wear properties. Based on these considerations attempts have been made to disperse various hard particles for example, $\text{Al}_2\text{O}_3$, $\text{TiO}_2$, $\text{SiC}$, $\text{WC}$, $\text{TiC}$, diamond etc, in a range of matrix materials like Ni, Cu, Cr, Co and Fe.

5.3.1.1 **Nickel-based-wear-resistant coatings**

**Nickel-alumina**: Nickel-alumina composite coatings have been investigated by several researchers [170, 173, 182, 193].

Increasing the bath load of $\text{Al}_2\text{O}_3$ increased the amount of $\text{Al}_2\text{O}_3$ in the coating. This trend was observed up to 200 g/l of $\text{Al}_2\text{O}_3$ by Pushpavanam et al [203]. However, Sinha et al [173] reported the codeposition increased up to a bath load of 100 g/l of $\text{Al}_2\text{O}_3$ and thereafter it remained constant. This difference in the behaviour at higher concentration has been attributed by the investigators to the use of sodium sulphate in their experiments. The pH seems to have little or no effect on the Ni-$\text{Al}_2\text{O}_3$ system. However, below pH 1.6 little [203] or no [173] deposition of $\text{Al}_2\text{O}_3$ is encountered.
Results of several investigators are in agreement that the amount of \( \text{Al}_2\text{O}_3 \) codeposited generally decreases with increasing current density. The temperature and time [170] practically have no effect on the incorporation of \( \text{Al}_2\text{O}_3 \) in the coating.

The effect of various additives on the codeposition of \( \text{Al}_2\text{O}_3 \) with nickel from a Watts bath has been investigated. Urea added as a brightening agent was detrimental to codeposition [182]. Anionic surfactants like sodium lauryl sulphate and sodium lignosulphonate have been shown to be useful in achieving uniform dispersions of \( \text{Al}_2\text{O}_3 \), whereas cationic surfactants such as cetyl trimethyl ammonium bromide and octadecyl trimethyl ammonium bromide result in brittle deposits [203].

An increase in the yield and tensile strengths by inclusion of alumina particles in nickel coatings have been observed [170,186]. Sautter [170] found the yield strength to increase by 4-5 times by increasing the volume percent of incorporated alumina in a nickel coating from 3.5 to 6. Greco [204] reports that in contrast to pure nickel coatings, the Ni-\( \text{Al}_2\text{O}_3 \) composite coatings retain their strength at higher temperatures.

**Nickel-Titania:** Codeposition of \( \text{TiO}_2 \) has been obtained from Watts [186,205] and sulphamate [171,183] baths. As with \( \text{Al}_2\text{O}_3 \), the content of \( \text{TiO}_2 \) in the nickel coating increases with increasing \( \text{TiO}_2 \) in the bath [204,206] and decreases with increasing current density [207].

The incorporation of \( \text{TiO}_2 \) particles in a nickel matrix increases the yield strength, ultimate tensile strength and microhardness as compared to pure nickel coatings [207]. The microhardness of Ni-\( \text{TiO}_2 \)
composite coatings is lower than that of Ni-Al₂O₃ coatings, at equal volume percentage of included particles [204].

**Nickel-refractory carbides and nitrides:** Refractory carbides and nitrides which have been successfully codeposited include TiC, WC, SiC and SiN. Kedward et al [163] observed that the wear resistance of Ni-WC coatings was better than that of Ni-TiC and Ni-Sn coatings. However, it was not high enough to allow the use of such coatings in aerospace applications.

A well known example of the use of Ni-SiC coating with 5% SiC is as sealing components in the Wankel-motor [208], such materials being attractive especially in view of their life span and permissible maximum load. Special attention has to be given to the choice of materials which come into contact with these coatings as they are highly abrasive.

5.3.1.2 **Chromium based coatings**

**Chromium-refractory oxides:** Early attempts to codeposit Al₂O₃ and SiO₂ with chromium, from hexavalent and trivalent Cr baths were unsuccessful [182,209].

In 1971 Skominas et al [210] reported that codeposition of Al₂O₃, SiO₂ and BrO₂ with chromium was possible from hexavalent baths. Addison and Kedward [211], investigated both hexavalent and trivalent electrolytes for codepositing Al₂O₃. It was observed that hexavalent baths were not suitable for codeposition but trivalent baths could codeposit alumina and chromium. However, there was a severe limitation on the thickness of coatings obtainable from trivalent baths, which may be a drawback in solving wear problems. Moreover, uniform coating
thickness could not be obtained from trivalent chromium baths based on chlorides because of their throwing power.

Young [209] showed that $\text{Al}_2\text{O}_3$ could only be deposited from hexavalent baths in the presence of thallium ions.

Wear properties of Cr-$\text{Al}_2\text{O}_3$ coating have been reported to be inferior to those of hard chromium coatings [209,211] especially at temperatures above $200^\circ\text{C}$. TiO$_2$ has been successfully incorporated [204], but volume per cent incorporated is much lower than that of TiO$_2$ in nickel coatings.

Chromium-refractory borides, carbides and diamond: Particles that have been incorporated with chromium include SiC, $\text{B}_6\text{Cr}$, TiC, $\text{Cr}_3\text{C}_2$, BrB$_2$, TiB$_2$ and diamond particles.

The addition of monovalent cations e.g. Tl$^+$, Ce$^+$, Li$^+$, NH$_4^+$ and Na$^+$, is necessary to codeposit chromium from the conventional hexavalent bath [209]. Of these, Tl$^+$ was the most effective for all carbides mentioned. When used in high concentrations Li$^+$, NH$_4^+$ and Na$^+$ had a deleterious effect on the properties of the chromium deposit. Addison Kedward [211] codeposited $\text{Cr}_3\text{C}_2$ particles with chromium from a trivalent bath. The wear resistance was inferior to that of hard chromium coatings. Composite Cr-ZrB$_2$ coatings exhibited good wear characteristics between 300-400$^\circ\text{C}$ but the wear resistance decreased above 400$^\circ\text{C}$. 

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Codeposition of diamond particles from hexavalent baths with Tl$^+$ ions has been reported by Young [209]. With an increase in Tl$^+$ ion concentration in the bath, the amount of diamond in the coating increased linearly. The wear resistance of Cr-diamond coatings was very good.

Another development using chromium as a matrix is that covered in a German patent [212]. Hard glossy layers of chromium are produced by codepositing refractory oxides. This is achieved by the novel method of adding the substances to the electrolytes in the form of their soluble salts. Under the action of the strong acid electrolyte the latter than decomposes and the oxides precipitate in colloidal form.

5.3.1.3 Copper based wear resistant coatings

Copper-alumina: Codeposition of alumina with copper proved difficult from acid baths [182,191] but was successful from cyanide baths [182]. The crystalline structure of alumina was observed to be of importance as $\gamma$-Al$_2$O$_3$ could not be deposited whereas $\alpha$-Al$_2$O$_3$ was successfully codeposited.

However, Roos et al [179] reported that both $\alpha$- and $\gamma$-alumina could be codeposited with copper from acid baths, but under identical conditions the amount of $\alpha$-alumina incorporated was much greater than $\gamma$-alumina. Roos observed that addition of Tl$^+$ added as thallium sulphate promoted codeposition of Al$_2$O$_3$ at all current densities, whereas NH$_4^+$ and Al$^3+$ were effective at low current densities. The codeposition of $\alpha$-alumina with copper has been found to increase the microhardness of the coatings [193].
Cu-\(\alpha\)Al\(_2\)O\(_3\) exhibit higher yield and ultimate tensile strengths and lower ductility compared with pure copper coatings. Increased Al\(_2\)O\(_3\) content in the coating increases yield and tensile strengths and lowers the ductility [193]. The use of ultrasonic agitation reduced the amount of incorporated alumina, but the distribution was more uniform and agglomeration of particles less pronounced [193]. This technique was used to overcome the blistering caused by annealing at high temperatures.

**Copper-Titania:** Chen et al [178] observed that, as in the case of Al\(_2\)O\(_3\), the crystalline form of TiO\(_2\) was important for successful codeposition. Rutile TiO\(_2\) could be successfully codeposited whereas anatase TiO\(_2\) could not be codeposited.

**Copper-carbides:** SiC particles have been incorporated in a copper matrix from acid [191,213] and fluoborate baths. The incorporation of SiC resulted in an increase in the hardness of the coating, the increased hardness was retained up to 900\(^\circ\)C. The abrasion resistance also improved as a result of the addition of SiC.

A good dispersion of zirconium carbide has been codeposited with copper from a cyanide bath [182].

### 5.3.1.4 Cobalt based wear-resistant coatings

The alumina content of cobalt coatings has been seen to increase with increasing bath load of alumina and decreasing current density [214,215]. The pH in the range 1.5-4.5 had no effect. The yield strength of Co-Al\(_2\)O\(_3\) coatings is higher than that of pure cobalt coatings. Co-Al\(_2\)O\(_3\) coatings produced with ultrasonic agitation [216] showed higher yield strength than coatings produced with mechanical agitation.
Kedward and co-workers \[163,180\] studied composite coatings with incorporations of \(\text{Cr}_3\text{C}_2\), WC and SiC. Cobalt-\(\text{Cr}_3\text{C}_2\) coatings exhibited good dry-sliding wear resistance and were superior to coatings containing WC and SiC. The Co-\(\text{Cr}_3\text{C}_2\) were also superior to nickel and chromium based composites and as a result they are used as wear control coatings on aero engines and have been developed on an industrial scale in Britain.

5.3.1.5 **Other metal based wear resistant coatings**

Silver-corundum composite coatings have been studied by Saifullin et al \[217\]. The coatings had a microhardness twice that of pure silver deposits. Titania has also been codeposited with silver \[218\]. Various investigators have incorporated \(\text{Al}_2\text{O}_3\) in an iron matrix. The ultimate tensile strength and microhardness are increased with the addition of \(\text{Al}_2\text{O}_3\) \[219\]. The wear resistance of the composite coatings was twice that of pure iron deposits \[220\].

Zinc based composite coatings with particles of SiC \[221\], \(\text{B}_4\text{C}\) and \(\text{Al}_2\text{O}_3\) \[209\] have been produced successfully. Incorporation of \(\text{TiO}_2\) can give uniform distribution and increases hardness with as little as 1% \(\text{TiO}_2\) in the coating \[222\]. Lead-WC and Lead-TiC composite coatings have been produced by Pini and Weber \[223\].

Gold-WC composite coatings from acid gold complex cyanide and alkaline gold complex sulphite baths have been produced by Larson \[224\]. The coating exhibited higher strength and hardness. Beulens et al \[185\] have observed that \(\text{Al}_2\text{O}_3\) can be incorporated into a gold coating. The amount of \(\text{Al}_2\text{O}_3\) embedded is dependent on pH and temperature. Best codeposition is obtained at pH 4, 60°C and low current densities.
5.3.2 Dry Lubricant Coatings

A composite coating may be expected to have good antifriction properties when soft particles having a low shear strength are incorporated in a metal matrix. Particles used to produce dry lubricant coatings include molybdenum disulphide, graphite and barium sulphate. Vest and Bazarre [225] have investigated the codeposition of MoS$_2$ with nickel from sulphamate baths. The pH was found to be of importance as increased pH resulted in decreased incorporation of MoS$_2$. The adhesion of the coatings decreased as a result of the inclusion of MoS$_2$ particles.

Some difficulty has been encountered in producing chromium deposits with MoS$_2$ particles. Young [209] found that deposits of Cr-MoS$_2$ were very poor, and that after two or three runs the bath became incapable of producing continuous chromium deposits. Konzina and Erganou [220] codeposited MoS$_2$ in a number of metallic matrices. They observed that inclusion of MoS$_2$ in silver coatings reduced the coefficient of friction of the coating. However, the inclusion of MoS$_2$ particles has practically no effect on the coefficient of friction of copper coatings, and only slightly increased that coefficient in the case of tin coatings.

The codeposition of graphite has been reported by several workers [191,209,211,225]. Martin [227] has reported encouraging results for a composite of copper and graphite when compared with conventional materials. Ghouse [228] considered the incorporation of graphite, MoS$_2$ and WS$_2$ with copper coatings. He found that greater incorporation of graphite particles was obtained compared with the other particles. Young has shown the possibility of codepositing graphite particles with chromium from hexavalent baths in the presence of Li$^+$ ions.
Composite coatings of barium sulphate - Cu have been produced from acid baths with the addition of promoters such as heavy monovalent ions (Tl⁺, Ce⁺, Rb⁺) and amino acids [191]. The pH of the electrolyte was found to have no effect but increased temperature reduced codeposition.

There has been considerable interest in codepositing PTFE particles in a metallic matrix in recent years. The properties of PTFE composites can be exploited in many situations that require dry lubrication of a coating coupled with wear resistance. Applications at present in use include: carburettor parts, mechanical handling assemblies, bearing cages and conveyor parts. Whereas systems for the inclusion of hard particles have been in use commercially for a number of years, the problems associated with codepositing PTFE have prevented satisfactory codeposition. Polytetrafluoroethylene (PTFE) is not easily wettable and when wetted it tends to agglomerate, thus stable dispersions are difficult to obtain [229].

However, a patent [230] has been published for producing an aqueous dispersion of positively charged polyfluorocarbon resin particles. Material made to this specification was available until recently; this product has now been withdrawn from sale, therefore workers are now endeavouring to find a replacement. However, problems are now encountered with the change of the polyfluorocarbon resin particles, they are negatively charged. For conventional electrodeposition the charge on the particles has to be reversed, one method of doing this is reported by Pearce and Hawes [229].

The use of electroless nickel-PTFE coatings to provide dry lubricity and good wearability is rapidly developing.
The use of electrolytic nickel-PTFE coatings with non-stick characteristics on moulds have been recently developed in Japan [231]. Helle [232] has reported yet another interesting application of metal-polytetrafluorethylene coatings. Due to their resistance to wetting by water, PTFE composite coated condenser pipes will not be covered by an insulating water film so that an increased heat flow can be obtained. Waterman [233] has produced a lead-based composite containing polymerised resinous material for use on a bearing surface.

5.3.3 Corrosion and Oxidation-Resistant Coatings
Electrolytic codeposition has also been employed to improve the corrosion resistance of electrodeposits. A well known application is in the production of microporous chromium layers by codeposition of non-conducting particles in the underlying nickel layer. Corrosion of the nickel thus occurs over an increased surface resulting in a smaller depth of attack.

Ni-Al₂O₃ composite coatings have better oxidation resistance in an oxygen-rich environment, compared with plain nickel coatings [186]. Good results are also reported for nickel-SiC composites [234]. Fine SiC particles cause a decrease in the oxidation rate, largely due to internal oxide-derived particles acting as barriers to Ni³⁺ diffusion through the NiO scale. The movement of oxygen through oxidation scales has been proved as an important factor in the oxidation characteristics of composites [235]. Withers [236] has produced cermets of nickel, chromium, platinum, rhodium and a cobalt-tungsten alloy with refractory oxides and MoS₂ to produce coatings against high-temperature oxidation.
5.3.4 Dispersion Hardened Coatings

The formation of dispersion hardened alloys has been widely investigated. Brown and Gow [219] have examined an Fe-Al₂O₃ composite coating and reported increased hardness and tensile strength compared with the pure metal. Sautter [170] has observed Ni-Al₂O₃ coatings and considers them feasible for producing dispersion strengthened rocket motor cases. In nickel coatings containing Al₂O₃, SiO₂, TiO₂ and ZrO₂ an increase in hardness is observed with increasing incorporation [204,237].

The hardness decreases with increased volume per cent embedded when graphite particles are used; this can be explained by the low shear strength of the graphite allowing easy deformation [238]. The codeposition of oxides and carbides with copper or nickel not only increases the hardness but also the yield and ultimate tensile strength, ductility, however, is decreased.

Dispersion strengthening can best be achieved after heat treatment. A uniform distribution of particles must be realised in order to obtain maximum retention of hardness after annealing. Codeposition promoters, e.g. aluminium sulphate, can result in an inhomogeneous distribution of alumina particles in Cu-Al₂O₃ composites, thus inferior hardness properties.

5.3.5 Nuclear Coatings

Kedward has codeposited fissile materials like UO₂ and Po with nickel for possible use in fuel elements. Neutron absorbing materials such as boron and its compounds codeposited with nickel could be used as reactor control materials.
5.4 MECHANISM OF CODEPOSITION

Electrolysis conditions to obtain a composite with well-defined characteristics cannot yet be described. Actual insight into the mechanism of codeposition is not sufficient to fully predict the influence of electrolysis conditions on codeposition. Based on the results of early workers [171] three possible mechanisms of codeposition are largely accepted:

i) Mechanical entrapment
ii) Electrophoresis
iii) Two-stage adsorption.

5.4.1 Mechanical Entrapment

One of the most basic conditions to obtain codeposition is that the particles must have the chance to reach the cathode. The inclusion of particles can be described as a chance process in which the particles are brought into contact with the cathode by agitation of the plating baths. If the metal deposition is sufficiently rapid, any particle that is delayed at the cathode will be trapped by the flux of the depositing metal and be engulfed in the deposit. Thus, cathodic efficiency can be important in determining whether codeposition is possible.

The effects of current density and addition agents on the amount of codeposition cannot be explained by a mechanism solely based on mechanical entrapment.
5.4.2 Electrophoresis

Electrophoresis is a phenomenon by which charged particles placed in a liquid move under the influence of an applied electric field. The nature of the surface charge on the particle determines the direction of movement. If the particle is positively charged, it moves towards the cathode. The surface charge can be very important in affecting electrophoretic transport towards the cathode. Foster and Kariapper [239] suggested that adsorption of suitable ions on a particle may produce a large positive charge on its surface and facilitate its electrophoretic transport towards the cathode and subsequent inclusion in the electrodeposit.

The findings of Tomaszewski [191] on the influence of monovalent cations on the codeposition of inert particles indicate that an adsorption process does take place.

Zeta potential measurements using the streaming potential have been reported by Hoffman [240] and Snaith [213].

[Note:

\[ V = \frac{DEZ}{4\pi\mu} \]  

(28)

where \( V \) = electrophoretic velocity

\( D \) = dielectric constant of the medium

\( E \) = applied potential gradient

\( Z \) = zeta potential

\( \mu \) = coefficient of viscosity of the medium.
Due to the high ionic strength of the solutions used for codeposition they concluded that, in agreement with theoretical predictions, no evidence of electrophoretic effects controlling the deposition of alumina was obtained. Snaith [213] also measured the zeta potential in Cu-SiC and Cu-CrB$_2$ systems. These observations supported the electrophoresis mechanism for the codeposition of SiC and CrB$_2$ with copper from acid baths.

However, Sykes and Alner [241] reported that the zeta-potential of Al$_2$O$_3$ in a Watts nickel and an acid copper bath would be very low and negative, and thus they concluded that electrophoretic transport of particles was not taking place in these cases.

5.4.3 Two-Stage Adsorption

Guiglielmi [196] has proposed a mathematical model for the electrocodeposition of inert particles based on two successive adsorption steps - Figure 17.

In the first step the inert particles are loosely adsorbed on the cathode and they are in equilibrium with the particles in suspension, being still surrounded by adsorbed ions and solvent molecules. The second step is thought to be field assisted and produces a strong and irreversible electrochemical adsorption of the particles. The strongly adsorbed particles are then engulfed in the depositing metal. Guiglielmi derived an expression relating the concentration of codeposited particles to the suspension concentration and the electrode overpotential:

$$ C' = \frac{W \cdot \gamma_0}{n \cdot F \cdot d \cdot V_0} e^{(A-B)\eta} \left( \frac{1}{K'} + C \right) $$  

(29)
where $C'$ = concentration of suspended particles
\[ \alpha = \text{volume fraction of particles in deposit} \]
\[ W = \text{atmospheric weight of deposited metal} \]
\[ n = \text{valence of metal} \]
\[ F = \text{Faraday constant} \]
\[ \eta = \text{overpotential} \]
\[ K' = \text{adsorption constant} \]
\[ i_0, A = \text{constants related to metal deposition} \]
\[ V_0, B = \text{constants related to particle deposition} \]

Guglielmi verified the validity of his model for the codeposition of TiO$_2$ and SiC with nickel from a nickel sulphamate bath.

Based on studies of adsorption of Al$_2$O$_3$ particles in nickel and copper electrolytes, Foster and Kariapper [239] showed that the surface charge on alumina particles was an important factor for codeposition. They concluded that codeposition occurred in nickel baths due to nickel ions being strongly adsorbed on the alumina surface, codeposition of γ-alumina did not occur in acid copper baths because cation adsorption on the alumina surface was very small. Addition of Tl$^+$ and Rb$^+$ to the acid copper bath produces a large positive charge on the alumina surface, thereby promoting codeposition.

Celis and Roos [242] also found that this model was valid for the codeposition of α-Al$_2$O$_3$ with copper from acidified copper sulphate baths with and without the addition of Tl$^+$ ions as promoter. They concluded from their results that the second adsorption step was rate-determining. In that step real contact between particles and cathode is created once an ion adsorbed on the particle is reduced at the cathode surface and they showed that only when the reduction of the
copper ions is under charge-transfer overvoltage control a considerable increase of the amount of embedded alumina particles is obtained with increasing current densities. When concentration overvoltage becomes predominant the amount of codeposited particles decreases with increasing current density. Once the applied cathodic overvoltage is large enough to reduce other ions absorbed onto particles e.g. $\text{H}^+$, higher codeposition is obtained [243].

A better insight into the mechanism of electrolytic codeposition is by considering the new development of incorporating fluoropolymer inclusions [232]. By using appropriate fluorocarbon surfactants it is possible to give the fluoropolymer particles a sufficiently high positive charge resulting in a strong affinity of the particles for the cathode. The simultaneous use of non-ionic surfactants is required to prevent flocculation and sagging of the particles. By changing codeposition parameters such as particle concentration in the bath, ratio of cationic/nonionic surfactant and the agitation of the bath, the amount of included polymer can be varied between 0 and 50%.

Overall, it may be stated that Guglielmi's model, based on two adsorption steps, is a valid representation of the process taking place during codeposition. However, further research of the reactions occurring in the hydrodynamic and electrochemical double layers is necessary to clarify the relative effects of the different codeposition parameters to determine optimum conditions for codeposition of composite coatings.
CHAPTER 6
MASS TRANSPORT CONSIDERATIONS

6.1 BASIS FOR TRANSFER PHENOMENA

The fundamental transport or transfer processes of momentum transfer, heat transfer and mass transfer are all basic to the operation of electrochemical reactors or cells, as well as to the classical unit operations of chemical and electrochemical engineering. The aspects of the transfer of momentum, occurring in moving media, are associated with fluid flow and with mixing. For heat transfer, all three traditional mechanisms of convection, conduction and radiation apply individually or collectively in electrochemical processes. Mass transfer, the most basic and important of all transfer processes for electrochemical cells, includes both mass being transferred from one phase to another distinct phase, and more frequently, mass being transferred within a phase from areas of high to low concentration. The basic mechanism of mass transfer is the same whether the phases are gas, solid or liquid.

The basic relations pertinent to the motions of a fluid are the equations for overall mass balance, overall energy balance, and momentum balance. These are then applicable to any analysis of transfer phenomena in electrochemical systems. The dimensionless Reynolds number (\(Re = \frac{\nu L}{\mu}\)), giving the ratio of the inertia forces to the viscous forces in the fluid stream, is used to help differentiate between laminar and turbulent (eddy motion) flow regimes. For application both to regular flow such as pipe, channel flow and even flow in a tank, and to complex flow situations which do not permit easy fundamental analysis, correlations based on Reynolds are available.
The essential applicability to transfer (heat and mass) phenomena in electrochemical systems is given by the relationship to Reynolds as well as Sherwood numbers. For flow situations we can then differentiate among laminar and turbulent regimes and a transition regime. The correlations cover measures for velocity profiles, for pressure drops due to friction, for friction dependence on surface roughness, for temperature gradient effects and geometric (diameter) effects.

6.2 TRANSPORT UNDER TURBULENT FLOW CONDITIONS

For the flow regime where turbulence or eddy motion occurs, the fluid motion next to a solid surface is considered to comprise a boundary layer whose thickness will vary but approaches a constant value under fully developed hydrodynamic flow conditions. The classical model for turbulence has treated it as a stochastic phenomenon with a well-defined mean on which a randomly fluctuating field is superimposed. Application to the relevant equations of fluid dynamics led to the inclusion of empirical observations of eddy diffusivity and eddy viscosity. This classical picture considers flow close to a solid surface to comprise three zones: a thin laminar sublayer film adjacent to the solid surface, where molecular diffusion prevails, an inviscid turbulent outer region where eddies tend to keep concentrations and other fluid properties uniform on a macroscale, an intermediate transitional buffer zone where both viscous and eddy transport are important.

Current ideas on turbulence tend to visualise some universal coherence structure, and some disturbance of the laminar sublayer, and turbulent "bursts" occurring in the buffer zone [54]. For our purposes it is adequate to recognise that models based on these developing concepts
of turbulence will have significant empirical aspects. Models to portray fluid turbulence include Prandtl mixing length and penetration models \([55, 56, 57]\). Because of the indeterminancy of the eddy diffusivity and of the thickness of the layers through which diffusion is taking place, the usual practice is to express the mass transfer flux in terms of a mass transfer coefficient, \(K_L\), thus:

\[
K_L = \frac{I_L}{A_C} \cdot \frac{d}{D}
\]

(30)

6.3 IONIC TRANSFER

In the cathodic reaction of metal deposition being carried out at a rate corresponding to the limiting current, the operative mechanisms of ionic transfer will be diffusion, convection and migration. Diffusion and convection arise from concentration differences in the electrolyte, while migration is the result of the applied potential field.

Electron transfer clearly involves an energy barrier and it can be shown that there is a very small rate of classical electron emission over the energy barrier for electrons at an electrode. There must \([244]\) therefore be tunnel transfers of electrons through the energy barrier from metal to the solution.

With the electrode reaction depleting the metallic ion to zero concentration (at the limiting current) next to the electrode surface, (more at the outer surface of the electrical double layer), the concentration difference provides the driving force for molecular diffusion. The original Nernst concept was limited to this process.
The concentration gradient has a corresponding density gradient which, by the force of gravity, will cause bulk flow of concentrated solution towards the electrode to replace the rising, less dense "stripped" solution. This process of free or natural convection is limited only by the immediate film of electrolyte next to the electrode which will remain stagnant because of viscous and surface frictional forces. Molecular diffusion ensues over this limited stagnant layer of electrolyte (equation 30). The imposition of externally forced fluid movement by agitation or any other form of forced convection will further narrow the region over which molecular diffusion takes place, and contribute to maintaining constant concentration throughout the bulk of the electrolyte.

6.4 DIFFUSION LAYER THICKNESS

Convection is a form of mass transport characterised by movement of substantial quantities of the solution relative to the electrode. Either solution or electrode, or both may move. Near the cathode, the solution becomes less dense as metal ions are plated out, this causes upward streaming of electrolyte. Conversely, downward streaming occurs at the anode. These effects have been called natural convection and may result in stratification of the plating bath, with layers of high density accumulating near the bottom of the tank.

As greater convection is often desired in electroplating processes, this may be supplied by stirring, by pumping the electrolyte, by moving the cathode electrode through the bath, or by bubbling of air through it, in our case by vibratory agitation. This forced convection which can eliminate stratification is usually called agitation. Agitation decreases the thickness of the diffusion film, thus increasing the diffusion current and the limiting current density. In
the immediate neighbourhood of the cathode, diffusion is the principal mode of transport. Therefore, with increasing agitation the effective thickness of the diffusion layer is decreased, hence the rate of diffusion (deposition) increases. The diffusion layer at a metal-electrolyte interface is of particular significance because it has considerable influence on the rates of the electrode reactions. The thickness of the layer is important because it has a major effect on the rate of a reaction and as it becomes thicker the rate of the diffusion decreases so that the reaction becomes slower. Agitation of the solution is generally beneficial as it reduces the layer thickness.

Convection generally gives laminar flow, the thickness of the layer is governed by the geometry of the surface, the coefficient of viscosity and density of the electrolyte, the diffusion coefficient and the velocity of the liquid. The rate of an electrochemical reaction is given by the current density. The maximum limiting current density of deposition of metal ions is very dependent on the thickness of the diffusion layer. It has been shown that, for a process involving iodine [245] the limiting current density was $2.89 \times 10^{-3}$ A/dm$^2$ and the thickness of the layer was estimated as 500 μm for a stationary disc electrode but when the disc was rotated at 50 rev per minute the values became $13.41 \times 10^{-3}$ A/dm$^2$ and 110 μm respectively, and at the higher speed of 250 rev per minute the values were $29.21 \times 10^{-3}$ A.dm$^2$ and 50 μm. Hence, agitation has a marked influence on both the limiting current density as well as the diffusion layer thickness.

That is, the rate of diffusion in gram-ions or moles per square centimetre per second is proportional to the concentration gradient (more correctly, the activity gradient) at the electrode, and the proportionality constant $D$ is called the diffusion constant.
(coefficient), with dimensions of square centimetre per second. The rate is conveniently expressed as:

\[ D(\text{c}_0 - \text{c}_E)/\delta_N \]  

(31)

where \( \text{c}_0 \) is the bulk concentration, \( \text{c}_E \) is the concentration in the immediate vicinity of the electrode surface, and \( \delta_N \) is the effective thickness or Nernst thickness of the diffusion layer. This is a useful term, but not an actual thickness as measured by the freezing or optical methods [246,247].

6.5 CALCULATION OF THE DIFFUSION LAYER THICKNESS FROM THE LIMITING CURRENT DENSITY THEORY

The thickness of the Nernst diffusion layer can be calculated from the limiting current density. This can be considered to be the value of the current density at which a change in polarisation produces little or no change in current density. Fick's first law of diffusion can be written [248] in this form:

\[ \frac{i_L}{nF} + i_D = -D \frac{dc}{dx} \]  

(32)

where \( i_L \) is the limiting current density, \( n \) is the number of electrons involved in the electrode process, \( F \) is the Faraday's constant, \( i_D \) is the diffusion flux, \( D \) is the diffusion coefficient and \( dc/dx \) is the concentration gradient at the interface.
The concentration profile can be considered to be linear within the small distance from the metal-electrolyte interface and then it asymptotically approaches the bulk value. The linear section can be extrapolated until it intersects the bulk concentration at a distance which is the thickness of the double layer, Figure 18. Hence, across the double layer, the concentration gradient \( \frac{dc}{dx} \) is equal to the change \( C_0 - C_x \) in concentration from the bulk solution to the interface over the distance:

\[
\frac{dc}{dx} = \frac{C_0 - C_x}{\delta}
\]

(33)

Therefore

\[
\frac{i_L}{nF} = i_D = -D \frac{dc}{\delta}
\]

(34)

When the rate of a reaction as measured by the current density reaches the limiting value \( i_L \), the concentration \( C_x \) of ions at the interface is zero, \( C_x = 0 \) and the relationship becomes:

\[
\frac{i_L}{nF} = -D \frac{C_0}{\delta}
\]

(35)

\[
\delta = \frac{nF C_0 D}{i_L}
\]

(36)

Therefore, the thickness of the Nernst diffusion layer can be estimated if the value of the limiting current density is known. In this work the limiting current density for the electrodeposition of
copper on stainless steel from the acid copper sulphate bath is shown in Tables 12, 13, 14 and 15, parallel various degrees of agitation, amplitude of vibration and from which the Nernst diffusion layer thickness was calculated based on equation (36). It is necessary to note that the value of the diffusion thickness depends on many other factors such as the composition of the electrolyte, the temperature, the viscosity, current density, diffusion coefficient and the electrode geometry.

6.6 CURRENT DENSITY

In electroplating processes the interest is not so much in the total weight of metal deposited as in its thickness, that is, both coverage thickness and the distribution of the deposit on the cathode. The average thickness will depend on both the total amount of metal deposited and the area over which the deposit is spread, and its distribution will depend upon how evenly the deposit covers the cathode. It is therefore important in electroplating to consider the variable called current density, defined as current in amperes per unit area of electrode. This may be amperes per square metre, A/m², milliamperes per square centimetre, mA/cm², amperes per square decimetre, A/dm², etc.

In all electroplating operations, current density is a very important variable. The character of the deposit, its distribution, the current efficiency, and perhaps, even whether a deposit forms at all may depend on the current density employed.
6.6.1 Current Density and Temperature

Operating temperatures for acid copper baths may vary from 18°C to 60°C but usually a temperature of between 20° and 35°C is used since in this range, little or no heating and cooling is required. Higher temperatures allow higher current densities to be used but tend to reduce throwing power and cause a higher rate of breakdown of addition agents. Current densities which can be used in acid copper deposition depend upon the electrolyte formulation, the rate and type of agitation used, the temperature of the electrolyte and the application. Decorative applications commonly use an average current density of 4-5 A/dm² whereas electroforming applications frequently use current densities of 15-20 A/dm².

The throwing power of the electrolyte is adversely affected by increasing the current density and high throwing power electrolytes are usually operated at relatively low current densities, 2-3 A/dm². For applications where maximum throwing power is required, current densities of 1 A/dm² may be required.

6.6.2 Limiting Current Determination

Cathodic limiting currents can be determined experimentally for the purpose of mass transfer analysis by the following four methods [141,249]:

1. By sweeping potential from zero either continuously or in steps known as the potentiodynamic method.
2. By current sweeps from zero until the potential shows a steep rise - the galvodynamic method.
3. By maintaining current constant and decreasing convective flow until the potential rises steeply.
4. By holding the potential constant at the limiting current equivalent value, the current is measured after the initial transient and before the rise caused by cathodic roughening - the potential step method.

In this work both (1) and (4) were used and the latter found particularly more convenient which in recent times has been shown to be very convenient for rough surfaces and those tending to become rough through incipient dendritic growth [249]. The technique is illustrated in Figure 19 defining limiting current and potentials. To establish the limiting current value $I_L$ from an equivalent limiting potential $E_L$, the polarisation measurements are made on a smooth cathode surface. The limiting potential $E_L$ is defined by:

$$E_L = \frac{E_1 + E_2}{2}$$  \hspace{1cm} (37)

Subsequently, the potential $E$ is applied potentiostatically and the steady-state current established in about 60-180 seconds which is used as a measure of $I_L$. After about 180 seconds and above, begins a gradual increase indicating dendritic growth roughening. This method is convincingly convenient in this study where potential sweeps produce highly serrated polarisation curves as shown in Figure 20 and current averaging achieved by damping of the potentiometric recorder or use of an analogue meter.

The criteria for improvement in each of the methods solution agitation could be related to the five reasons listed in Chapter 1, but in terms of mass transfer several options exist, either use of a mass transfer parameter such as limiting current density ($i_L$), mass transfer coefficient ($K_L$), dimensionless number (Sh) or use of an enhancement factor (EF) relating the performance under agitative conditions such that:
EF = \frac{i_L(\text{ag})}{i_L(0)} = \frac{K_L(\text{ag})}{K_L(0)} = \frac{Sh(\text{ag})}{Sh(0)} \quad (38)

where

Sh = \frac{i_L \cdot d}{nFCD} \quad (39)

d represents the diameter of the agitator disc (cm), \( n \) is the ionic charge of copper (charge per ion in deposition), \( F \) is the Faraday constant (A.S mol\(^{-1}\)), \( C \) is the concentration of copper (\( \text{Cu}^{2+} \)) ions (\text{mol cm}^{-3}), \( D \) the diffusion coefficient (cm\(^2\).s\(^{-1}\)) and \( i_L \) is the limiting current density (mA cm\(^{-2}\)). The electrode reaction is controlled by mass transfer process in this case, that is, the diffusion rates of the reactive species. Namely, according to the diffusion layer concept [248], the diffusion current, \( i \), is given as follows:

\[ i = \frac{nFD (C_X - C_O)}{\delta} \quad (40) \]

where \( i \) is the current density, \( C_O \) is the concentration of reactive species at the interface, and \( \delta \) is the thickness of the diffusion layer. When the concentration of reactive species at the interface is zero, \( C_O = 0 \), the current density shows some critical value. In the case of a static bath, the diffusion coefficient, \( D \), is approximately \( 10^{-5} \) cm\(^2\)/sec and the thickness of the diffusion layer, \( \delta \), is about \( 10^{-2} \) cm. The maximum concentration gradient, \( C_O = 0 \), corresponds to the limiting current, \( I_L \):

\[ I_L = \frac{nFD C_O}{\delta} \quad (41) \]
Equation (41) means that the limiting current increases with the concentration of reactive ion and temperature or by decreasing the thickness of the diffusion layer. The reduction in the diffusion layer thickness is the most effective method. The thickness of the diffusion layer is decreased by increasing the flow rate of the electrolyte. For example, the thickness of the diffusion layer becomes less than $1 \times 10^{-3}$ cm in the stirred bath compared with $2 \times 10^{-2}$ cm in the static bath [311]. The limiting current density is defined as:

$$i_L = I_L/A$$  \hspace{1cm} (42)$$

where $A$ is the effective area of the working electrode (cm$^2$) and $I_L$ is the limiting current (A).

The virtue for the selection of vibratory agitation for study is specially enormous because it is particularly effective in composite electroplating where it is necessary to maintain second phase particles in suspension in the electrolyte in such a way that they can be systematically and quantitatively incorporated in the electrodeposits. There is evidence to suggest that of all the several alternatives such as solution pumping, cathode bar reciprocation, rotary stirring, fluidisation etc, vibratory agitation may be best [18].

Vibratory solution agitation was induced in the process tank electromechanically and to the solution. Systematic studies have been reported for both vibrated electrodes [19-22] usually in the context of electroanalysis or electrode kinetic studies in chemistry, and for enhanced mass transfer in solution [23-29]. Detailed behaviour varies
from one mode of operation to another and also in the case of whether the vibration is longitudinal or lateral and whether it is applied to a cylindrical, flat or disc type electrode. The degree of agitation is expressed quantitatively as an amplitude of movement, \( a \), which can be incorporated in a dimensionless Reynolds number as:

\[
Re = \frac{100 \cdot a \cdot d}{v}
\]

(43)

\( a \) is the vibrational amplitude (mm), \( v \) is the kinematic viscosity of the electrolyte (cm\(^{-2}\) s\(^{-1}\)). Indeed, few fundamental studies have been made for this mode of agitation and no two studies are directly comparable. For example, a vibratory disc electrode was used [25], vibration achieved by longitudinal shaft reciprocation, and results obtained were of the form:

\[
Sh = 0.39 \, Re^{0.585} \, Sc^{0.33} \, (r/R)^{0.235}
\]

where \( r \) and \( R \) were the radii of the disc and cylindrical shaft respectively.

Fahidy [22] reported a correlation for a similar arrangement, that is, horizontal disc electrode vibrating longitudinally as:

\[
Sh = 0.07 \, Re^{0.75} \, Sc^{0.5}
\]

In this regard, there is no definitive quantitative description yet as different interpretations exist.
6.7 THROWING POWER

Among the many characteristics of electrodeposits, the most commonly specified by end-users are macroscopic thickness uniformity and minimum and/or maximum thickness. The capability of a plating bath to give uniform thickness distribution is normally referred to as its throwing power, which is usually experimentally determined in a Haring-Blum cell, Figure 21, by measuring the mass deposited on two equipotential cathodes placed at different distances from a central anode. This phenomenon was defined by them in their paper [52] as a number derived from the derivation of the actual metal distribution from the primary current distribution. They considered it a property of the solution, which it is not. Hence, the concept of throwing power may properly be considered as describing a property of a solution, but any numerical value assigned to it has no meaning outside the apparatus on which it was measured. A numerical value is then computed using one of the following empirical formulae:

Haring-Blum equation [52]:

\[
TP \ (HB) = \frac{(K-M) \times 100}{K} \quad (44)
\]

Heathley equation [250].

\[
TP \ (He) = \frac{(K-M) \times 100}{(K-1)} \quad (45)
\]

Field equation [251].

\[
TP \ (Fi) = \frac{(K-M) \times 100}{(K+M-2)} \quad (46)
\]
where $K$ is the distance between the far cathode and anode divided by the distance between the near cathode and anode, and $M$ is the mass of metal deposited on the near cathode divided by the mass of metal deposited on the far cathode.

For a bath that exhibits perfect throwing power ($M=1$), the three equations give numerical values of $TP(HB) = 100(K-1)/K$, $TP(He) = 100$, and $TP(Fi) = 100$. For one that exhibits the lowest throwing power, the three equations give $TP(HB) = -\infty$, $TP(He) = -\infty$, and $TP(Fi) = -100$ percent. However, none of these equations takes into consideration the effect of actual interelectrode distances, which have been found to have a significant effect on solution throwing power [252]. Other proposed methods for describing throwing power include current and metal distribution and a combination of both, usually on a graphical basis. The various methods and their limitations were covered extensively by Vagramayam and Solov'eva [253]. Kardos and Foulke [254-262] gave an excellent review on the application of mass-transfer theory to such problems.

The drawbacks of -100 and +100 percent or even -infinity can be very confusing and with the importance of throwing power for printed circuit boards and in particular multilayer circuits as well as electrodeposition processes in general, there is a case for modifying the Field's formula to eliminate negative values. An alternative formula [53] for the Haring-Blum cell is:

$$TP = \frac{K-M.100}{K+M+1}$$  \hspace{1cm} (47)
Sulphates, Chlorides and Fluoborates of copper, zinc, nickel and tin are examples of acid plating baths which exhibit low but positive throwing powers, the nature of the metal is also a factor. The principal reason is that cathode efficiencies in these baths remain near 100 percent at high as well as low current densities. The throwing power in acid copper plating solutions is inversely proportional to current density and proportional to the degree of agitation. Therefore, to attain maximum throwing power, it is necessary to plate at minimum practicable current density and maximum solution flow (solution agitation).

Throwing power in acid copper sulphate solution is dependent upon the concentration of both the copper sulphate and sulphuric acid. Also, the use of deposit growth modifying additives not only improves the mechanical properties of the deposits but can also improve the throwing power. The throwing power of acid copper sulphate solutions improves with:

1. Decrease of current density.
2. Decrease of solution temperature.
3. Increase of solution agitation.
5. Increase of addition agents to a minimal level, above which throwing power decreases.

An increase in the concentration of sulphuric acid considerably increases the conductivity of the electrolyte and hence improves the throwing power.
"Plating without rejects" is an ideal that requires an understanding of the processes involved. The requirements and properties of the copper deposit (plate) will vary somewhat with the application or intended use of the deposit. Similarly, the troubles for one application may be insignificant for another - for instance, brightness may not be required or even desired for heat-treat stopoff job. Typical applications and uses for copper plating in general are shown in Table 16.

To discuss the effects of common variables, it is important to define some terms that are sometimes misunderstood in relation to their influence in electrodeposition processes, discussion of which is better explained by graphic representation of the very most important variables.

a) CATHODE EFFICIENCY: For a given amount of direct current, a definite quantity of metal is theoretically deposited. The ratio of the actual to the theoretical amount of metal deposited (per Faraday's Law) is a measure of cathode efficiency. The amount of current that is not being used to deposit the desired metal usually goes to produce hydrogen gas and/or heat - neither of which is an efficient use of current in a plating operation.

b) ANODE EFFICIENCY: For a given amount of direct current (dc) amperage, a definite quantity of metal theoretically dissolves from a "soluble" anode. The ratio of the actual to the theoretical amount dissolved is a measure of anode efficiency.
c) THROWING POWER: This is a measure of how evenly a metal is deposited over the surface, from the high-to-the-low-current density areas. A number for throwing power can be derived from a standardised laboratory test using a Haring cell. Throwing power does not refer to how far down in a deep recess the metal is deposited, it refers only to plate (deposit) thickness distribution. This aspect has been dealt with more elaborately in the previous section above.

d) COVERING POWER: This is defined as the capability of a plating solution to deposit metal on the surfaces of recesses or deep holes (through-holes). No standardised tests are published but the term is frequently used.

Each of the above characteristics or properties is affected by the chemical make-up of the bath and the operating conditions. Hence, understanding these effects can help in establishing optimum conditions. Furthermore, it is necessary to examine some of these variables in some more detail.

6.8.1 Cathode Efficiency

When thick copper plate (deposit) is required in a fixed plating time, it is important to select those conditions that maximise cathode efficiency. Often the temptation is to increase the current density to get more plating. This procedure has a negative effect. To put this into perspective, a bath operating at 95 per cent efficiency at about 3 A/dm$^2$ may drop to below 70 per cent at 6-7 A/dm$^2$ as can be seen in Figure 22.
Higher temperatures (up to 71.11°C or 160°F) increase the cathode efficiency, see Figure 23. Above this, the increase is smaller. The change can be significant, 35 per cent at 26.67°C or 80°F can increase to 90 percent at 71.11°C or 160°F. However, higher temperatures have an adverse effect as this can greatly affect the properties of the electrolyte.

Agitation improves cathode efficiency, with the biggest benefit being in the low ranges. Above a certain agitation rate, no further increase occurs. With high turbulence, the cathode efficiency can decrease. This is represented in Figure 24.

6.8.2 Anode Efficiency

It is important to consider any changes in operating parameters with regard to the effects on the anode as well as the cathode. This will help to avoid long-range problems associated with them.

Current density has a pronounced effect on the anode when it exceeds a certain value for a given bath. This limit, or point at which the anode polarises, varies with the bath chemistry, conditions and contaminant. For example, high free cyanide, aggressive agitation, and the type and concentration of additives or anode aids can increase this current density limit.

Free cyanide aids anode efficiency, however, some compromise is suggested because of the reverse effect on the cathode [264]. Agitation benefits anode corrosion (dissolution). If anodes are bagged, the solution movement on the anode surface is decreased drastically and other conditions have to be maximised to be successful. Anode efficiency aids are designated to allow high anode current densities before polarisation sets in.
6.9 MICROELECTRODES AND SENSORS

6.9.1 Applications and Uses

Microelectrodes have been used by different workers and researchers to mean different things, for example, what is micro to an engineer may be macro to an electroanalytical chemist, and this has led to the use of the term ultra-microelectrode by some workers. Therefore, the situation has become more clearly defined and would probably be accepted that, to be a microelectrode, one of the dimensions should certainly be less than 20 microns. However, in view of the small dimensions involved in the construction of microelectrodes, one can see immediately that microelectrode construction is liable to present some enormous problems.

The use of microelectrodes has grown rapidly and are advantageous for several reasons. First, very small currents (rates of reactions) as low as $\times 10^{-17}$ A, can be measured with relative ease. Second, iR drop is reduced when working with microelectrodes. Third, capacitative charging currents, the limiting factor in all transient electrochemical techniques, are reduced to insignificant proportions at electrodes of sufficiently small area. Fourth, the rate of mass transport to and from the electrodes increases as the size of the electrode increases, moreover, steady states of mass transfer are rapidly established. By the consequence of reduced capacitative charging currents and increased mass transport rates, microelectrodes exhibit excellent signal to noise (S/N) characteristics.

The unusual properties of microelectrodes also allow electrochemical measurements to be made on novel systems - those that are not amenable to conventional electroanalysis. The high mass transfer rates allow
electroanalytical measurements to be made at low substrate concentrations. Other applications include the measurement of the kinetics of fast electrode reactions and of the kinetics of fast reactions in solution coupled to electrode reactions, for example, using the radius dependence of the limiting currents that become kinetically controlled by the reaction in solution. These applications are dependent on three of the special properties because of the spherical or quasi-spherical, concentration, and potential fields surrounding the microelectrode, the reduction of iR losses, decreased capacitative currents and increased mass transport rates [265-272].

One of the best known examples is the use of microelectrodes to stimulate and monitor physiological processes. The application of microelectrodes also provides new opportunities for simplifying and extending research into well known systems. For example, it becomes possible to investigate the deformation of single, or at most, a few growth centres [273-289]. Finally, as indicated in many literatures, microelectrode systems are easily implemented and involve relatively low costs.

6.9.2 Sensors
The concept of sensors for electroplating process control is not new but has become more closely defined in recent years, substantially due to the initiative of Turner [290]. The use of sensors has traditionally been to monitor the process solution through pH, temperature, conductivity and metal ion concentration but using electronic feedback systems a considerable degree of automation is now feasible [291-292].
The need to measure local or general mass transport rates arises in several ways but it is not always necessary to measure such rates in absolute terms. For example, a change in mass transport, usually an increase, may often be quite adequately considered as a degree of process enhancement or as an enhancement factor. This may be caused by, or related to several distinct situations, that is, enhancement due to:

a) increased diffusion rates as a consequence of increased solution temperature;

b) increased cathode surface areas caused by electrodeposited roughening as nodular or dendritic growth develops;

c) increased agitation which decreases the cathode diffusion layer thickness.

This study is concerned with the third possibility and has adopted a well-established strategy which is well-developed in the other cases.

Sensors based on galvanic couples have found several applications. For example, Tomashov [293] devised a "galvanic corrosion battery" and similarly Sereda [294,295] developed a sensor based on galvanic current flow between a Zn-Pt couple and used it to measure the "time of wetness", a parameter defined arbitrarily as the time for which the voltage drop across a 1 megohm shunt resistor exceeded 0.2V. These devices were used in a study of test panels exposed to the atmosphere. Also Mansfeld and Kenkel [296,297] evaluated this system for use as "atmospheric corrosion monitors" (ACM).
In the light of these applications of microelectrode probes or sensors, it has enabled us to assess and determine the current distribution (localised current) in our system, especially on the surface of the printed circuit boards (PCB). This of course can be related to the rates of mass transfer over the whole surface of the board. From experiments carried out, it is therefore evident that the current density decreases from the edge to the centre. This technique provides the opportunity for the determination of localised current density, hence it becomes possible to investigate the formation of growth centres - deposit thickness growth, also, it is possible to investigate the probability distribution of the reaction rates of ensembles of experiments and hence the higher moments of the kinetic parameters of the kinetic processes. The interpretation of the higher moments of the reaction rates is highly diagnostic of the mechanism of the reactions, the measurement and interpretation of electrochemical "noise", therefore promises to be a further important area for the application of sensors to analytical and physical problems.

In conclusion, microelectrodes or sensors can be used in a variety of ways to study both coupled homogeneous chemical reactions and heterogeneous electron transfers as well as metal deposition. Therefore, the development of microelectrode probes or sensors has made possible a range of new experiments in the area of nucleation and phase growth.
CHAPTER 7

EXPERIMENTAL TECHNIQUE

7.1 VIBRATORY AGITATION

7.1.1 Introduction
Experimental work has been carried out to prepare acid copper sulphate solution able to produce satisfactory copper deposits employing vibratory agitation method as a means of stirring the electroplating bath.

The effect of operating variables, system variables, and equipment variables, such as current density, diameter, geometry and orientation of agitator disc as well as tank, solution volume, etc were investigated. The characteristics of vibratory agitation and copper deposition especially in through-holes and recesses and limiting current density distribution were studied by a means of linear sweep potentiodynamic, potential step and sensor techniques.

The optimum parameters for copper deposition from acid copper sulphate baths using vibratory agitation were obtained, analysis of the data obtained were made and necessary correlations for the results were also derived.

7.1.2 Experimental and Arrangement
Previous work (as mentioned in the literature review) on agitation for electrodeposition of copper has been centred around using gas sparging (air agitation) and employing cyanide, fluoborate, pyrophosphate and recently sulphate baths. Little or no work has been carried out
previously using vibratory agitation as a means of bath stirring for copper deposition.

Vibratory agitation was achieved by the use of a vibratory motor (Chemap A.G., model E1) which develops longitudinal vibrations in its axis shaft (instead of the more usual rotational motion) at the frequency used in the primary power supply - in this case conventional alternating current at 50 Hz. The shaft and agitator discs are made of 316-type stainless steel and are inert in the electroplating solution. The disc can be attached or detached from the shaft by means of a swivel-screw threaded into the shaft. Flat, perforated and unperforated discs were employed (diameters of 4, 5, 7.5, 10 and 12.5 cm), the perforated holes (9 mm diameter) being truncated to provide jet spouts of liquid. Amplitudes of vibration were varied by a variac controller. This was shown to be simply related to the input voltage or power and calibrations obtained by using several techniques including stroboscope methods. Some fluid damping occurred such that the calibration held good only if the fluid density, viscosity, etc were constant. Agitation provided by the vibratory motor is controlled potentiostatically. Powering of the motor is provided by the variac and voltage and current utilised were measured by means of digital multimetres. The schematic as well as the actual electroplating rig used in this work is shown in Figures 25 and 26. Thompson Ministat series "E" supplied the power for the electroplating process. The Ministat is capable of providing ± 12A at ± 18V driven by a conventional potential/time sweep rate. The digital multimeter measures the current and the potentiometric chart recorder provides the potential-current polarisation curves.
Experiments have been carried out at various levels of scale-up, typically tank sizes of 2 litres, 5 litres, 10 litres and 25 litres, and the same general pattern of behaviour has been noted. It is therefore important to appreciate the fact that the tank shape and volume size, diameter and thickness of the agitator disc are equally influential parameters and may be factors in governing the magnitude of mass transport analyses of vibratory agitation.

The reference electrode used throughout the work is a mercury/mercury sulphate (Hg/Hg₂SO₄) type. For polarisation study, soluble copper anodes (15 cm²) and vertical sheet cathodes (3 cm²) were employed with a remote junction reference electrode in a sodium sulphate salt bridge. Similarly, soluble copper anodes (216 cm²) and stainless steel cathodes (156 cm²) and (120 cm²) respectively were employed in a 25 litre bath having a total electrolyte volume of 20 litres.

7.1.3 Amplitude Measurements
Vibrational amplitude was measured by several methods. A "Xenon" stroboscope enabled the image of the vibrating shaft to be slowed down or "frozen" and was calibrated against a rotating shaft motor and provided a check on the frequency of vibration.

By providing a travelling microscope and a graduated graticule lens a marker line on the mirror attached to the shaft could be observed and a direct measurement of amplitude made from the maximum and minimum positions.

A further but less accurate check was provided by a "Chemap Indicator" (Alfa-Laval Ltd) - a self-adhesive strip attached to the shaft coupling - which exhibits two arrows during operation and by observing intersection points the amplitude can be measured to ± 0.1 mm.
7.1.4 Solutions Used

Both dilute and concentrated acid copper sulphate solutions whose electrochemical characteristics were well known were used for electroplating. The dilute solution was used for the polarisation and mass transport study. However, the copper sulphate solution was of high acidity to ensure that the transport number of \( \text{Cu}^{2+} \) ion was almost zero.

\[
\begin{align*}
\text{CuSO}_4 \cdot 5\text{H}_2\text{O} & \quad 3.75 \text{ g/l} \quad (0.015\text{M}) \\
\text{H}_2\text{SO}_4 \quad (98\%) & \quad 26.65 \text{ ml/l} \quad (0.5\text{M}) \\
\text{Deionized water (litre)} & \quad \text{pH} = 0.6
\end{align*}
\]

For deposition thickness and distribution study it became necessary to maintain a higher concentration of both copper sulphate and sulphuric acid similar to what exists commercially for the production of printed circuit boards. So a fairly typical "high throw" formulation was used.

\[
\begin{align*}
\text{CuSO}_4 \cdot 5\text{H}_2\text{O} & \quad 75 \text{ g/l} \quad (0.3\text{M}) \\
\text{H}_2\text{SO}_4 \quad (98\%) & \quad 120 \text{ ml/l} \quad (2.25\text{M}) \\
\text{Deionized water (litre)} & \quad \text{pH} = 0.6
\end{align*}
\]

For these studies, vertical flat sheets of stainless steel were used to simulate typically printed circuit boards in a production unit.

For the establishment of the effect of vibratory agitation in the electrodeposition process for the production of printed circuit boards, a typical commercial electrolyte was used in combination with addition and carrying agents.
Lea Ronal pre-purified Copper Gleam Concentrate 250 ml/l
Sulphuric Acid (98%) 120 ml/l
Copper Gleam 125L Carrier 16 ml/l
Copper Gleam 125L Additive 2.5 ml/l

The reference electrode used remained the same type throughout the duration of this work.

7.1.5 Pretreatment (Cleaning)

To give good adhesion, the pretreatment of the parts (panels) to be plated is very important. Cleaning is the removal of undesirable materials from a base material and is normally limited to the surface. The unwanted material may be mist or oxide films, metal fines, shop dirt such as dust or paper, rust preventatives, buffing or polishing compounds, wax, oil, fingerprints, grease and even water in some cases.

Cleaning is one final step in preparing a metal surface for plating. Preceding steps of fabrication, cutting of sample panels to desired size, marking out of the effective area and taping with polytetrafluoroethylene (PTFE) tape etc have each contributed to the surface finish in order to obtain a satisfactory electroplate. The surface to be clean has a direct effect on the cleaning materials because of the possibility of excessive corrosion, formation of oxide or other form of film coating on the sample. Many non-ferrous metals such as copper and copper alloys require milder treatment. It is therefore essential that metal or sample panels to be plated be free of scale and oxide for quality plating. Hence, as cleaning solvents, acetone, 50% nitric acid and cold water as well as deionized water were used at room temperature.
Samples are firstly cleaned with acetone, followed by nitric acid dip and sequentially rinsed with cold water and deionized water respectively. As earlier mentioned, type of cleaning and cleaning materials depends upon the type of sample panel.

Therefore, cleaning and subsequent plating of printed circuit boards, commercial cleaning solvents and procedure were used.

<table>
<thead>
<tr>
<th>Cleaner</th>
<th>Time</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ronclean PC960* † (30% v/v concentration in tap water)</td>
<td>3 minutes</td>
<td>45-50°C</td>
</tr>
<tr>
<td>Water Rinse</td>
<td>2 minutes</td>
<td>cold</td>
</tr>
<tr>
<td>Pattern Prep 24</td>
<td>1 minute</td>
<td>30°C</td>
</tr>
<tr>
<td>Water Rinse</td>
<td>2 minutes</td>
<td>cold</td>
</tr>
<tr>
<td>10% Sulphuric Acid</td>
<td>1 minute</td>
<td>cold</td>
</tr>
</tbody>
</table>

* Proprietary to Lea Ronal Company

Then the plating process is carried out as required.

7.1.6 Determination of Deposit Thickness

The coating thickness determination on stainless steel flat surfaces was carried out by employing an X-ray fluorescence thickness testing computer (Fisherscope 1000). This gives the actual amount of copper deposit on the sample.
Through-holes deposit thickness measured by microsection was made by cutting cross sections of the test panel, supported using sample clips (pins) and mounted in Bakelite using a mounting press, and left to set for 24 hours. The samples were then ground, polished and etched using 5g of ammonium persulphate dissolved in 100 mls of 10% ammonia solution. The etching treatment was simply to differentiate clearly between the plated deposit and the electroless laminate substrate, and rinsed with cold water for about 2 minutes.

Measurement was made using a specially equipped microscope with a camera. The calibration scale was in micrometres.

7.2 AIR AGITATION

7.2.1 Experimental and Calibration

The equipment for air agitation as used in this work is a simple air pump (Whisper 1000 "aquarium pump") operating at mains frequency - 50 Hz. Attached to the air pump is airline tubing of 4 mm diameter. Along the line is a check-valve, connecting the main line is a "Tee" connector. At the end of the tubings are airstones which produce and scatter (distribute) the air bubbles in the solution contained in a tank of 25 litres. The assembly is shown schematically in Figure 27.

The pump calibration ranges from 0-14 digital units. Ten small units (lines) 1 mm apart make a digital unit. That is, fourteen divisions, each having ten sub-divisions. The degree of agitation provided by the pump is controlled by the calibration on the knob of the pump. Every digital increase of the calibration accounts for the corresponding increase in the solution agitation. The pumping rate of the air-pump is from 3 l/min (at 0 which is the base) up to 10 l/min at 14
The flow rate is represented in the plot of air flow rate in litres per minute to pump setting (calibration), Figure 28.

For electroplating processing, air was introduced externally through the air stones via the tubing to the bottom of the tank between the vertical parallel electrodes. The characteristics of the air bubbles and the type of agitation generated were studied. An even distribution of bubbles is realised only above a certain level of agitation, which is solely dependent on the pump setting (calibration). This increase in the pump calibration accounts for the increase in the gas (air) flow rate, liquid velocity which of course is relative to the velocity of the rising bubbles.

As it is often made in the study of mass transfer, it is useful to correlate the results by expressing the data in terms of dimensionless analysis. Considering that a forced flow sets in when the bubbles rise and the corresponding rising velocity increases as the flow rate increases, it is found:

\[ Sh = F(Ar^*, Sc) \]  

(48)

where \( Sh \) and \( Ar^* \) are the Sherwood and Archimedes numbers and \( Sc \) is the Schmidt number.

### 7.3 SENSOR ELECTRODE

#### 7.3.1 Principles of the Method

The key to the method is the well-known Nernst limiting current equation:
which for two sets of experimental considerations can give rise directly to an enhancement factor:

\[ \text{EF} = \frac{I_L'}{I_L''} \]  

where \( I_L' \) and \( I_L'' \) are the values of the limiting currents under agitative and non-agitative conditions respectively when \( I_L' > I_L'' \). When one parameter only is varied to produce enhancement, the following relationships apply with respect to situations a, b and c already cited. Equally, these also express the degree of enhancement in the system – see also Section 6.6.2 (equation 38).

\[
\begin{align*}
(a) \quad \frac{I_L'}{I_L''} & = \frac{D'}{D''}; \\
(b) \quad \frac{I_L'}{I_L''} & = \frac{A'}{A''}; \\
(c) \quad \frac{I_L'}{I_L''} & = \frac{\delta'}{\delta''}
\end{align*}
\]  

(51a,b,c)

The principle has been used successfully in several instances. Considering first the case of electrode surface area, a previous study used this approach to measure surface areas of deliberately machine-roughened cylinder electrodes and a comparison was favourably made with geometrical/measurement measurements of the true surface area [298,299]. An analogous method due to Puippe [299,300] is the basis of the 'DIM' instrument for assessing areas of intricate electronic or jewellery components prior to electroplating. In the case of agitation or flow rates, a change in the limiting current has been suggested as a means of assessing the degree of flow [146] although little data has apparently been published.
These two types of study have led to the idea of using a limiting current technique with a small probe or sensor electrode to assess the degree of agitation (or flow) within a large reactor vessel or electroplating cell. While akin to a microelectrode technique, the practicable size of the electrode is much bigger although could be equally well used as such as in the studies of Wragg et al [301].

7.3.2 Experimental
In order for the sensor/probe to be used quickly and effectively, a rapid method of measuring the limiting current \( I_L \) is required; in this study of agitation a model acid copper sulphate solution has been employed whose mass transport characteristics have been determined previously. Gabe and Makanjuola [249] have shown that by establishing the potential/current curve in the vicinity of the limiting current a potential \( E_L \), equivalent to the limiting current \( I_L \), can be defined (see Figure 20) so that when applied potentiostatically the limiting current value can be quickly measured even when the degree of agitation employed is substantially increased. By monitoring the current/time function, Figure 29, steady state conditions exist after 20-40 seconds after which the current rises slowly as rough growth develops. As the agitation is increased the minimum time reduces to \( x \) 10 seconds (see Figure 29) and the precise value of limiting current becomes less certain (Figure 20).

The solution characteristics were as follows:

<table>
<thead>
<tr>
<th>Solution:</th>
<th>0.3M CuSO(_4); 2.25M H(_2)SO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature:</td>
<td>18°C</td>
</tr>
<tr>
<td>Diffusion coefficient:</td>
<td>( D = 5.84 \times 10^{-6} \text{ [cm}^2 \cdot \text{s}^{-1}] )</td>
</tr>
<tr>
<td>Viscosity:</td>
<td>( = 1.0184 \times 10^{-2} \text{ [cm}^2 \cdot \text{s}^{-1}] )</td>
</tr>
</tbody>
</table>
Plating tanks of up to 25 litres volume were employed and the cathodes were flat sheets of stainless steel suspended vertically to simulate typically printed circuit boards in a production unit. Agitation was achieved by conventional air agitation or disc vibratory agitation as already described, both applied at the centre-bottom of the tank. Limiting current values measured in the tank without agitation were used as baseline values \((I_L)\) relative to which Enhancement Factors \((EF)\) were obtained as in equations 50 and 51c.

The sensor was typically a small wire-tip electrode with an associated luggin probe or sintered glass remote reference electrode, that is, a two-electrode assembly which is schematically represented in Figure 30. Both calomel (SCE) and mercurous sulphate (MMS) reference electrodes have been used. The two-electrode probe can be moved around the tank and its position recorded in three dimensional coordinates. Alternatively it can be placed adjacent to the work pieces and "dead" agitation zones identified.

An X-ray fluorescence method of thickness testing on the sheet cathodes (Fischer Instruments) was employed to make a comparison of thickness and equivalent thickness values assuming >90% cathode current efficiency.
8.1 RESULTS: VIBRATORY AGITATION

8.1.1 Characteristics and Mass Transfer
The degree of vibratory agitation was controlled by alternating current voltage from the variac or variable auto-transformer which was calibrated in terms of amplitude of movement. The motor calibration is shown in Figure 31.

Increase in applied voltage results in a corresponding increase in the amplitude and consequent increase in the solution agitation. Calibration and degree of agitation relative to the types of eddies produced differed for perforated and unperforated agitator discs, indicating that greater energy was required for the latter to give similar amplitudes of vibration because the unperforated discs act as lift pumps or hydraulic pistons, hence they produce inferior agitation as the fluid is being diverted laterally around the edge of the disc. The perforated discs produce superior agitation. Initially, the agitation was found to be essentially laminar up to a critical amplitude or control voltage whereupon an eddying pattern became apparent and flow was becoming markedly turbulent, because the perforations in the disc allowed fluid to pass through and jet upwards creating large eddy-type circulation hence increasing the degree of agitation.
When inert particles were added to the electrolyte the calibration changed: in the case of fine low density alumina almost imperceptibly but in the case of high density iron powder quite substantially Figure 32.

The limiting current technique was used to study the enhancement of mass transfer in relation to vibrational amplitude. For this purpose only perforated agitator discs were employed and solutions with and without particles were investigated. The experimental data obtained are given in Figure 33, the data being plotted on logarithmic scales to demonstrate clearly the transition from laminar to turbulent flow at an amplitude of 0.45-0.6 mm. These experimental data obtained for both the simple copper sulphate "model" electrolyte and for a composite coating electrolyte based on the "model" composition containing additionally 1 and 5 g/l of alumina (Al₂O₃) particles (size 3 μm, allotrope). Analyses of the data have shown that the presence of particles has only a marginal effect on the mass transport correlation.

When plotted as a mass transfer correlation the transition remained equally clear - Figure 34 - giving obvious differences in behaviour within the two regimes. These data disregard Schmidt number as a separate variable and utilise values of physical parameters for the solution.

A laminar–turbulent transition was also apparent for amplitude, a = 0.04-0.06 for solution without particles (Re = 2500) as shown in Figure 35. Below this transition the laminar region showed relative insensitivity of mass transport to agitation while in the turbulent region marked enhancement occurred. The relationships from graph calculations (Figure 35) were as follows:
Laminar regime \( \text{Sh} = 29.7 \, \text{Re}^{0.037} \, \text{Sc}^{0.33} \)

Turbulent regime \( \text{Sh} = 0.16 \, \text{Re}^{0.82} \, \text{Sc}^{0.33} \)

In both cases the power dependence for Schmidt (Sc) number was essentially assumed because the data represented such a narrow range of values: \( 1800 < \text{Sc} < 3200 \). Again, with the inclusion of the data for the composite deposits (containing \( \text{Al}_2\text{O}_3 \) particles) the dependence changes slightly to give values of Sherwood number approximately the same as Reynolds number \( (\text{Sh} \approx \text{Re}^{0.91}) \), and to obtain a full correlation, values of Schmidt number (Sc) need to be varied over at least an order of magnitude and this has not been possible. However, for \( 1779 < \text{Sc} < 3057 \) and \( 2500 < \text{Re} < 20,000 \) the correlation has been found to take the form:

\[
\text{Sh} = 0.164 \, \text{Re}^{0.82} \, \text{Sc}^{0.33}
\]

or

\[
\text{Sh} = 1.94 \, \text{Re}^{0.84} \text{ at Sc = 1779}
\]

A degree of enhancement has been defined as the ratio of limiting current density (or Sh) obtained with vibratory agitation to that obtained in still solutions; values compare favourably with those obtained by other agitation methods:

- still solution: 1
- cathode reciprocation: 2-4
- air agitation: 2-4
- vibratory agitation: 3-20
Similarly, the effectiveness of the prevailing agitation can be expressed simply as the value of the diffusion layer thickness, $\delta$, typical values are as follows:

<table>
<thead>
<tr>
<th>Method</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>natural convection</td>
<td>0.1 - 0.2 mm</td>
</tr>
<tr>
<td>planar/annular surfaces</td>
<td>0.01 - 0.2 mm</td>
</tr>
<tr>
<td>rotating cylinders</td>
<td>0.005 - 0.05 mm</td>
</tr>
<tr>
<td>gas-generating electrode</td>
<td>0.002 - 0.04 mm</td>
</tr>
<tr>
<td>surface abrasion/scraping</td>
<td>0.01 - 0.1 mm</td>
</tr>
<tr>
<td>ultrasonic agitation</td>
<td>0.005 - 0.01 mm</td>
</tr>
<tr>
<td>vibratory agitation</td>
<td>0.0003 - 0.0014 mm</td>
</tr>
</tbody>
</table>

The study of the effect of varying superficial velocity on mass transfer coefficients of electrodes of different diameters as shown in Figure 36, reveals that (i) the values of the mass transfer coefficients increase with increase in superficial velocity and the improvements in coefficients with flow normal to the electrode compared to those with flow parallel to the electrode are 3-6 fold; (ii) the values of the mass transfer coefficients increase with decrease in the electrode diameter.

Detailed experimental study of the limiting current density distribution revealed an uneven distribution from the top of the plating tank to the bottom. The limiting current was found to be high at the top and much higher at the bottom of the tank, whereas the middle maintained a low limiting current value, and moreover, the limiting current value increased with increase in vibratory agitation rate - Figures 37 and 38. This experiment was repeated with the electrode at different positions in the tank and the same trend was observed.
8.1.2 Composite Electrodeposition Studies

Codeposition of inert particles within a metallic matrix has been developed for practical uses in the last few years, but its mechanism is not yet fully understood. Investigations have shown that vibratory agitation is a principal factor which can enhance particle incorporation because it has the advantage of maintaining full particle buoyancy not swirling shear effects of agglomerate disintegration and also, the region at which to operate (mild turbulence) can easily be determined.

The stirring (agitation) rate of the electrolyte containing the inert particles has a considerable influence on the amount incorporated in the deposit. The effect of the vibrational agitation rate on the incorporation of alumina from acid copper sulphate solution containing 40 and 75 g/l of alumina particles (size 3 μm, α allotrope) is shown in Figure 39a,b. The figure demonstrates that at low vibrational agitation rates, the amount of alumina particles incorporated was low, that is, about 1 per cent by weight. The alumina incorporation or content increased as the vibratory agitation rate was progressively increased, rising to a maximum at agitation rates between 170-180. With further increases in the degree of agitation the incorporation of alumina particles decreased drastically to less than 1.5 per cent. This result indicates that the maximum amount of alumina was incorporated at intermediate vibratory agitation rates.

From visual observation, at the lowest vibrational agitation rates a considerable amount of the alumina particles were resting at the bottom of the tank and not in suspension, therefore there were practically less alumina particles available for codeposition. At the higher vibrational agitation rates, the solution at this moment is in
a turbulent state and particle agglomeration was noted with the higher agitation rates, while the low incorporation could have been due to the alumina particles striking the cathode surface too fast to allow incorporation. The current density was maintained at 3 A/dm² throughout the course of this investigation.

8.1.3 Limiting Current and Deposition Thickness Distribution

Variations occur in the limiting current values from the top of the plating tank to the bottom. This is corroborated by the deposition thickness distribution on the surface of the plated panel. The results of the deposition thickness, as measured by the Fischerscope 1000 -X-ray fluorescence (coating thickness testing computer), are shown in Figures 40a-43b, plated at constant potential but at different plating times.

At low current density, the surface diffusion is fast compared with electron transfer, while at higher current density, surface diffusion is no longer fast compared with electron transfer and in this case further nuclei must form, then the layer or deposit becomes less ordered. With further increase in the current density, outward growth of the layer becomes of increasing importance and problems arising from mass transfer control in solution can arise, hence dendrites can occur and once this form of growth commences, it predominates totally because of the enhanced rate of mass transfer. In the completely mass transport controlled potential region the deposit becomes a powdered texture.
8.1.4 Through-Hole Plating

It is increasingly appreciated that manufacturers of printed circuit boards have two main problems of metal distribution. Firstly, poor metal distribution within through-holes which may be caused by ion depletion, i.e. concentration polarisation effects, or by secondary distribution characteristics which may be changed by pulse current techniques, this latter behaviour has been highlighted extensively [305]. Secondly, metal distribution and throwing power effects across the whole board (thickness deposit distribution). This characteristic is susceptible to change by varying modes of agitation and jigging patterns within the plating tank.

Through-hole plating was carried out employing both vibratory and air agitation methods with the board placed vertically and horizontally in the tank. The cathode reciprocating method (cathode mechanical movement) was also employed. Board positions also varied vertical/horizontal). Similarly, plating was carried out with and without additives and carriers respectively. The respective effects of position, location at different points and positions in the tank as well as the effects of additives and carriers and duration of plating time were noted. Each of these were found to have some characteristic effect on the deposit thickness in the through-holes as well as on the surface of the printed circuit board. Through-holes of different diameters were plated. Printed circuit boards with through-holes of smaller diameters present more problems with regard to metal distribution down the holes especially with the air agitation method than with vibratory agitation. The big holes have diameters of 0.8 mm while the smaller holes are of 0.3 mm diameter.
Figure 44 shows the effect of the absence of addition agents. Here, it can be seen that the deposit in the through-hole is very rough and non-uniform.

Figures 45 and 46 show the effect of the presence as well as the absence of one or the other in each case. Figure 45 was plated with 125LX Additive but without 125BL Carrier, while in Figure 46 the 125BL Carrier was present and 125LX Additive absent. In the two photographs (figures) the difference as well as the influence is very distinct in each case.

Then plating was carried out with both of the addition agents employing cathode reciprocation, air and vibratory modes of solution agitation, increasing the plating time from 45 minutes to 60 minutes per sample in all cases. The positioning of the boards in the tank were varied in terms of vertical and horizontal, while a specific location in the tank and distance from the bottom as well as from the agitator disc was maintained. Similarly, the current density was maintained at 3 A/dm² throughout this investigation.

The results of this investigation are shown in Figures 47, 48, 49, 50 and 51. These photographic representations show the deposit thickness in the through-holes as well as on the surface of the printed circuit board (PCB). The vertical arm of the photographs shows the deposit on the surface while the horizontal arm is the deposit in the through-holes.

These figures demonstrate the type of deposit thickness as well as distributions in terms of uniformity and smoothness in a plated through-hole employing different types of solution agitation methods.
8.2 RESULTS FOR AIR AGITATION

8.2.1 Bubbles in Motion

Bubbles in free rise or fall in infinite media under the influence of gravity are generally grouped under the following three categories:

a) Spherical, bubbles whose interfacial tension and or viscous forces are much more important than inertia forces;

b) Ellipsoidal, bubbles which are oblate with a convex interface around the entire surface; and

c) Spherical-cap or ellipsoidal-cap, bubbles which adopt flat or indented bases and lack the semblance of fore- and aft-symmetry.

These types of bubbles may look very similar to segments cut from spheres or from oblate spheroids of low eccentricity.

For bubbles rising or falling freely in infinite media a generalised graphical correlation is prepared in terms of the Eotvos number, Eo; Morton number, M; and Reynolds number Re [136,137]. The resulting plot is shown in Figure 60. This graphical correlation dealing with shape regime shows the boundaries between the three principal shape regimes. In view of the values of both Reynolds and Eotvos numbers as obtained in this work, bubble shape regimes are within two or more boundaries (see Table 18).
Bubbles are ellipsoidal at relatively high Reynolds and immediate Eotvos number while spherical- or ellipsoidal-cap regimes require that both Eo and Reynolds numbers be large. Even though the boundaries between the principal shape regimes are somewhat arbitrary, nevertheless, Figure 60 is a useful tool for demonstrating the wide range of bubble behaviour as observed in this work.

Figures 61a,b,c,d and 62a,b,c show different types and shapes of bubbles. These are individual bubbles selected out of several bubbles to demonstrate the different shapes of bubbles involved in this work, while Figures 63a,b are shown photographically to demonstrate the coalescence of the bubbles.

8.2.2 Bubble Distribution
The distribution of the bubbles in the plating tank has been observed to vary according to the bubble volume. This is dependent on the pump calibration - that is, the volume of air pumped per minute. At low flow rates the bubbles are sparsely distributed. As the flow rates increase, the electroplating tank is then gradually filled with bubbles.

Therefore, in Figures 64-70 are shown the distribution patterns of bubbles in the electroplating tank used in this work, at different air flow rates.

8.2.3 Electrodeposit Thickness
The analysis of the electrodeposits has shown that air as a means of stirring electrodeposition baths is poor in terms of deposit thickness and distribution, especially if used without the aid of other means of solution stirring, for example, in combination with cathode movement.
Although it produces uniform deposits on planar surfaces but it has poor quality deposits in crevices especially in plated through-holes of printed circuit boards.

As the overall fluid velocity increases due to increase in bubble volume and velocity, one would expect a corresponding enhancement of mass transfer rate when translated in terms of enhancement factor (EF) or rates of deposit thickness. Typical enhancement factors obtained under the scope of this work are shown in Table 18 for air agitation and Table 19 for vibratory agitation.

Enhancement is related to plating rate. This is expressed by taking front and back (both surfaces) of plated panels showing deposition rates as measured by the X-ray fluorescence Fisherscope 1000 thickness (coating) testing computer, the results of which are represented in Figures 71.1-73.3, plated at 10, 15 and 20 minutes respectively. However, enhancement factor values can be estimated to be approximately four times more than the calculated values if based on thickness values as represented graphically in Figure 71.1.

Comparative representation of deposition rates employing vibratory agitation are shown in Figures 74.1 to 77.3.

In view of the deposition rates using the two types of agitation methods, one can conveniently arrive at the conclusion that the air agitated solution plating rate is not sensitive to the degree of agitation, whereas by contrast vibratory agitation provides marked enhancement. Also for high technology, high speed processes, vibratory agitation is obviously advantageous, while air agitation is ideal for a jobbing-shop but really it is of little value for enhancement both from scientific and technological points of view.
8.3 RESULTS FOR MICROELECTRODE

8.3.1 Sensor-Electrode

The sensor has been used to measure the variation of agitation in large plating tanks, produced by non-symmetrical or localised agitators which lead in industrial processes to variable degrees of electrodeposit thickness on large cathode work pieces. Such sources of variation are often attributed to "throwing power" effects but in practice they may be due to both true throwing power effects and local variability in agitation due to flow shielding by irregularly shaped or contoured cathodes. The sensor has also been used to compare agitation techniques in terms of process rate enhancement, this being one particular reason for the use of agitation.

In these experiments, variations in degree of agitation in the tank have been measured from top to middle to bottom and from side to centre to side. However initially a calibration was attempted in relation to deposit thickness by use of a large vertical sheet, simulating a printed circuit board, on which coating thickness was measured also by X-ray fluorescence after electrodeposition at a normal current density, for example, 1 A/dm², current densities were measured separately. Figure 78 shows the very good agreement which was obtained. It also illustrates that for vibratory agitation marked enhancement occurs at the bottom, relatively little at the middle and rather more at the top near the meniscus interface.

By using the sensor in small increments of height from top to bottom and variable vibratory agitation rate, a very detailed pattern of agitation could be obtained, this is illustrated in Figure 38.
Variations across the tank (corner-centre-corner) were investigated in a similar manner using three vibratory agitation levels and the probe in bottom, middle and top positions as shown in Figures 79-81. It can be seen that the tank walls "drag" effect extends for about 7 cm and is more marked at the middle level - see Figure 80. These figures also illustrate how the degree of agitation can be interpreted as an enhancement factor. If the same effect is studied on a side to centre to side basis the "drag" effect appears more marked - Figures 82 and 83 - with a very sharp peak of agitative effectiveness at the centre.

It is interesting to compare air agitation in this context. This is not the place to consider air agitation characteristics in detail as it has already been discussed in other sections, but it is worth noting that air agitation can produce a more even or uniform effect but that the degree of enhancement does not increase markedly with air flow rate for a given pattern of air bubble distribution as shown in Figure 84. The figure demonstrates that below 3 litres per minute the bubble release or evolution is spasmodic or erratic giving rise to bursts of activity creating an impression of high mass transfer at 3-4 litres per minute. However, when "steady-state" the bubble agitation has developed at 4-5 litres per minute the pattern of agitation is remarkably uniform giving limiting current density ($i_L$) values of 12.05-12.25 mA/cm$^2$ which represents a very narrow range.

This is found for air flow rates of 4.5-10 litres per minute which is a wide range of flow rates. Thus, it may be considered to be extremely good for uniformity but relatively poor for increasing deposition rate.
CHAPTER 9
DISCUSSION

9.1 DISCUSSION OF VIBRATORY AGITATION

The origin of vibratory agitation may be traced to the technology of composite electrodeposition where it is one of about five or six possible methods of dispersing particles in an electroplating solution. While it is difficult to state which is the best method it does have some advantages because the requirements of agitation are initially to disperse the particles and thereby transport them in a non-aggregative form to the growing cathode surface.

Sufficient agitation is a common requirement to the macroscale, miniscale and microscale characteristics of plating of complete panels. The consequence of insufficient agitation is inadequate mass transport which in turn results in large ion concentration gradients at the cathodic surface. Mass transport limited plating results in poor quality deposits and the conditions at which the deposit occurs at the bulk of the plating solution. For these reasons, vibratory agitation in electrodeposition process is an important aspect for the electroplating of copper in the "through-holes" of printed circuit boards.

Flow and mass transfer rates are characterised by Reynolds and Sherwood numbers respectively. The driving force of mass transfer at this moment being related to the concentration gradient of the reacting species or to the concentration difference between electrode and bulk solution. Consequently, the migration flux can be very much
decreased by increasing the conductivity of the solution, thereby lowering the electric field strength. Thus, in this work an adequate amount of supporting or inert electrolyte was added.

The calibration of amplitude against input power or voltage was found to be always of a paralinear form and must be considered to be essentially a characteristic of the mechanical or inertial restraints of the vibratory motor. While a linear relation would have been ideal, the reproducibility is excellent up to the effective limit of approximately 3.8 mm in some cases. The accuracy of the two methods of measurement of amplitude is also worth noting. From experimental points of view the Travelling Microscope Vernier method is believed to be most accurate and even convenient with results varying by only $\pm 2\%$ and due primarily to focusing variations. The Chemap Indicator has a degree of convenience and was used primarily to provide a second means of calibration: its accuracy is less good partly because of the way in which it has to be used at particular amplitudes when visual coincidence occurs.

The differences in behaviour for baths of differing sizes was noted initially in studies of the flow patterns generated. Purely in flow terms no difference can exist and analysis of the data obtained shows that any damping due to vessel constraints is negligible and the experimental data is absolutely predictable as should be expected if the definition of Reynolds number is correct. This cannot be assumed to imply that the effects of agitation on an electroplating process, however, is unaffected and is consequently considered in detail in this work.
The structure of the growing layer (deposition) will largely be determined by the relative rates of mass transport (this may be diffusion, convection or migration) of the metal-bearing species to the electrode surface and diffusion across the surface into a position in the lattice in the plating process, and the current density employed. Above a certain critical Reynolds number, characteristic for a given flow system, the nature of fluid flow changes drastically, it passes from laminar to turbulent motion. While in steady laminar flow, the fluid particles follow in definite streamlines, turbulent flow is characterised by a random chaotic motion of eddies superimposed on the main stream motion by the vibratory agitation.

The eddies which are produced by vibratory agitation carry momentum and mass toward regions of lower concentration of these quantities. Because the moving entities are very large, consequent mass transport rates are considerably higher in turbulent flow than in laminar flow. Therefore, the effectiveness of vibratory agitation is measured by the mass transfer numbers, limiting current, enhancement factors and the throwing power ability of the system.

The choice of definition for the Reynolds number was based on that given by previous authors [141,144,154]. However, other options became evident through the critical dimension. No attempt was made here to prove the correctness of this definition but further detailed investigative work on scale-up of vibratory agitation suggests that a more precise definition was necessary (see equation 25). This would take account of the fact that when the gap becomes narrow, eddy circulation cannot take place.
Fundamental analysis of the mass transport behaviour is usually based on the use of classical dimensionless correlations (see equation 26a) where the Sherwood number expresses the rate of deposition as a mass transport coefficient, the Reynolds number describes the flow behaviour and the Schmidt number defines the solution's physical properties. The special definition of Reynolds number in a vibratory system has been discussed (see equation 24) and Sherwood number is primarily dependent upon limiting current density $i_L$ (see equation 39).

Generally, the data of Figure 35 as well as some other related figures disregard Schmidt number as a separate variable of course (one solution of constant diffusion coefficient $D$ and kinematic viscosity was used throughout) so must yield a constant which includes the value for Schmidt number ($Sc$). Thus two equations can be derived:

for $a < 0.45$ or $Re < 2000$

$$Sh = 375 \ Re^{0.037}$$

(52)

for $a > 0.55$ or $Re > 2500$

$$Sh = 1.4 \ Re^{0.84}$$

(53)

At low laminar regime relatively little mass transfer enhancement occurs and the particles in a composite plating bath are probably not fluidised. In the turbulent regime substantial enhancement occurs and the agitation is highly effective. Close scrutiny of the data suggests that the indice value increases as the solution becomes pseudo-viscous due to particle dispersion and 5 g/l alumina ($Al_2O_3$) particles the "best fit" value of $a = 0.91$. 

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From the pattern of vibratory agitation observed it may be reasonably deduced that the two regions thus described are laminar and turbulent in character although clearly of a special geometric pattern arising from the geometry of the perforated disc employed as agitator. Furthermore, it is clear that for practical purposes the laminar region is quite unsuitable for use because its effectiveness for agitation is poor and in electrodeposition processes as well as composite plating it provides inadequate throwing power and particle dispersion.

The effectiveness of vibratory agitation for commercial electroplating processes can be defined in several ways. Using the principle of enhancement factor (EF) it is clear that in the laminar regime little enhancement occurs and it is not a practicable proposition. However, in the turbulent regime enhancement factors of up to 3-30 were obtained compared with 2-4 for air agitation and cathode reciprocation and 5-50 for turbulent flow past a flat electrode surface. Some typical Enhancement Factors are given in Tables 19 and 20.

For electroplating in a large tank or vat the relative size of the agitator disc and the relative position of the cathode surface in relation to the disc within the tank are clearly important. The results have been normalised with respect to the relative sizes by using modified Reynolds and Sherwood numbers (see equations 25 and 27). The effect of varying mass transfer within the tank was established by using a small cathode probe and determining limiting current densities at various positions in relation to the agitator disc and at various degrees of vibratory agitation. Figures 85 and 86 give the data obtained and show common general patterns and some detailed differences. Positions just below or alongside the disc are
less effective and those just above more effective; this behaviour is apparent from the pattern of eddy turbulence shown in Figure 12. The data can be analysed numerically by determining the mass transfer correlation for each set of data. The equation coefficients are given in Table 21 and show detailed differences for the same general pattern of behaviour.

The applications envisaged for vibratory agitation must be considered in relation to process requirements and its relative efficacy when compared with other agitative systems. When compared with air agitation it is likely to be more expensive in energy terms, but, as with cathode movement, it is non-oxidative. If process rate enhancement is important then vibratory agitation is clearly very effective and must stand on its own merit. As indicated already, vibratory agitation to date has been used primarily in electrodeposition of composite coatings where it provides not only agitation but particle buoyancy in an advantageous manner. It has been argued that for this application it may provide the best mode of agitation because the particles must be dispersed, must be made buoyant and must be allowed to have adequate substrate residence time to be efficiently co-deposited.

However, excessive agitation tends to reduce incorporation as particles can be swept away from the surface before incorporation can take place. It is clear from this investigation that once the transition or critical amplitude is exceeded particle distribution in the bed, and consequently in the composite electrodeposit is good. Local distribution attributable to particle agglomeration is not so satisfactory, but the presence of a small amount of surfactant is helpful in this respect.
9.1.1 Plating of Printed Circuit Boards

As already mentioned, printed circuit boards have problems of metal distribution, especially within through-holes, and throwing power effects across the whole board, which is liable to change due to changes in the modes of agitation within the plating tank.

The agitation pattern within a vibratory agitated tank has been studied in several ways, but notably by measuring deposit thickness over large boards placed vertically and horizontally in the tank and noting the precise location of each thickness value. A limiting current micro-electrode (sensor) method has also been employed to measure the local limiting current density and hence localised enhancement factors. The limiting current density increased with an increase in amplitude of vibration and was used to study the mass transfer rate in relation to vibrational rate. In the laminar regime, flow is near stable and does not contribute much to the diffusion process hence little enhancement occurs. At higher vibration (high limiting current density), a secondary flow pattern forms (Taylor vortices) and finally the flow becomes turbulent.

By using the limiting current technique a mass transfer type of correlation can be obtained for every coordination position in the tank and the changing pattern can clearly be seen in Figure 38. Thus, the greatest enhancement occurs at the bottom of the tank nearest the source of agitation. If the confusion is avoided by taking bottom, middle and top curves only, it may be seen that two patterns emerge (see Figure 40) with a position at the bottom of the board giving greatest enhancement and consequently greatest deposit thickness but that the other patterns tend to converge minimising variability in enhancement of deposit thickness. This difference also covers a laminar-turbulent transition.
In practical terms this manifests itself as variations in deposit thickness of course and this has been checked by X-ray fluorescence thickness testing measurements. The agreement between the two techniques is very good, the pattern being virtually identical and the difference in absolute value being entirely attributable to a cathode current efficiency of 90-97%. The high value at the top near the solution surface is perhaps most surprising but has been clearly seen as due to reflection of the vibratory agitation pulses causing circulating eddies within the tank and ripples on the solution surface.

The consequence for metal distribution over the whole board is that the board size and position should be related to the tank size and solution volume in order to minimise deviation of deposit thickness from the preferred norm. Thus, in the context of Figure 78 if the board is placed between positions marked 10 and 25 cm the deviation is reduced substantially from 4.1 ± μm to 3.4 ± 0.2 μm and this has clear implications for improved metal distribution.

The use of air agitation gives not dissimilar effects but detailed differences necessarily occur due to the resistive nature of air bubbles and their tendency to cling to surfaces especially those with capillary crevices such as through-holes. Metal distribution within holes will only be affected by agitation if metal depletion occurs and the solution is effectively stagnant. This is increasingly likely to occur with high aspect ratio holes where capillary forces are increased. Otherwise, a different approach is required and pulsed current techniques may be appropriate [309]. Of course the use of concentrated plating electrolytes is advantageous in reducing the possibility of complete depletion in a stagnant hole but even partial
depletion will increase polarisation effects and make nodular growths more likely.

9.1.2 A Sensor to Study Agitation Behaviour

The variation of agitation within a large electroplating tank has always been known in a qualitative manner and the art of jigging irregularly shaped components to produce evenly coated products is one obvious manifestation of this knowledge. To establish the effect quantitatively is more difficult although various throwing power cells (Haring, Hull) purport to do this in various ways. However none effectively include agitation as a parameter. Similarly the use of limiting current methods is well-established as a means of assessing reactor performance on overall cathode deposition rates edge effects being clearly recognised as edge build-up or edge burning. The equivalence of deposit thickness and current density is implicit in the use of the Hull cell but when limiting current densities are employed the current efficiency is invariably invoked as a reason for caution. In this light Figure 78 demonstrates a remarkable level of agreement. No specific claim for the Faradaic equivalence is made but it should be noted, that the discrepancy is attributable primarily to current efficiencies of less than 100%.

It should be noted that the limiting current density technique is designed to be one near 100% efficient because the selection of an acid copper sulphate electrolyte and the selection of an appropriate control potential (-0.85V vs SCE) is an attempt to operate under conditions where hydrogen evolution has not commenced (see Figure 20). Thus, the sensor technique is believed to correlate well with deposit thickness for this metal system.
Investigation of the pattern of agitation within the electroplating tank has revealed several interesting features, some of which are already known in a qualitative manner. Thus, wall "drag" effects are well appropriated and components are kept towards the centre of a tank. Equally, components are suspended in the middle of the tank in depth terms on the basis that agitation at the top and bottom is atypical. The nature of this atypical behaviour is only guessed at however.

The bottom of the tank is clearly well-agitated with both vibratory and air techniques because it is near the source of agitative power. A damping effect within the solution is also recognised as higher positions are taken. However, enhancement at the top is not generally appreciated but here vibratory and air agitations can be distinguished.

It has been pointed out that to be successful vibratory agitators must be designed to allow circulatory eddies to develop; thus the vibrator plate must leave a substantial gap between itself and the tank wall. However, it is equally important that the vibratory waves must be able to reflect off the top electrolyte interface or surface in order to circulate outwards; this they do with a consequent increase in local agitation near the solution surface. In contrast air bubbles do not circulate but on rising to the surface disperse into the air through the interface and if a bubble raft forms, an effect especially prevalent in chromium plating solutions where hydrogen gas is also present, plating is substantially inhibited and not enhanced. However air agitation does have the virtue of giving a more uniform level of agitation throughout the tank.
For this reason it is simplistic to assume that a common mass transport analysis of the whole tank can be made for vibratory agitation. Closer examination of the data in Figure 38 reveals two distinct mass transport patterns which are shown more clearly in Figures 40a-43b. These may be related to patterns of turbulence which become prevalent at higher degrees of agitation, of above a critical value, but which also depend upon the geometrical restrictions of flow and proximity to the source of agitation. If the curves of Figures 40a-43b are considered individually (bottom, middle and top) on their own merit, it could be seen that the transition region is peculiar to each respective curve, nevertheless the two patterns are clear cut for an equation. In comparison, air agitation in which perhaps enhancement is less, but agitation more uniform exhibits one mass transport pattern and therefore, only one mass transport correlation might be used.

The degree of enhancement is a measure of the effectiveness of the agitation technique in relation to high speed electrodeposition. On this basis air is singularly poor although somewhat better than cathode bar reciprocation which is merely designed to eliminate stagnation. Using the enhancement factor (EF) as a measure of agitation, the values results, as shown in Chapter 7 (7.1.1) the range representing not only variation within the tank but also variation with degree of agitation.

9.1.3 Optimum Plating Conditions

The use of a solution containing 3.75 g/l hydrated copper sulphate and 26.65 ml/l sulphuric acid (98%) were found to be satisfactory for all plating trials. Lower copper sulphate and sulphuric acid concentration solutions resulted in reduced cathodic efficiency as well as poor
throwing power, and therefore was not suitable for plating of printed circuit boards and flat sheet of stainless steel, to enable deposition thickness and distribution study.

Consequently, higher concentrations of both hydrated copper sulphate and sulphuric acid were used - 75 g/l and 120 ml/l respectively. The effect of higher acidity is important to the solution. A pH of 0.6 was maintained as this was found to be ideal.

Although increasing the temperature improved the conductivity of the solution, all plating processes were carried out under room temperature conditions as there was no reason for employing high temperatures because the conducting power of the electrolyte was good enough. This may result in the use of higher current densities and this would result in inferior deposits.

The copper electrodeposits obtained from the electrolyte with no addition agents were of inferior quality. Good, bright and smooth deposits were obtained with the addition agents at current densities of 2.5-3.5 A/dm². At higher current densities 5-7 A/dm² the brightness of the deposit is lost. However, the value of the current density depends upon the sizes of the board, tank and volume of electrolyte. Also at higher current densities the deposits were spongy, loosely attached and easily removed by gentle rubbing over the surface.

9.1.4 Addition Agents

Hull Cell trials for the plating solution containing 75 g/l hydrated copper sulphate, 120 ml/l sulphuric acid (98%) and a range of addition agents, selected on the basis of having previously been used for acid
copper sulphate plating for printed circuit boards, showed that the throwing power of the solution improved. Deposited copper thickness and distribution on the surface as well as in the through-holes were uniform and smooth.

9.1.4.1 Description of Copper Gleam 125L

Copper Gleam 125L (solution proprietary to Lea-Ronal UK Ltd) provides a bright extremely ductile copper deposit from a stable solution with high throwing power. This type of addition agent is designed specifically for through-hole plating of printed circuit boards.

The combination of excellent throwing power and the ability to fill cavities in the epoxy-resin created by poor drilling and the ability to meet all known thermal shock requirements, e.g. BS 9760 and MIL P551100 is unique to the Copper Gleam 125L and 125B types of addition agents. These characteristics ensure freedom from outgassing and excellent hole-filling during wave soldering even when the copper thickness is at minimum permitted by specification, particularly in combination with the Ronamet through-hole metallisation system. The solution is stable, easy to use and control, economical and has excellent resistance to both organic and metallic pollution and frequent purification or replacement is not required. A specialised Hull cell technique for quantitative measurements is used to control the additive level.

The Copper Gleam 125L process is outstanding in its numerous features by the ability to plate small diameter holes in relatively thick boards (greater than 5:1 aspect ratio) with a surface to hole ratio of close to 1:1 and the ability to cover substrate defects by its excellent micro-levelling characteristics. It has been found that at
vigorous vibratory agitation deposition rate was not less than 37.5 microns/hour at 3 amp/dm² at about 100 per cent cathode efficiency under all normal operating conditions.

The replenishment is carried out by the addition of ca. 300 ml Copper Gleam 125L additive/1000 ampere hours, dependent on operation. To raise the copper concentration by 10 gm/l, 33 ml/l Lea-Ronal Purified Copper Concentrate (300 gm/l chloride free) is added.

However, it is important to note that:

1. For maximum throwing power boards are racked rigidly vertical above the agitator disc normal to anode electrode, so as to produce sluicing action through the holes. Vigorous vibratory agitation is essential for maximum deposition.

2. High chloride levels (greater than 100 ppm) cause the formation of greyish-white films on the anode and excessive additive consumption. Anode polarisation may occur. The chloride can be reduced using Lea-Ronal Copper Gleam Chloride Reducer as a dressing on the filters, and the anode cleaned by etching and rinsing prior to re-use.

3. Too high an anode surface area increases additive consumption.

4. Anode bagging is essential.

5. Higher temperatures permit higher current densities but the throwing power decreases as bath temperatures and current density are increased. High temperature will also promote high additive consumption.
9.1.5 **Experimental Techniques**

The prime objectives of the project were to develop an agitative system for electrodeposition processes for the production of printed circuit boards and connectors which would be an alternative to air agitation methods already in use in industry. The process development in a laboratory needed to consider the control problems that would arise in an industrial situation. However, the use of elaborate and sophisticated techniques and equipment were thought to be inapplicable to an industrial situation. The experimental techniques were developed not only to produce accurate results showing the effects of the parameters but also to produce results that were reproducible enabling comparison with other methods of solution agitation.

The type of electroplating tank used was of a suitable size for the quantity of solution required for the purposes of the project. However, where larger quantities of solution are desired, as for industrial applications, a corresponding larger tank would be necessary.

The polarisation study and data were obtained efficiently with the equipment used. The potentiostat, chart recorder as well as the digital multimeters worked satisfactorily throughout the course of the project, and the electrical contacts needed regular cleaning to ensure good contact in the electrical circuit. The different sizes of baths (tank) and other necessary appliances were creditable in their respective uses. The reference electrode with its remote junction glass tip was effective in determining quick and accurate reference potentials without problems. The use of flat sheets of stainless steel to simulate printed circuit boards during deposit thickness studies was perfect.
The analysis of the electrodeposits by X-ray fluorescence coating thickness computer (Fischerscope 1000) was found, although tedious, to be accurate and not too difficult.

9.2 **COMPOSITE ELECTRODEPOSITION**

Composite coatings incorporating non-metallic particles in metal matrices can be formed by electroplating in solutions containing suspensions of appropriate powders. Research on the electrodeposition of composite coatings by various researchers has resulted in the production of sound, coherent materials based on different metals and a wide variety of alloys.

Composite materials generally display improved mechanical and chemical properties compared with those of the metallic matrix, resulting in a wider range of applications. Particularly composites may offer significant improvements in hardness, wear resistance, oxidation resistance and frictional characteristics. Due to time limitations, only one type of particle has been investigated. This was a hard alumina whose incorporation should result in the formation of composites with improved properties for abrasion and wear resistance.

9.2.1 **Experimental Techniques**

To minimise complications regarding solution characteristics and quality of the electrodeposits, acid copper sulphate solution was used in this investigation. The type of equipment used for electrodeposition, as well as the agitation devices, have been discussed in earlier sections. In the literature, simple methods of agitation, such as air or impeller agitation, have been reported as being adequate for the formation of a composite coating. However, it
was thought that the simple air agitation process in view of its characteristic behaviour would not be able to produce homogeneous composites as desired for the present studies, hence vibrational agitation was only investigated.

Initially rotational agitation was studied using magnetic stirring and rotating blades [310]. Both of these methods were suitable for stirring the electrolyte containing the particles to be codeposited, but at the same time produced very large eddy currents. However, it was further discovered that deposits produced with rotary agitation exhibited areas depleted of particles and areas where the particles were to be found as agglomerates. Therefore, these phenomena strengthened the favour for vibratory agitation for this investigation and because the rotary method was not considered as adequate to achieve a regular distribution in a deposit as it could not maintain a regular dispersion of the particles in the electrolyte. Vibratory agitation as achieved with the Vibromixer produced favourable suspensions of particles without any detrimental turbulence effects provided the limit is not exceeded.

Excessive agitation tends to reduce incorporation as particles can be swept away from the surface before incorporation can take place. However, it is clear from this investigation that once the transition or critical amplitude is exceeded particle distribution in the bed, and consequently in the composite electrodeposit is good. Local distribution attributable to particle agglomeration is not so satisfactory but the presence of a small amount of surfactant is helpful in this respect. Local eddying around the perforations of the agitator disc were considered to be insufficient to be a cause for concern. The vibrational agitation had the advantage of not producing foam when agitating in the presence of surfactants, foaming was clearly evident with the use of rotary stirrers [310].
9.2.2 Current Density

The effect of current density on the amount of particles codeposited was important. In the codeposition of alumina with copper from the acid copper sulphate electrolyte at low current densities, when the reduction of copper was most probably under charge-transfer overvoltage control, the amount of embedded particles was high. This indicates that the rate of codeposition may probably be determined by the formation of a real contact between the particles and the cathode. This contact could be the result of the reduction of copper ions adsorbed on the particles.

At increased current densities, where the reduction of copper ions was most likely under concentration overvoltage control, the amount of codeposited particles gradually decreased. This observation is also in agreement with the observation of Celis and Roos [242,243] for the codeposition of copper and alumina from copper sulphate solutions. Clearly at lower current densities the influence of physical adsorption prevails but above 2 A/dm² electrochemical forces seem to dominate.

9.2.3 Hydrodynamics

It can be deduced from the results that under laminar flow conditions a low constant number of particles were embedded and at this stage there was a considerable amount of sedimentation of the particles in the bath. As the agitation was increased the number of particles in suspension increased and this had the effect of increasing the amount of particles codeposited due to the quasi-turbulent flow. However what was not evident is the agglomeration of codeposited particles. The probable deduction may be because of the absence of swirling. Consequently, vibratory types of agitation provide complete particle buoyancy and not swirling shear effects of agglomerate disintegration.
The increase in turbulent flow continued due to increase in agitation rate until complete development of turbulence took place and although more particles were then in suspension, the flow rate was too rapid to allow particles to codeposit and thus reduced codeposition was only to be expected.

Therefore, under conditions of vigorous agitation particles impinge on the growing deposit, adhere momentarily and either become entrapped or re-enter the bath. Whether entrapment occurs depends not only on the size of the particles, but also on the time of contact (residence time) with the cathode surface and hence with vigorous agitation (higher turbulence) the particles move around in the solution faster than with mild agitation and hence residence time is less. However, the time of contact with the cathode surface is further related to the velocity and the angle of impact and to the precise site on the growing deposit at which impact occurs. The surface of the cathode due to the growing deposit is unlikely to be uniform, and it is possible that preferential entrapment could occur at certain sites, for example, steps, kinks in a step and vacancies as well as sites of nodule growths.

Where agglomerates are produced by agitation, they consist of irregularly shaped particles which, if they adhere momentarily on the cathode surface, could be included by a thickness of deposit very much less than their overall individual sizes. Under these circumstances, adherence of the agglomerates onto the cathode surface need only be for a very short time, probably a fraction of a second, for entrapment to occur. Hence, the time of contact with the cathode surface is a critical factor determining the amount of codeposition and this is influenced by rate of agitation.
9.2.4 A Model of Codeposition

The electrolytic codeposition of particles, especially inert particles with metal, has recently gained importance for the production of composite coatings. However, the theoretical mechanism of codeposition has not yet been completely elucidated.

The results obtained from this investigation employing vibratory agitation are now used here to attempt to explain some features of the electrodeposition of composite coatings. The production of reproducible composite coatings requires first of all a homogeneous suspension of particles in the plating bath. Assuming codeposition can be readily obtained in this system, the particles have to move from the bulk of the suspension to the surface of the cathode electrode to be incorporated.

From this viewpoint, the mechanism of codeposition should thus be based on two fundamentals:

1. the formation of an adsorbed layer of appropriate ions onto the particle;
2. the reduction of a number of ions belonging to the particle cloud.

The overall process could thus be divided into five steps which take place consecutively, namely:

a) formation of ionic cloud
b) convection
c) diffusion
d) adsorption and reduction
e) deposition.
The evolution of a particle from the bulk of the solution into the metal matrix via these five steps is shown schematically in Figure 87.

The first phenomenon taking place when a particle such as alumina is brought into the bath is ADSORPTION of ions and molecules from solution onto the particles. This causes the accumulation of a certain charge on the particle surface which can be reflected by its zeta potential value. The adsorption which is physicochemical in nature, creates on the particle surface an ionic double layer which is influenced by the composition of the plating bath.

In the experimental set-up with vibratory agitation, the particle surrounded by its double layer, was brought into contact with the electrode by convective diffusion. The first step of this mass transport (i.e. the second step in the process of codeposition) takes place by FORCED CONVECTION and drives the particles to the hydrodynamic boundary layer. This process is purely physical in nature and is concerned with the bulk of the solution. The intensity of this mass transport phenomenon is determined by the speed of agitation. The process itself is immediately influenced by the position of the electrode in the solution, by the mode and rate of agitation - flow regime, by the presence of other phases such as gas bubbles or other particles.

Once at the hydrodynamic boundary layer, the particles move on to the electrode surface by DIFFUSION and reach the diffusion layer. The diffusion rate can be evaluated from the diffusion coefficient 'D' and this is influenced by other parameters such as temperature, solution composition, viscosity and agitation velocity. Every species in solution has its own diffusion layer depending upon ionic diffusion
(Nernst diffusion layer) and its diffusion coefficient. Particles (have a Prandtl diffusion layer dependent upon viscosity primarily) and free ions in solution have therefore a markedly different diffusion layer thickness.

The last step of reduction of ions in the process of codeposition is associated with the particle and is preceded by an adsorption of the particle with the ionic cloud at the electrode surface. The adsorption can be considered as an electro-physico-chemical process and takes place very near the electrode itself. Therefore, every factor affecting the electrode surface and the double layer on the particle strongly influences the adsorption process. Once the overpotential and resident time is sufficiently high to reduce enough ions from the layer around the particle, the latter is irreversibly fixed in the metal matrix and can be considered as incorporated by electrodeposition. The nature of this last step is undoubtedly electrochemical and therefore depends strongly on the potential of the electrode.

On the other hand, codeposition appears to be determined by the reduction reaction and of course by every electrolysis parameter. Consequently, codeposition requires the formation of an adequate ionic cloud around the particle, and the role of this cloud is two-fold:

a) adsorbed cations causing a positive charge on the particles increase the attraction of the particles towards the negatively charged cathode;

b) the adsorbed cations act as a screen between cathode and particles because as long as some of these ions are not reduced, only a loose adsorption condition is realised.
This ionic cloud can be built up in several ways depending on the nature of particles and solution. The adsorption of the ions may take place immediately on the surface of the particles or indirectly via hydrogen bonds with the hydration sheath, the latter being dependent on pH of the solution.

The ideal codeposition process arrangement therefore requires:

a) steady state conditions to be realised, having no concentration, pressure or temperature variations occurring during the process;

b) a uniformly accessible surface is necessary - no edge effects must exist;

c) a homogeneous suspension of particles in solution to be maintained, this requires a minimum vibrational agitation rate that is necessary to prevent sedimentation of the particles and an overall wettability of the particles and aid of surfactant where necessary.

9.2.5 Scanning Electron Microscope Study

A distribution study of the alumina particles on the surface of the electrode was carried out using the scanning electron microscope (SEM). The distribution pattern, as revealed by the X-ray photographs in Figures 93a-95c, shows good distribution on the surface of the cathode electrode.

The whitish dots represent the incorporated alumina particles. The codeposition process was carried out at different degrees of vibratory agitation rate and, as can be seen in each case, the density of the
white dots on the right hand side of the photographs indicates the amount of alumina particles incorporated at the different degrees of agitation rate.

At vibrational amplitude of 0.016 mm or agitation rate of 70 less particles are incorporated as the system was operating at laminar regime and therefore the particles have not yet developed buoyancy; hence most of the particles were resting at the bottom of the tank. The stirring effect at this point is so minimal that there was little or no particle dispersion in the tank, hence very little amount of particles were codeposited. However, the top section of the sample panel showed that more alumina particles are incorporated than at the middle or bottom. The probable reason for this is that, the smaller particles that were able to break up at this rate of agitation came up to the surface and were accordingly trapped on the electrode surface. At the agitation rates of 140 (a = 0.053 mm) and 210 (a = 0.114 mm) respectively, more particles were incorporated. At these instances, the particles have fully developed buoyancy in the solution and less particles are sedimented because there is complete particle dispersion.

Nevertheless, between the two agitation rates, more particles are incorporated at the vibrational amplitude, a, of 0.053 mm than at a = 0.114 mm. This is because at the agitation rate of 210 (a = 0.114 mm) there is fully developed turbulence of the solution and as a result, the alumina particles are in constant movement within the tank. The constant chaotic movement of the particles makes it difficult for the particles to be trapped on the cathode surface. However at agitation rate of 140 (a = 0.053 mm) the particles are fully and individually incorporated because the electrodeposition process is operating at an
intermediate turbulent regime. Therefore, the use of vibratory agitation in the electrodeposition of composite coatings has made it possible to predict at what degree of solution agitation codeposition could be carried out.

Consequently, electrodeposition of composite coatings in laminar regimes do not give any reasonable amount of particle incorporation. Similarly, at higher turbulent regimes the residence time of the particles on the surface of the cathode electrode is drastically reduced, thereby making it difficult for any appreciable amount of particles to be incorporated. While at intermediate solution turbulence (transition) an optimum degree of particle incorporation is achieved. This is illustrated in Figure 96. This figure demonstrates that at the vibrational amplitudes of 0.041-0.053 mm - the onset of turbulence, particles incorporation is at maximum. This is in good agreement with the findings of Celis et al (see Figure 16), where the rotating disc electrode (RDE) was used instead. However, there exists an important difference in the two systems (vibratory and rotation) in terms of the configuration of the curves. In the system using rotating disc electrodes there is a sharp drop of particle incorporation at the onset of transition regime which later begins to increase at a rotation speed of 500 rpm. While in the case of vibratory agitation there is a gradual but systematic increase of particle incorporation. A logical explanation of this behaviour rests with the type of agitation or eddies generated in the solution by these two methods.

It can be said that the alumina particles effectively follow in the rotational direction of the disc electrode. In contrast the vibratory agitation method produces eddies that move in the direction of propagation in which also rotational eddies may be possible (see Figures 12 and 13).
However, it is appreciated that dots mapping (X-ray) analysis on rough surfaces is not very precise as many incorporated particles may be buried in the outgrowths (nodules). As a result the true interpretation of these results involves some considerable difficulties.

Further surface analysis was also carried out in order to determine the percentage concentration by weight of some certain elements in the deposit. The results of this study are shown in Table 22. Similarly, in Table 23 are the results of the percentage composition of copper, alumina particles incorporated and oxygen at agitation rates of 70 \((a = 0.016 \text{ mm})\), 140 \((a = 0.053 \text{ mm})\) and 210 \((a = 0.14 \text{ mm})\) respectively, and at different sections of the sample panels.

The results of this analysis (Table 23) agree with the alumina mapping X-ray analysis (Figures 93a-95c). Moreover, it is interesting to note that, as the degree of alumina particle incorporation increases, the percentage composition of copper in the deposit decreases and vice versa. The composition of oxygen follows the same trend as the alumina particles' composition. Still the higher percentage of alumina composition at the vibratory agitation rate of 70 \((a = 0.016 \text{ mm})\) "top" follows the same line of explanation or reasoning as in the above.

9.2.5 Commercial Feasibility

Electrodeposited composite coatings have the potential of being used in four main commercial areas:

a) wear resistant coatings
b) dry lubricant coatings
c) heat treatable metal alloys
d) nuclear control coatings.
The composite coatings incorporating alumina, titania or polytetrafluoroethylene (PTFE) with lead-tin or copper have great potential as bearing overlays with improved wear resistant properties. Small amounts of particle incorporation are sufficient in improving the wear resistance, hence additional cost to the production of an overlay is insignificant compared to the longer life given to the material product.

A conventional electroplating bath (e.g. acid copper sulphate, lead-tin fluoroborate, etc) can be easily changed into a composite plating bath by the simple use of a vibromixer and addition of the desired particle to be incorporated. Therefore, the only increased cost for a composite coating is the equipment cost of a vibromixer, power requirements in this regard do not require any special considerations. There are no special effluent problems associated with the codeposition of particles, only those related to the electrolyte concerned. However, there is a foreseeable problem related to the filtration of a composite plating tank. The operation of composite plating production units by both Bristol Aerojet and Rolls Royce under licence have shown that with normal metal finish step process control, decontamination is only required at fairly infrequent intervals.

The laboratory work has shown that acid copper coatings with codeposited alumina can be reproduced consistently once the optimum plating parameters have been researched. Although no work was carried out with lead-tin during the course of this project, works by other researchers have shown that lead-tin with titania and alumina are equally good. The process can lend itself very comfortably to commercial applications for a wide range of uses.
In conclusion, the obvious application for vibratory agitation is in the electrodeposition of composite coatings where the virtues of having buoyant suspended particles in solution are apparent. Unlike some other agitation methods it does enable a full range of particle incorporation tendencies to be obtained as can be seen in Figure 39. This arises because initially the particles develop buoyancy and the degree of incorporation increases as more particles are fully and individually suspended. Thereafter a fall in the rate of incorporation occurs due to the increasing turbulence creating very low particle residence times on the cathode surface and incorporation becomes more difficult. Other agitation methods cause immediate "swirling" as buoyancy occurs and the pattern is therefore different.

In this type of process increased rates of deposition are less important than consistent incorporation of the second phase particles and while other methods of agitation can achieve this, the degree of freedom may be substantially reduced. Thus, it is believed that vibratory agitation is particularly well-suited to this type of process.

9.3 DISCUSSION OF AIR AGITATION

9.3.1 Mass Transfer Correlations

A typical mass transfer geometry under forced convection conditions is that related to channel flow electrodes under either laminar or turbulent conditions. The corresponding equations and figures for the rate of mass transfer have been derived either empirically or analytically, and exhibit an explicit dependence on both the length of the electrode and channel gap. Usually, the maximum rate equations for mass transfer are expressed in dimensionless form.
For laminar flow, the mass transfer problem is solved for the electrode located either within the hydrodynamic entrance length region or in the region where the hydrodynamic profile is completely developed. Whereas, for turbulent flow the rate of mass transfer increases more rapidly with Reynolds number than in laminar flow. These are flows for which the viscous forces obey the relationship:

\[ \nu = -\mu \frac{\partial U_x}{\partial y} = -\nu \frac{\partial (\rho U_x)}{\partial y} \quad (54) \]

otherwise known as Newton's law of viscosity and are called laminar flows. These imply flow dominated by forces due to molecular friction for which the only random motion is Brownian motion of the molecules leading to molecular diffusion. In more rapid flows, local instabilities occur which cannot be cancelled by the molecular viscous forces. This type of flow is called the turbulent flow and it displays viscous stresses of kinetic origin which depend on the properties of the flow. This turbulent viscosity tends to zero when the velocity of the fluid tends to zero and especially at the wall where the fluid velocity is in fact zero. The behaviour of the fluid in the neighbourhood of the walls is quite important since the transport phenomena at the electrodes are also affected.

Therefore, different dimensionless groups are chosen to describe different characteristics behaviour of particular forced convections. For example, Reynolds number expresses the ratio of the forces of inertia to the molecular shear forces (also known as viscous forces). Therefore, it is effectively possible to show that the inertial force of a flow corresponds to the rate of transport of momentum of the flow.
In Figure 52 the mass transfer coefficient is plotted versus the gas voidage fraction. This suggests that we plot the mass transfer coefficient $K_L$ as a function of the void fraction, and one can see that it is in fact possible to represent the results as a function of a single variable which combines the influence of the air bubble and the liquid flow. It therefore seems that the flow behaviour in a bubble agitated solution and thus the mass transport in such an agitation mode are determined to a large extent by the volumetric voidage fraction of the air.

The fact that the mass transport increases with the bubble concentration suggests that it is rather the motion of the bubbles which plays the dominant role. The fluid dynamics of agitated two-phase systems are governed not only by inertia and viscous forces, but also by gravitational forces, whereby in the case of gas bubbles in a liquid these forces are determined by the properties of the liquid [302]. Therefore, the characteristic dimensionless group to be used for the description of bubble motion is the Archimedes number [303]:

$$\text{Ar}^* = \frac{d^3 g \Delta \rho}{v_L^2 \rho_\infty}$$  \hspace{1cm} (55)

where $d$ is the characteristic length, otherwise the bubble diameter; $g$, the gravitational force; $\Delta \rho$ is the density difference between the liquid and the gas (air); $v_L$ is the kinematic viscosity of the plating electrolyte and $\rho_\infty$ the average density. The average density of the two-phase system ($\rho_\infty$) is calculated by the relation:

$$\rho_\infty = (1-c) \rho_L + c \rho_g$$  \hspace{1cm} (56)
and the voidage fraction \( \varepsilon \), is defined by:

\[
\varepsilon = \frac{A_R \cdot N_b}{X}
\]  

(57)

where, \( A_R \) is the average bubble size (cm); \( N_b \) is the number of bubbles per 648 \( cm^3 \) while \( X \) is the denominator used in calculation (648 \( cm^3 \)).

The second term on the right side of equation (56) can be neglected if we take into account that \( \rho_g \ll \rho_L \). Thus, the Archimedes number describing the motion of a bubble dispersion becomes:

\[
Ar^{**} = \frac{d^3 g}{v_L^2} \cdot \frac{\varepsilon}{1-\varepsilon}
\]  

(58)

Hence, it has been attempted to represent the experimental results by means of a dimensionless equation of the form:

\[
Sh = f(Ar \cdot Sc)
\]  

(59)

Since no dependence of the mass transfer coefficient on the height and breadth of the bath between the electrode could be found, the bubble diameter has been used as the characteristic length in \( Sh, Ar^* \) and \( Ar^{**} \). The following correlations have been obtained from the experimental data:

\[
Sh = 0.9578 \ (Ar^* \cdot Sc)^{1/3}
\]  

(60)

and

\[
Sh = 0.5719 \ (Ar^{**} \cdot Sc)^{1/3}
\]  

(61)
Graphic analyses of equations (515) and (518) are represented in Figures 53 and 54. In another correlation for the experimental analysis of the mass transfer rate expressed in Sherwood number takes the form:

$$Sh_{exp} = \frac{i_0d}{nC_oF_D}$$

(62)

and results of which are represented in Figures 55 and 56. The above correlations were modified to account for the equivalent hydraulic diameter (see equation 27). This modified version or form of correlation was also applied to the Archimedes numbers:

$$Ar^+ = \frac{d^3g\Delta \rho}{\nu L^{2/3} \rho_\infty} \left[ \frac{d_1-d_2}{d_2} \right]$$

(63)

and

$$Ar^{++} = \frac{d^3g \varepsilon}{\gamma L^{2/3} (1-\varepsilon)} \left[ \frac{d_1-d_2}{d_2} \right]$$

(64)

Representation of the modified dimensionless groups interpreting the mass transfer results are shown in Figures 57 and 58. This is in consideration of the fact that the bubble and the tank diameters are the only relevant characteristic lengths. The power (1/3) used in equations (60) and (61) is used with the plausible assumption that the data represented such a narrow range of values. However, the ideas of the stirring mechanism of bubbles justifies its use in the formation of the dimensionless groups. It is worth noting that equations 60 and 61 are practically identical with the correlations found for mass and heat transfer under turbulent free convection conditions [303-307] if one replaces the Archimedes number by the Grashof number.
Therefore, the motion of a bubble dispersion can be considered as a kind of natural convection.

The analogy with turbulent free convection can be explained by considering the fact that a rising bubble displaces liquid creating thus a velocity component perpendicular to the direction of motion. Also the velocity of the bubbles is usually large enough so that turbulent eddies are formed in the wake of the bubbles. This transverse motion of the liquid constitutes in an analogous way as the fluctuations in 'normal' turbulence, the major contribution to mass transport. In view of the turbulence in the surrounding of the individual bubbles and the mass transfer coefficient a function of the velocity component, taking into account that the rising velocity of the bubble is described by the Archimedes number, we arrive at the conclusion that mass transfer from a liquid stirred by rising bubbles to a vertical wall can be characterised by an Archimedes number.

9.3.2 Influence of Bubbles on Electrolyte Resistance

The presence of bubbles in the electrolytic solution gives rise to a heterogeneous system exhibiting a resistance that is different to that of the electrolytic solution itself. Various models have been proposed to evaluate the apparent conductivity, $R_c$, of the bubble-electrolyte system.

The equations derived from the various models are assembled in Table 17. These equations tend to the $K/K_o$ ratio for $\varepsilon_g \to 0$ and $\varepsilon_g \to \infty$. It is evident that the void fraction should be kept as low as possible ($\varepsilon_g \to 0$) to minimise ohmic drop due to the presence of bubbles.
independent of the rate of bubble production. The experimental values of the conductivity ratio \( \frac{K}{K_L} \) (\( K \) is the effective conductivity of the dispersion and \( K_L \) that of the air-free solution as the reference) as a function of the air voidage fraction are represented in Figure 59 together with the theoretical correlations given by Maxwell and other workers who were the early individuals to calculate the effective conductivity \( K \) of a two phase dispersion (see Table 17). That is, the air voidage leads to a diminution of the electrical conductivity of the electrolyte which results in higher energy losses. A graphical representation of the IR drop of the electroplating solution plotted against the air voidage is shown in Figure 88.

Similarly, a graph showing results using theoretical model and photomicrograph data - Figure 89 represents close configurational agreement of our laboratory experimental results and the predicted model (Figure 59).

The current density value and its eventual distribution in the solution depends in the case on the air voidage fraction (conductivity of the electrolyte). Therefore, due to the increasing volume of air bubbles, there is increased air voidage fraction and eventual ohmic drop, thus, causing non-uniformity in current distribution in the electroplating tank. The experimental variable of major interest was the gas (air) flow rate, because it determines the buoyancy energy, which would be a major parameter affecting the bubble size distribution, coalescence characteristics, air voidage fraction in the system, and gas-liquid interfacial area depending on the flow regime - laminar or turbulent. As the pump setting (calibration) is increased from the "base point" to 14 (maximum) so also the volume as well as the air flow rate is increased. Under this condition low transfer
rates may be achieved due to the current entering the electrolyte becoming "flooded". This is the phenomenon where the air flow rate is so high that the current is passing through a gas phase and therefore cannot have reasonable contact with the electrolyte resulting in poor conductivity of the plating solution.

This loss in conductivity is higher at the top (surface) of the electrolyte. This is because the top is the zone of the bubble "raft" formation and it is most probable that the effect of the air voidage is higher at this zone.

Percentage of air voidage is plotted against air-flow rate as shown in Figure 90. This result relates to the power of the air pump, size, height and diameter of the tank and the volume of the electrolyte as used in this investigation. However, it is in good agreement with the findings of V. Sahajwalla et al [312] who carried out similar investigations using a two-element electroresitivity probe coupled to a microcomputer and tanks of greater height and diameter and water bath.

9.3.3 Voidage Fraction in Electrical Cell

The low curve in Figure 59 represents the correlation given by Bruggermann based on Maxwell's equation and implies the assumption of a large size range of the particles. He further assumed that the field around a particle can be better represented if one uses for the conductivity of the surrounding medium the average value of the mixture rather than that for the continuous phase. De La Rue and Tobias [308] have studied the conductivities of suspensions of solid particles (glass beads and sand) up to a voidage of 0.4. In the case of large particle size-range their results were in rather good
agreement with the Bruggermann equation, in accordance with the assumption underlying this model. For narrow size-ranges, however, the conductivity value tended to be somewhat higher and to lie between Bruggermann and Maxwell-Rayleigh (Tobias and Prager - see Figure 59).

The results of the study reveal, as seen in the figure, that in the case of air bubbles in an electroplating solution Maxwell's relation is higher and may seem to be more appropriate to Bruggermann's. This can probably be explained by the fact that the size range of bubbles in moderately concentrated electrolytes is rather narrow and that therefore Maxwell's model is more appropriate in this case.

In practice the gas voidage fraction will usually take values of about 0.1-0.2 and $K/K_L$ is about 0.85-0.75. These values are in very good agreement with the experimental results obtained in this study as shown in Table 18.

Based on these five classical models analysis of the solution conductivities as a function of agitative air voidage was carried out and represented graphically. Both predicted and laboratory experimental data are shown in Figures 91 and 92 respectively. In both cases, the experimental conductivity ratio lies close to the "linear" curve and can be said to be in agreement. However, more is still to be learnt about the behavioural characteristics of these models as some uncertainty remains owing to the impossibility of accurately determining the direction of movement of a bubble as well as its size with respect to the bubbler in a given medium.
AGITATION AND PRINTED CIRCUIT BOARD PRODUCTION

In the production of printed circuit boards there exist two problems of great concern:

a) through-hole continuity and uniformity
b) uniform distribution over board.

For through-holes, avoiding stagnation within holes is essential. Therefore, uniformity of agitation is very necessary. In this respect, air is better than vibratory agitation if the board is vertical, although the degree of enhancement is lower - this is vividly illustrated in Figures 71.1-73.3 and Figure 84.

However, if horizontal boards are used air agitation may not be best due to air entrapment on the lower side of the board and in contrast vibratory agitation producing jet effects at the holes will give a better deposit continuity and uniformity in the holes as well as uniform distribution over the surface of the boards. If the board is tilted there is the possibility of achieving continuity as well as uniformity in the hole.

For board distribution problems air is best but additional use of vibratory agitation may enable distribution and enhancement to be improved greatly.

Scale-up pilot plant plating exercise could be usefully carried out.
Dimensional analysis as a basic concept underlying the theory of transport processes and electrochemical cells is important and very familiar. In analysing laboratory data for reacting systems, the various rate-constants, transfer coefficients, transport properties, and tank dimensions must be combined in such a way that dimensional consistency is maintained.

The basis of dimensional analysis is the theory of similitude. By similarity transformation or suitable combination, the large number of variables and parameters in a system of differential equations describing the operation of a tank or reactor may be reduced to a few dimensionless groups. The use of dimensionless groups implies the idea of scale-up. In this sense, the strategy of pilot-plant operation, i.e. the question of which dimensionless groups to use is essential for correct scale-up, hence an important factor in the electrochemical process development.

The heart of the philosophy of electrochemical process development is that one should start out with a definite preliminary choice of cell type and capacity based on cell feed preparation electrolysis, recovery of products and power supply.

9.5.1 Similarity and Dimensional Analysis
Similarity may be defined as to size, shape or composition. Although size and shape are easily visualised as spatial, shape is usefully defined as a spatial-temporal characteristic, for example, a time-dependent development of concentration profiles, as in unsteady-state diffusion.
Shape factors are dimensional ratios characterising a certain shape, for example the aspect ratio (width/height) or a rectangular channel (tank or cell). Scale ratios, on the other hand, are dimensional ratios characterising the scale-up, from one size to another size of similarly shaped bodies. The first extension of similarity concept is mechanical similarity if considered in a geometric sense, where a distinction may be made between kinematic and dynamic similarity. The first refers, for example, to the velocity profiles of fluids or particles within fluids. The second implies that the force ratios determining the kinematically similar profiles are identical. It is easily seen that in a uniform stream (laminar) exemplifies a situation where kinematic similarity, for example, the ratio of longitudinal and transverse velocity components, is the result of dynamic similarity. In this case, the ratio of inertial force to viscous force near the tank or pipe wall is characterised by Reynolds number.

In practice, mechanical (dynamic) similarity can never completely be realised since it would require identical ratios for all relevant forces in the system. These may include:

- pressure forces
- inertial forces
- viscous stresses
- gravitational forces
- interfacial tension
- electrical fields

Thus, one can at most expect certain regions of a tank or reactor and "regimes" of tank operation where similarity exists between two tanks or reactors. This is the significance of the laminar and turbulent
regimes in, for example, pipe flow. Hence, it is necessary in projects where mass transport is evident, to identify these two regions for the purposes of scale-up operations commercially. If heat transfer by convective conduction cannot be neglected, then not only geometric but also kinematic similarity is required. Thus, geometrically similar systems are thermally similar when corresponding temperature differences bear a constant ratio to one another and when the systems, if moving, are kinematically similar.

Mass transfer similarity, like heat transfer similarity with neglect of radiation, requires geometric and kinematic similarity. These conditions are satisfied in the well-known applications to either laminar or turbulent transport. Thus, for fully developed laminar flow, the mass transfer rates at high Pr or Sc numbers are correlated by identical functional relations:

\[
\text{Nu} = K \text{Re}^a \text{Pr}^b \tag{66}
\]

or

\[
\text{Sh} = K \text{Re}^a \text{Sc}^b \tag{67}
\]

where K is a constant and directly related to the stress at the wall. Such groups are used to characterise "regimes" in which particular force ratios are valid. Dimensionless groups have proved to be very useful in scaling up equipment such as agitated vessels, as well as in defining heat and mass transfer rates and regimes in a system.
10.1 VIBRATORY AGITATION FOR ELECTRODEPOSITION PROCESSES

1. Electrodeposition enhancement is obtained by vibratory agitation considering the relative turbulent motion that can be generated by its agitative systems. In this mode of solution agitation there is no danger of oxidation of the solutions' constituents, compared to air agitation. Moreover, vibratory agitation is reproducible and controllable by the input voltage or power to the vibromixer.

2. The size and geometric dimensions of the plating bath as well as the agitator disc can influence the electroplating process using the vibratory agitation method by way of data analysis. Position within the plating tank is very important and the amplitude of vibration may be measured satisfactorily by either of the two methods employed.

3. The Reynolds Number can be defined as \( Re = \frac{100 \, d \, a}{v} \), where \( d \) is the disc diameter, \( a \) is the amplitude of vibration at 50 Hz frequency and \( v \) is the kinematic viscosity of the solution. A laminar-turbulent transition was identified, which in this work occurred at a vibratory amplitude of \( a = 0.41 \, \text{mm} \) or \( Re = 2500 \). In the laminar flow regime mass transport obeys the relationship:
\[ Sh = 29.7 \ Re^{0.037} \ Sc^{0.33} \]
for \( Re < 2000 \)

In the turbulent flow regime mass transport obeys the relationship:

\[ Sh = 0.16 \ Re^{0.82} \ Sc^{0.33} \]
for the ranges \( 2500 \leq Re \leq 20,000 \) and \( 1800 \leq Sc \leq 3200 \)

4. Perforated and flat discs induce different patterns of agitation, indicated by differing power/amplitude calibrations, but not represented in assessment by Reynolds Number alone. Onset of eddying patterns of agitation was noted at approximately 120V input voltage, corresponding to an amplitude of vibration of 0.41-0.6 mm or \( Re = 1800-3000 \). Most importantly, enhancement of electrodeposition obtained by vibratory agitation was typically by a factor within the range 3 to 40, but with modified Reynolds found to be as high as 80.

5. With vibratory agitation particles can be codeposited in an electrodeposit in a uniform manner although the absence of shear mixing action may allow particle agglomeration. Electrodeposition in the laminar flow region is not recommended as this region is ineffective. Particle dispersion for composite plating is effective only in the turbulent region and maximum particle incorporation taking place at the transition region (intermediate turbulence).
As a general conclusion, it is clear that, by using the conventional approach of mass transport correlation analysis, it is possible to systematise vibratory agitation as used in electroplating cells. The scatter of the results is such that positions within the cell (tank) are important but the general form of the correlation is unaffected. Using this type of basic information it is now feasible to establish a mode of use for vibratory agitators in large electroplating installations.

10.2 COMPOSITE COATINGS

1. The ability of an inert particle to be codeposited is dependent upon its crystalline form; α-alumina codeposits more readily than γ-alumina. Also, the amount of codeposited alumina particles is less when vibrational agitation is either in the laminar or at very high turbulence, hence codeposition is best at intermediate turbulence.

2. The amount of codeposition decreases with an increase in current density. An increase in the concentration of particles leads to an increase in the amount of codeposition. Processing parameters have shown the process of electrodeposition to be no more difficult to operate than other electroplating processes, hence the cost of producing a composite coating may be within the same order as other electrodeposited coatings.
10.3 **AIR AGITATION**

1. The effective conductivity depends on the flow rates of the air produced and of the electrolyte. This study suggests the importance of the flow pattern in understanding the dependence of gas-liquid mass transfer on the design and operating parameters of air-agitated tanks and it also has implications for the efficient operation of air-agitated tanks.

2. Increases in both the velocity and turbulence levels as well as the increase in gas-liquid mass transfer depends on the diameter of a given tube in a given tank diameter. Also, an increase in the volume of air in the electroplating tank results in an increase in the value of the air voidage fraction.

3. For a given air velocity, higher air voidage, higher mass transfer rates are achieved until a point where increase in bubble(s) velocity do not yield a corresponding increase in the rate of mass transfer. This is as a result of ohmic drop due to increase in the air voidage, hence there is loss of conductivity of the electroplating solution. Uniformity of mass transport tends to decrease with increasing air agitation rate.

4. Air bubbles may adhere to the workpiece especially in holes and recesses thereby providing localised insulation and obstruction to electrodeposit growth. There is danger of oxidation of the solutions' constituents by using air alone as a means of solution agitation in the electrodeposition process.
5. For air agitation no transition is noted and correlation of the type are obtained:

\[ Sh = \text{constant } Ar^x \cdot Sc^y \]

or

\[ Sh = 0.9578 \: Ar^{0.33} \: Sc^{0.33} \]

and

\[ Sh = \text{constant } Ar^{x*} \cdot Sc^y \]

or

\[ Sh = 0.5719 \: Ar^{0.33} \: Sc^{0.33} \]

6. The smaller the holes of a printed circuit board (PCB), the more difficult it is to use air for solution agitation in the electrodeposition process. By and large it can be said that air agitation is probably an attractive mode of agitation for electrochemical cells. This is particularly true of systems which are not sensitive to oxygen and where therefore air can be used for the agitation.
10.4 SENSOR

1. A sensor has been developed to assess the degree of agitation within an electroplating cell. It can be moved around the tank and its position recorded in three dimensional coordinates. The sensor has been used to compare agitation techniques in terms of process rate enhancement.

2. By the use of the sensor, it is possible to measure the variation of agitation in large plating tanks, produced by non-symmetrical or localised agitators. Also, using the sensor in small increments of height from top to bottom or corner to corner and variable vibratory agitation rate a very detailed pattern of agitation could be obtained.
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<table>
<thead>
<tr>
<th>Composition</th>
<th>I oz/gal</th>
<th>II oz/gal</th>
<th>III oz/gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper Fluoborate, Cu(BF₄)₂</td>
<td>35.5</td>
<td>71.0</td>
<td>72.0</td>
</tr>
<tr>
<td>Fluoboric Acid, HBF₄</td>
<td>2.4</td>
<td>4.8</td>
<td>4.8</td>
</tr>
<tr>
<td>Boric Acid, H₃BO₃</td>
<td>2.4</td>
<td>4.8</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>1.2-1.7</td>
<td>0.2-0.6</td>
<td>below 0.3</td>
</tr>
<tr>
<td>Solution Type (pH)</td>
<td>Copper Content g/l</td>
<td>Current Density A/dm²</td>
<td>Cathode Efficiency %</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------</td>
<td>-----------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Cyanide (9-12)</td>
<td>12-25</td>
<td>1-6</td>
<td>40-70</td>
</tr>
<tr>
<td>Pyrophosphate (7-8)</td>
<td>20-40</td>
<td>1-8</td>
<td>95</td>
</tr>
<tr>
<td>Sulphate (1)</td>
<td>40-75</td>
<td>2-10</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Fluoborate (&lt;1)</td>
<td>60-120</td>
<td>7-35</td>
<td>&gt;95</td>
</tr>
</tbody>
</table>
### Table 3: Solutions for Electrodeposition of Copper

<table>
<thead>
<tr>
<th>Solution</th>
<th>Composition</th>
<th>Process Conditions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline cyanide</td>
<td>CuCN 20-80 g/l</td>
<td>pH 10-12</td>
<td>Agitation preferred</td>
</tr>
<tr>
<td></td>
<td>NaCN 20-80</td>
<td>cd 0.5-10 A/dm²</td>
<td>Used widely as a 'strike' process</td>
</tr>
<tr>
<td></td>
<td>NaOH 10-40</td>
<td>T 20-70°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rochelle salt 20-30</td>
<td>Eff. 30-80%</td>
<td></td>
</tr>
<tr>
<td>Pyrophosphate</td>
<td>Cu pyro 50-200 g/l</td>
<td>pH 8-9</td>
<td>Used as a 'strike' in some cases</td>
</tr>
<tr>
<td></td>
<td>K pyro 100-250 g/l</td>
<td>cd 1-5 A/dm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NH₄OH 1-2</td>
<td>T 30-60°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₃Citr 10-20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid sulphate</td>
<td>CuSO₄ 100-250 g/l</td>
<td>pH &lt;1</td>
<td>Cheapest solution</td>
</tr>
<tr>
<td></td>
<td>H₂O₄ 40-120</td>
<td>cd 0.5-10 A/dm²</td>
<td>for thick deposits.</td>
</tr>
<tr>
<td></td>
<td>Levellers 1-10 mg/l</td>
<td>T 20-50°C</td>
<td>Levellers necessary</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Eff. &gt;90%</td>
<td></td>
</tr>
<tr>
<td>Acid fluoroborate</td>
<td>Cu(BF₄)₂ 200-450 g/l</td>
<td>pH 0.5-2</td>
<td>Electroforming</td>
</tr>
<tr>
<td></td>
<td>KBF₄ 15-30</td>
<td>cd 20-50 A/dm²</td>
<td>solution, agitation required</td>
</tr>
<tr>
<td></td>
<td>K₃BO₃ 15-30</td>
<td>T 30-50°C</td>
<td></td>
</tr>
<tr>
<td>ALLOY AND SOLUTION</td>
<td>COMPOSITION</td>
<td>PROCESS CONDITIONS</td>
<td>DEPOSIT</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------------</td>
<td>--------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Cu-Zn, Cyanide</td>
<td>CuCN 20-70 g/l</td>
<td>pH 10-12</td>
<td>70% Cu</td>
</tr>
<tr>
<td></td>
<td>Zn(CN)₂ 10-50</td>
<td>cd 0.5-4 A/dm²</td>
<td>30% Zn</td>
</tr>
<tr>
<td></td>
<td>NaCN 4-15</td>
<td>T 25-40°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NaOH 5-30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Sn, Cyanide</td>
<td>K₂SnO₃ 60 g/l</td>
<td>pH 10-12</td>
<td>Speculum alloy</td>
</tr>
<tr>
<td></td>
<td>CuCN 40</td>
<td>cd 2-10 A/dm²</td>
<td>50% Cu</td>
</tr>
<tr>
<td></td>
<td>KCN 90</td>
<td>T 60-70°C</td>
<td>50% Zn</td>
</tr>
<tr>
<td></td>
<td>KOH 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Ni, Sulphate</td>
<td>CuSO₄ 0.125M</td>
<td>pH 9</td>
<td>30% Cu</td>
</tr>
<tr>
<td></td>
<td>NiSO₄₂ 0.475M</td>
<td>cd 1-5 A/dm²</td>
<td>70% Ni</td>
</tr>
<tr>
<td></td>
<td>Na₃Cit 0.2M</td>
<td>T 20°C</td>
<td></td>
</tr>
<tr>
<td>Electrolyte Composition (g dm(^{-3}))</td>
<td>Copper Sulphate</td>
<td>Copper Fluoborate</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>----------------</td>
<td>------------------</td>
<td></td>
</tr>
<tr>
<td>CuSO(_4).5H(_2)O</td>
<td>210-240</td>
<td>Cu(BF(_4))(_2)</td>
<td>225-450</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>52-75</td>
<td>HBF(_4)</td>
<td>enough to maintain pH at 0.15-1.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Copper Sulphate</th>
<th>Copper Fluoborate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>18-32</td>
<td>21-54</td>
</tr>
<tr>
<td>Agitation</td>
<td>Vibratory, air or mechanical</td>
<td>Air or mechanical</td>
</tr>
<tr>
<td>Cathode current density (A dm(^{-2}))</td>
<td>1-10</td>
<td>8-44</td>
</tr>
<tr>
<td>Anodes</td>
<td>Soluble copper, cast or electrolytic</td>
<td>Soluble copper, cast or electrolytic</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th>Copper Sulphate</th>
<th>Copper Fluoborate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>205-380</td>
<td>140-345</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>15-25</td>
<td>5-25</td>
</tr>
<tr>
<td>Hardness (Vickers, 100g load)</td>
<td>45-70</td>
<td>40-80</td>
</tr>
<tr>
<td>Internal stress (MPa)</td>
<td>0-10</td>
<td>0-105</td>
</tr>
<tr>
<td>(tensile)</td>
<td>(tensile)</td>
<td>(tensile)</td>
</tr>
<tr>
<td>PROPERTY</td>
<td>OPERATING CONDITIONS</td>
<td>SOLUTION COMPOSITION</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------------------------------</td>
<td>-----------------------------------------------------------</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>Increases with increasing solution temperature</td>
<td>Increases with increasing copper fluoroborate concentration</td>
</tr>
<tr>
<td></td>
<td>Increases with increasing cathode current density</td>
<td>Relatively unaffected by fluoboric acid concentration</td>
</tr>
<tr>
<td>Elongation</td>
<td>Increases with increasing solution temperature</td>
<td>Increases with increasing copper fluoroborate concentration</td>
</tr>
<tr>
<td></td>
<td>Decreases with increasing cathode current density</td>
<td>Relatively unaffected by fluoboric acid concentration</td>
</tr>
<tr>
<td>Hardness</td>
<td>Decreases with increasing solution temperature</td>
<td>Decreases with increasing copper fluoroborate concentration</td>
</tr>
<tr>
<td></td>
<td>Increases with increasing cathode current density</td>
<td>Relatively unaffected by fluoboric acid concentration</td>
</tr>
<tr>
<td>PROPERTY</td>
<td>OPERATING CONDITIONS</td>
<td>SOLUTION COMPOSITION</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>Decreases slightly with increasing solution temperature</td>
<td>Relatively independent of changes in copper sulphate or sulphuric acid concentration within the range suggested in Table 9</td>
</tr>
<tr>
<td></td>
<td>Increases significantly with increase in cathode current density</td>
<td></td>
</tr>
<tr>
<td>Elongation</td>
<td>Decreases with increasing solution temperature</td>
<td>High acid concentrations, particularly with low copper sulphate concentration, tend to reduce elongation slightly</td>
</tr>
<tr>
<td></td>
<td>Increases slightly with increasing cathode current density</td>
<td></td>
</tr>
<tr>
<td>Hardness</td>
<td>Decreases slightly with increasing solution temperature</td>
<td>Relatively independent of copper sulphate concentration</td>
</tr>
<tr>
<td></td>
<td>Relatively independent of change in cathode current density</td>
<td>Increases slightly with increasing acid concentration</td>
</tr>
<tr>
<td>Internal stress</td>
<td>Increases with increasing solution temperature</td>
<td>Relatively independent of copper sulphate concentration</td>
</tr>
<tr>
<td></td>
<td>Increases with increasing cathode current density</td>
<td>Decreases very slightly with increasing acid concentration</td>
</tr>
</tbody>
</table>
## TABLE 8: COMPARISON OF COPPER PLATING SOLUTIONS

<table>
<thead>
<tr>
<th>Property</th>
<th>Acid Copper Sulphate</th>
<th>Alkaline Copper Cyanide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valency</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Polarisation</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Throwing power</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Plate on zinc?</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Cost</td>
<td>Low</td>
<td>Higher</td>
</tr>
<tr>
<td>Grain size</td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td>Strength</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Hardness</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Appearance</td>
<td>Dull/matt</td>
<td>Semi-bright</td>
</tr>
<tr>
<td>Addition agents necessary?</td>
<td>Yes</td>
<td>Perhaps</td>
</tr>
</tbody>
</table>
### TABLE 9: TYPICAL FORMULATION FOR ACID COPPER ELECTROLYTES

<table>
<thead>
<tr>
<th>Type of Solution</th>
<th>Copper Sulphate g/l</th>
<th>Sulphuric Acid g/l</th>
<th>Chloride Ion mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard (decorative and electroforming)</td>
<td>200-250</td>
<td>50-100</td>
<td>80-200</td>
</tr>
<tr>
<td>High throwing power (for printed circuit boards)</td>
<td>50-100</td>
<td>110-220</td>
<td>30-80</td>
</tr>
</tbody>
</table>

### TABLE 10: ACID COPPER ELECTROLYTES

<table>
<thead>
<tr>
<th>Composition</th>
<th>Traditional Bath</th>
<th>High-Throw Bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper, Cu$^{2+}$ as sulphate</td>
<td>56 g/l</td>
<td>19 g/l</td>
</tr>
<tr>
<td>Sulphuric acid, (H$_2$SO$_4$)</td>
<td>56 g/l</td>
<td>190 g/l</td>
</tr>
<tr>
<td>Chloride, mg/l Cl$^{-}$</td>
<td>60 mg/l</td>
<td>60 mg/l</td>
</tr>
</tbody>
</table>
### TABLE 11: THERMAL SHOCK PERFORMANCE VS INTERNAL STRESS AND HARDNESS

<table>
<thead>
<tr>
<th>System</th>
<th>Hardness(^a)</th>
<th>Internal Stress(^b)</th>
<th>Thermal Shock(^c)</th>
<th>Levelling(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mpa (lb/in(^2))</td>
<td>Mpa (+lb/in(^2))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No additives</td>
<td>95</td>
<td>+7.9 (+1140)</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Levelling system</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New(^e)</td>
<td>100</td>
<td>+19.7 (+2850)</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Used</td>
<td>140</td>
<td>+6.9 (+1000)</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Combined thermal-shock and levelling system</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New(^e)</td>
<td>115</td>
<td>-16.6 (-2400)</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Used</td>
<td>107</td>
<td>-36.2 (-5247)</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Thermal-shock system</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New(^e)</td>
<td>92</td>
<td>+35.2 (+5100)</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Used</td>
<td>100</td>
<td>-8.3 (-1200)</td>
<td>Good</td>
<td>Poor</td>
</tr>
</tbody>
</table>

\(^a\) Measurements with a Koop indenter and a 25g load.

\(^b\) Measurements using a dilatometric method [7]. Negative values indicate a compressive stress.

\(^c\) Circuit board segments (5 x 5 cm) were plated in a 3 litre cell at 0.3 A/dm\(^2\) for 1.5 hr and then subjected to thermal-shock testing per MILP--51110.

\(^d\) "Poor" levelling is characterised by the deposit's conformity to the irregularities of the circuit board surface. "Good" levelling is characterised by a smooth deposit, void of any influence of board irregularities.

\(^e\) "New" systems were evaluated in freshly prepared 3 litre baths. "Used" systems were tested after 66 A-hr/l of operation.
TABLE 12: EFFECT OF VIBRATORY AGITATION ON NERNST DIFFUSION LAYER THICKNESS, $\delta$, IN A 25 LITRE BATH WITH 22 LITRES OF ELECTROLYTE AND SAMPLE AREA = 156 cm$^2$. PLATING TIME 20 MINUTES PER SAMPLE AT CONSTANT POTENTIAL

<table>
<thead>
<tr>
<th>Vibratory Agitation Rate</th>
<th>Vibrational Amplitude, $a$, mm</th>
<th>Limiting Current Density, $i_L$, mA/cm$^2$</th>
<th>Nernst Diffusion Layer Thickness, $\delta$, $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.0113</td>
<td>299.24</td>
</tr>
<tr>
<td>20</td>
<td>0.002</td>
<td>0.0115</td>
<td>294.03</td>
</tr>
<tr>
<td>30</td>
<td>0.003</td>
<td>0.0119</td>
<td>284.15</td>
</tr>
<tr>
<td>40</td>
<td>0.005</td>
<td>0.0121</td>
<td>279.45</td>
</tr>
<tr>
<td>50</td>
<td>0.006</td>
<td>0.0125</td>
<td>270.51</td>
</tr>
<tr>
<td>60</td>
<td>0.014</td>
<td>0.0138</td>
<td>245.03</td>
</tr>
<tr>
<td>70</td>
<td>0.016</td>
<td>0.0144</td>
<td>234.82</td>
</tr>
<tr>
<td>80</td>
<td>0.020</td>
<td>0.0151</td>
<td>223.93</td>
</tr>
<tr>
<td>90</td>
<td>0.026</td>
<td>0.0165</td>
<td>204.93</td>
</tr>
<tr>
<td>100</td>
<td>0.027</td>
<td>0.0174</td>
<td>194.33</td>
</tr>
<tr>
<td>110</td>
<td>0.041</td>
<td>0.0181</td>
<td>186.82</td>
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<tr>
<td>120</td>
<td>0.042</td>
<td>0.0187</td>
<td>180.82</td>
</tr>
<tr>
<td>130</td>
<td>0.050</td>
<td>0.0194</td>
<td>174.3</td>
</tr>
<tr>
<td>140</td>
<td>0.053</td>
<td>0.0199</td>
<td>169.92</td>
</tr>
<tr>
<td>150</td>
<td>0.056</td>
<td>0.0201</td>
<td>168.23</td>
</tr>
<tr>
<td>160</td>
<td>0.059</td>
<td>0.0204</td>
<td>165.75</td>
</tr>
<tr>
<td>170</td>
<td>0.079</td>
<td>0.0208</td>
<td>162.57</td>
</tr>
<tr>
<td>180</td>
<td>0.080</td>
<td>0.0210</td>
<td>161.02</td>
</tr>
<tr>
<td>190</td>
<td>0.098</td>
<td>0.0240</td>
<td>158.01</td>
</tr>
<tr>
<td>200</td>
<td>0.112</td>
<td>0.0219</td>
<td>154.4</td>
</tr>
<tr>
<td>210</td>
<td>0.114</td>
<td>0.0226</td>
<td>149.62</td>
</tr>
<tr>
<td>220</td>
<td>0.115</td>
<td>0.0231</td>
<td>146.38</td>
</tr>
</tbody>
</table>
TABLE 13: EFFECT OF VIBRATORY AGITATION ON NERNST DIFFUSION LAYER THICKNESS, $\delta$, IN A 25 LITRE BATH WITH 12 LITRES OF ELECTROLYTE AND SAMPLE AREA = 120 cm$^2$. PLATING TIME 20 MINUTES PER SAMPLE AT CONSTANT POTENTIAL

<table>
<thead>
<tr>
<th>Vibratory Agitation Rate</th>
<th>Vibrational Amplitude, $a$, mm</th>
<th>Limiting Current Density, $i_L$, mA/cm$^2$</th>
<th>Nernst Diffusion Layer Thickness, $\delta$, $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.0107</td>
<td>316.01</td>
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<tr>
<td>20</td>
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<td>0.0121</td>
<td>279.45</td>
</tr>
<tr>
<td>30</td>
<td>0.003</td>
<td>0.0142</td>
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<tr>
<td>40</td>
<td>0.005</td>
<td>0.0147</td>
<td>230.02</td>
</tr>
<tr>
<td>50</td>
<td>0.006</td>
<td>0.0152</td>
<td>222.46</td>
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<tr>
<td>60</td>
<td>0.014</td>
<td>0.0155</td>
<td>218.15</td>
</tr>
<tr>
<td>70</td>
<td>0.016</td>
<td>0.0158</td>
<td>241.01</td>
</tr>
<tr>
<td>80</td>
<td>0.02</td>
<td>0.0163</td>
<td>207.45</td>
</tr>
<tr>
<td>90</td>
<td>0.026</td>
<td>0.017</td>
<td>198.9</td>
</tr>
<tr>
<td>100</td>
<td>0.027</td>
<td>0.0201</td>
<td>168.23</td>
</tr>
<tr>
<td>110</td>
<td>0.041</td>
<td>0.0204</td>
<td>165.75</td>
</tr>
<tr>
<td>120</td>
<td>0.042</td>
<td>0.0207</td>
<td>163.35</td>
</tr>
<tr>
<td>130</td>
<td>0.05</td>
<td>0.0208</td>
<td>162.57</td>
</tr>
<tr>
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<td>0.053</td>
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<td>135.8</td>
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<tr>
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<td>0.056</td>
<td>0.0258</td>
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<tr>
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<td>0.059</td>
<td>0.0262</td>
<td>129.06</td>
</tr>
<tr>
<td>170</td>
<td>0.079</td>
<td>0.0288</td>
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</tr>
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<td>0.0308</td>
<td>109.78</td>
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<td>100.64</td>
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<tr>
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<td>0.112</td>
<td>0.035</td>
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<tr>
<td>210</td>
<td>0.114</td>
<td>0.037</td>
<td>91.39</td>
</tr>
<tr>
<td>220</td>
<td>0.115</td>
<td>0.0378</td>
<td>89.45</td>
</tr>
<tr>
<td>Vibratory Agitation Rate</td>
<td>Vibrational Amplitude, a, mm</td>
<td>Limiting Current Density, ( i_L ) mA/cm²</td>
<td>Nernst Diffusion Layer Thickness, ( \delta ), µm</td>
</tr>
<tr>
<td>-------------------------</td>
<td>-------------------------------</td>
<td>--------------------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.0113</td>
<td>299.24</td>
</tr>
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<td>20</td>
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<td>0.0114</td>
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<td>0.0127</td>
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<td>0.014</td>
<td>0.0139</td>
<td>243.26</td>
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<td>0.016</td>
<td>0.0146</td>
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<tr>
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<td>0.026</td>
<td>0.0149</td>
<td>226.94</td>
</tr>
<tr>
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<td>0.027</td>
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<td>120</td>
<td>0.042</td>
<td>0.0155</td>
<td>218.15</td>
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<td>210</td>
<td>0.114</td>
<td>0.0281</td>
<td>120.33</td>
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</table>
TABLE 15: EFFECT OF VIBRATORY AGITATION ON NERNST DIFFUSION LAYER THICKNESS, $\delta$, IN A 25 LITRE BATH WITH 22 LITRES OF ELECTROLYTE AND SAMPLE AREA = 156 cm$^2$. PLATING TIME 10 MINUTES PER SAMPLE AT CONSTANT POTENTIAL.

<table>
<thead>
<tr>
<th>Vibratory Agitation Rate</th>
<th>Vibrational Amplitude, $a$, mm</th>
<th>Limiting Current Density, $i_L$, mA/cm$^2$</th>
<th>Nernst Diffusion Layer Thickness, $\delta$, $\mu$m</th>
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<tbody>
<tr>
<td>0</td>
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<td>0.003</td>
<td>0.0139</td>
<td>243.26</td>
</tr>
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<td>40</td>
<td>0.005</td>
<td>0.0141</td>
<td>239.81</td>
</tr>
<tr>
<td>50</td>
<td>0.006</td>
<td>0.0149</td>
<td>226.94</td>
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<td>0.0154</td>
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</tr>
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<td></td>
</tr>
<tr>
<td>----------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Undercoat for other deposits to protect basis metal or promote adhesion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. For surface improvement in buffing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Levelling properties offer substitute for mechanical finishing.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Selective heat treating</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Soldering</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>6. Lubricity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Printed circuit boards</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Rotogravure, printing rolls</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Electroforming</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Decorative</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hardware, cabinetry, hinges, pulls</td>
</tr>
<tr>
<td>2. Lamps, lighting fixtures</td>
</tr>
<tr>
<td>3. Shelves, brackets etc.</td>
</tr>
<tr>
<td>Model</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>Linear</td>
</tr>
<tr>
<td>Maxwell/Rayleigh</td>
</tr>
<tr>
<td>Tobias</td>
</tr>
<tr>
<td>Bruggemann</td>
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<tr>
<td>Praeger</td>
</tr>
<tr>
<td>Air Pump Setting</td>
</tr>
<tr>
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</tr>
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</tr>
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<td>2</td>
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<tr>
<td>12</td>
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<tr>
<td>14</td>
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</table>

TABLE 18: GENERAL TABLE OF DATA FOR AIR AGITATION RESULTS OBTAINED
<table>
<thead>
<tr>
<th>$A_r^*$</th>
<th>$A_r^{**}$</th>
<th>$i_L (\text{A})$</th>
<th>$1000 \text{ E.F.} = \frac{i_L(\text{aq})}{i_L(0)}$</th>
<th>$K_L = \frac{i_L}{A_c} \frac{d}{D}$</th>
<th>$Sh_{\text{exp}} = \frac{i_L d}{Z \text{CoFD}}$</th>
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<td>Sh' = 0.9578 ((\text{ScAx}')^{1/3})</td>
<td>Sh'' = 0.5719 ((\text{ScAx}'')^{1/3})</td>
<td>(Sh_{\text{exp}} = \frac{i_L d_2}{ZC_{\text{FD}}} \left[ \frac{d_1 - d_2}{d_2} \right])</td>
<td>(Ar^* = \frac{1}{\nu} \left[ \frac{g^{3\Delta p}}{L} \right] \left[ \frac{d_1 - d_2}{d_2} \right])</td>
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<td>1518</td>
<td>1111390</td>
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<td></td>
</tr>
<tr>
<td>( Ar^{**} = \frac{13g}{v_L^2} )</td>
<td>( \frac{e}{1-e} )</td>
<td>( \frac{d_1 - d_2}{d_2} )</td>
<td>( d_{eq} = (6v_b/\pi)^{1/3} )</td>
<td>( E_0 = \frac{\rho_L d_{eq}}{\delta = 0} )</td>
<td>( Re_D = \frac{\rho_L u_D d_{eq}}{v_L} )</td>
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<td>60.45</td>
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<td>Re = 1000 (Low Turbulent)</td>
<td>Re = 10000 (High Turbulent)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-------------------</td>
<td>----------------------------</td>
<td>-----------------------------</td>
<td></td>
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<td>Fig. 85</td>
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<td>1.42</td>
<td>5.9</td>
<td>51.8</td>
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<td>Fig. 86</td>
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<tr>
<td>△</td>
<td>1.22</td>
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<td>29.3</td>
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<td>1.25</td>
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<td>21.6</td>
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<tr>
<td>x</td>
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<td>+</td>
<td>1.1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>□,□</td>
<td>0.9</td>
<td>1.6</td>
<td>22.0</td>
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</table>

Solution: \( 0.015\text{M CuSO}_4 \cdot 5\text{H}_2\text{O} + 0.5\text{M 98\% H}_2\text{SO}_4 \)

Temperature: 18°C

\( D \text{ Cu}^{2+} = 5.84 \times 10^{-6} \text{ cm}^2/\text{s} \)

\( v = 1.0184 \times 10^{-2} \text{ cm}^2/\text{s} \)
<table>
<thead>
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<th>Mode of Agitation</th>
<th>Enhancement Factor</th>
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<tr>
<td>Still solution</td>
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<tr>
<td>Natural convection</td>
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<tr>
<td>Cathode reciprocation</td>
<td>2-4</td>
</tr>
<tr>
<td>Air bubbling</td>
<td>2-4</td>
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<tr>
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<td>3-30</td>
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<td>Turbulent flow</td>
<td>5-50</td>
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<td>Ultrasonic agitation</td>
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### Table 21: Mass Transfer Correlation Coefficients for Data of Figures 85, 86

<table>
<thead>
<tr>
<th>Data Points</th>
<th>Indice α</th>
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<td>Figure 86 △,*</td>
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<td>x</td>
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* Sh = constant Re$_{i}^{α}$. Sc$^{0.33}$
### TABLE 22: SURFACE CONCENTRATION DEPTH (wt %)

<table>
<thead>
<tr>
<th>Vibratory Agitation Rate</th>
<th>Sample Surface Section</th>
<th>Copper (wt %)</th>
<th>Alumina (wt %)</th>
<th>Oxygen (wt %)</th>
<th>Carbon (wt %)</th>
<th>Chlorine (wt %)</th>
<th>Sulphur (wt %)</th>
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<tr>
<td></td>
<td>Top</td>
<td>71.0</td>
<td>4.3</td>
<td>13.4</td>
<td>2.4</td>
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<tr>
<td></td>
<td>Middle</td>
<td>73.6</td>
<td>1.4</td>
<td>14.4</td>
<td>3.1</td>
<td>7.5</td>
<td>0</td>
</tr>
<tr>
<td>(a=0.016)</td>
<td>Bottom</td>
<td>72.2</td>
<td>2.1</td>
<td>13.6</td>
<td>2.5</td>
<td>9.5</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Top</td>
<td>72.2</td>
<td>2.1</td>
<td>13.6</td>
<td>2.5</td>
<td>9.5</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>68.3</td>
<td>3.9</td>
<td>11.6</td>
<td>11.5</td>
<td>4.5</td>
<td>0.2</td>
</tr>
<tr>
<td>140</td>
<td>Bottom</td>
<td>72.7</td>
<td>2.6</td>
<td>13.3</td>
<td>3.4</td>
<td>7.5</td>
<td>0.5</td>
</tr>
<tr>
<td>(a=0.053)</td>
<td>Top</td>
<td>72.9</td>
<td>3.4</td>
<td>12.3</td>
<td>3.1</td>
<td>7.7</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>72.5</td>
<td>2.9</td>
<td>11.6</td>
<td>5.4</td>
<td>7.2</td>
<td>0.5</td>
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<tr>
<td>210</td>
<td>Bottom</td>
<td>72.7</td>
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<td>12.5</td>
<td>3.1</td>
<td>8.8</td>
<td>0.6</td>
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<tr>
<td>(a=0.114)</td>
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</table>

*a* = vibrational amplitude (mm)
### TABLE 23: COMPOSITION AT 0.4 μm DEPTH, wt %

<table>
<thead>
<tr>
<th>Vibratory Agitation Rate</th>
<th>Sample Surface Section</th>
<th>Copper (wt %)</th>
<th>Alumina (wt %)</th>
<th>Oxygen (wt %)</th>
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</thead>
<tbody>
<tr>
<td>70 (a=0.016)</td>
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<td>94.45</td>
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</tr>
<tr>
<td></td>
<td>Middle</td>
<td>98.45</td>
<td>0.85</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>98.75</td>
<td>0.65</td>
<td>0.6</td>
</tr>
<tr>
<td>140 (a=0.053)</td>
<td>Top</td>
<td>96.55</td>
<td>1.6</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>95.75</td>
<td>2.15</td>
<td>2.15</td>
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<td></td>
<td>Bottom</td>
<td>93.8</td>
<td>2.75</td>
<td>3.45</td>
</tr>
<tr>
<td>210 (a=0.114)</td>
<td>Top</td>
<td>96.45</td>
<td>1.85</td>
<td>1.7</td>
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<tr>
<td></td>
<td>Middle</td>
<td>96.15</td>
<td>1.9</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>95.5</td>
<td>2.2</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\( a^* \) = vibrational amplitude (mm)
FIGURE 1. Cathode potential–current density curves for a copper sulphate bath with various addition agents
FIGURE 2: Cross-sections of copper-plated printed circuit boards: (a) traditional copper bath (b) high throw bath
FIGURE 3: Copper density from a bath with no levelling agent reproduces imperfections in the surface of drilled holes.

FIGURE 4: Copper deposit from a bath with levelling agent smooths imperfections in drilled holes.
FIGURE 5: Foldover in non-uniform copper deposited in a bath containing no levelling agent

FIGURE 6: Uniform copper density on a multilayer board from a bath containing a levelling agent
Fig. 7. Wake angle $\Theta_w$ for spherical-cap bubbles as a function of bubble Reynolds number.

Fig. 8. Effect of surface tension on bubble volume under constant flow conditions.
FIGURE 9. Effect of surface tension on bubble volume for small orifice diameters under constant pressure conditions

FIGURE 10. Effect of surface tension on bubble volume for large orifice diameters under constant pressure condition
FIGURE 11. Typical perforated agitator disc.

Disc diameter \hspace{1cm} 100mm
Plate thickness \hspace{1cm} 1mm
Perforation hole diameter \hspace{1cm} 3mm
Hole truncation diameter \hspace{1cm} 9mm
Number of holes \hspace{1cm} 52

FIGURE 12. Observed patterns of vibratory agitation for a round disc in a concentric 2 litre beaker
(a) unperforated flat disc (b) perforated disc.
FIGURE 13. Schematic representation of observed patterns of vibratory agitation in a concentric 2 litre beaker employing perforated discs of different sizes:
(a) 5cm diameter.
(b) 10cm diameter.
(c) 12.5cm diameter.
FIGURE 14. Liquid / Air process. Liquid drawn from Electrolyte (A) through a tube (B) connected to a peristaltic pump (C) and recirculated through inlet port (D).

FIGURE 15. Plate pumping process.
A. Perforated plate.
B. Containing vessel.
FIGURE 16. Weight percentage (Wt %) of embedded alumina (Al₂O₃) in copper Vs. rotation speed of RDE.²
FIGURE 17. Schematic representation of important adsorption phenomena in codeposition - on inert alumina particles - on cathode surface.
FIGURE 18. Schematic representation of metal ion concentration near cathode during deposition: $C_0$, concentration of ion in the bulk solution; $C_E$, concentration at the electrode surface; $\delta_H$, effective or Nernst thickness of diffusion layer.

FIGURE 19. Schematic polarization curve defining limiting currents and potentials.
FIGURE 20. Polarization curves showing limiting current values at increasing vibratory agitation rates and the equivalent limiting potential $E = (E_1 + E_2)/2$.

FIGURE 21. The Haring - Blum cell for the determination of the throwing power of a plating bath.
FIGURE 22. Effect of current density on cathode efficiency.

FIGURE 23. Effect of temperature on cathode efficiency.

FIGURE 24. Effect of agitation on cathode efficiency.
Agitation generally improves cathode efficiency.
FIGURE 25. Schematic representation of the electroplating system employed (vibratory agitation) for electro-deposition process.
FIGURE 26: Actual vibratory agitation ring
FIGURE 27. Schematic experimental set-up showing external gas (air) introduction into an electrochemical cell for the measurement of the rate of mass transfer or rate of electrodeposition.
FIGURE 28. Volume of air (flow rate) pumped per minute using a two-way pump connected via Tee connector. Fourteen divisions, each having ten sub-divisions.

FIGURE 29. Relationship of limiting current density and time using the sensor electrode technique at different degrees of vibratory agitation under potentiostatic control.
FIGURE 30. Typical schematic representation of the electrode (working electrode) and the reference electrode used in this study.

- Working electrode
- Insulated sheath (glass)
- Wire probe
- Reference electrode
- Flexible transparent polymer tubing
- Adhesive banding
- Remote liquid junction bridge
- Sintered glass electrode
FIGURE 31. Relationship of applied voltage to vibrator motor and the amplitude of vibration for perforated disc of 10cm diameter at constant potential.

FIGURE 32. Relationship of applied vibrator voltage and the amplitude of vibration for flat and perforated discs in two different media.
FIGURE 33. Relation of cathodic (electrodeposition) limiting current density to amplitude of vibratory agitation (laminar/turbulent transition at $a = 0.45$).

FIGURE 34. Mass transfer correlation for one solution condition ($Sc = 1779$) using a perforated disc. Copper sulphate solution containing suspended particles.
FIGURE 35. Relation of cathodic (electrodeposition) limiting current density to the amplitude of vibratory agitation (laminar/turbulent transition at $a = 0.041$).

FIGURE 36. Effect of varying superficial velocity on mass transfer coefficient of electrodes of different diameters.
FIGURE 37. Limiting current density distribution profile along electrode/solution interface, positions 0 is to the bottom of the tank, 15 is the middle and 35 is the top (surface) of the tank.

FIGURE 38. Limiting current density distribution profile, determined by sensor, from top to bottom of a vertical flat sheet cathode at various vibratory agitation rates.
FIGURE 39a Effect of vibratory agitation rate on the degree of particle incorporation in composite electroplating, alumina with copper from acid copper sulphate solution (40g/l Alumina in suspension).

FIGURE 39b Effect of vibratory agitation rate on the degree of particle incorporation in composite electroplating, alumina with copper from acid copper sulphate solution (75g/l Alumina in suspension).
FIGURE 40a. Effect of vibratory agitation rate on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156cm$^2$ and plating time = 20 minutes per sample at constant potential.

FIGURE 40b. Effect of vibratory agitation rate on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156cm$^2$ and plating time = 20 minutes per sample at constant potential.
FIGURE 41a Effect of vibratory agitation rate on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120cm² and plating time = 20 minutes per sample at constant potential.

FIGURE 41b Effect of vibratory agitation rate on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120cm² and plating time = 20 minutes per sample at constant potential.
FIGURE 42a. Effect of vibratory agitation rate on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm$^2$ and plating time = 15 minutes per sample at constant potential.

Legend
- □ 1 Bottom
- □ 2 Top
- ♦ 3 Middle

FIGURE 42b. Effect of vibratory agitation rate on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm$^2$ and plating time = 15 minutes per sample at constant potential.
FIGURE 43a. Effect of vibratory agitation rate on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm$^2$, and plating time = 10 minutes per sample at constant potential.

FIGURE 43b. Effect of vibratory agitation rate on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm$^2$, and plating time = 10 minutes per sample at constant potential.
FIGURE 44: Photograph of the Plated-Through-Hole showing the effect of the absence of addition agents

FIGURE 45: Photograph of Plated-Through-Hole without the Carrier Agent
FIGURE 46: Plated-Through-Hole without the 125LX Additive but with Carrier Agent

FIGURE 47: Plated-Through-Hole, employing the cathode reciprocation (cathode movement) method with the panel in vertical position
FIGURE 48: Plated-Through-Hole, using air sparging as a means of solution agitation and the panel in vertical position

FIGURE 49: Plated-Through-Hole, with the panel in horizontal position and air as means of solution agitation
FIGURE 50: Plated-Through-Hole, employing vibratory agitation for solution agitation with the panel in vertical position

FIGURE 51: Plated-Through-Hole vibratory agitation as means of solution agitation with the panel in horizontal position
FIGURE 52. Plot of mass transfer coefficient, $K_L$ vs. gas voidage fraction, $e$.

FIGURE 53. Dimensionless representation of the mass transfer results of calculated Sherwood and Archimedes numbers.

FIGURE 54. Dimensionless representation of the mass transfer results of calculated Sherwood and Archimedes numbers.
FIGURE 55. Relationship between Sherwood number obtained by experimental data analysis and Archimedes number.

FIGURE 56. Relationship between Sherwood number obtained by experimental data analysis and Archimedes number.
FIGURE 57. Modified dimensionless representation of the mass transfer results for Sherwood and Archimedes numbers.

FIGURE 58. Modified dimensionless representation of the mass transfer results for Sherwood and Archimedes numbers.
FIGURE 59. Relationship between loss of conductivity ratio, \( (K/K_L) \) and gas voidage fraction (\( \varepsilon \)) expressing influence of bubbles on electrolyte resistance.
\[ Eo = g \Delta \rho \frac{d_e^2}{\sigma}, \]

FIGURE 60. Shape regimes for bubbles in unhindered gravitational motion through liquids.

\[ \text{Re} = \frac{\rho d_e U}{\mu}. \]
FIGURE 61: Photographic representation of selected bubbles showing types and shapes
FIGURE 62: Different bubble types and shapes
FIGURE 63: Photographic representation showing coalescence of bubbles during electrodeposition process
FIGURE 64: Photograph showing bubbles distribution at the flow rate of 3 litres per minute in a 25 litre tank

FIGURE 65: Photograph showing bubbles distribution in an electroplating tank of 25 litres at an air flow rate of 6 litres per minute
FIGURE 66: Photograph showing bubbles distribution at an air flow rate of 7 litres per minute in a 25 litre tank

FIGURE 67: Photograph showing distribution of bubbles in an electroplating tank of 25 litres at an air flow rate of 8 litres per minute
FIGURE 68: Photograph showing bubbles distribution at an air flow of 9 litres per minute in an electroplating tank of 25 litres

FIGURE 69: Bubbles distribution in an electroplating tank of 25 litres at the flow rate of 9.5 litres per minute
FIGURE 70: Photograph showing bubbles distribution at maximum flow rate of 10 litres per minute
FIGURE 71.1. Effect of air agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120cm² and plating time = 20 minutes per sample (top of bath) at constant potential.

FIGURE 71.2. Effect of air agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120cm² and plating time = 20 minutes per sample (middle of bath) at constant potential.

FIGURE 71.3. Effect of air agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120cm² and plating time = 20 minutes per sample (bottom of bath) at constant potential.
FIGURE 72.1. Effect of air agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120cm² and plating time = 15 minutes per sample (top of bath) at constant potential.

FIGURE 72.2. Effect of air agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120cm² and plating time = 15 minutes per sample (middle of bath) at constant potential.

FIGURE 72.3. Effect of air agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120cm² and plating time = 15 minutes per sample (bottom of bath) at constant potential.
 FIGURE 73.1. Effect of air agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120 cm² and plating time = 10 minutes per sample (top of bath) at constant potential.

 FIGURE 73.2. Effect of air agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120 cm² and plating time = 10 minutes per sample (middle of bath) at constant potential.

 FIGURE 73.3. Effect of air agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120 cm² and plating time = 10 minutes per sample (bottom of bath) at constant potential.
FIGURE 74.1. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120 cm$^2$ and plating time = 20 minutes per sample (top of bath) at constant potential.

FIGURE 74.2. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120 cm$^2$ and plating time = 20 minutes per sample (middle of bath) at constant potential.

FIGURE 74.3. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 120 cm$^2$ and plating time = 20 minutes per sample (bottom of bath) at constant potential.
FIGURE 75.1. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm² and plating time = 20 minutes per sample (top of bath) at constant potential.

FIGURE 75.2. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm² and plating time = 20 minutes per sample (middle of bath) at constant potential.

FIGURE 75.3. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm² and plating time = 20 minutes per sample (bottom of bath) at constant potential.
FIGURE 76.1. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm² and plating time = 15 minutes per sample (top of bath) at constant potential.

FIGURE 76.2. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm² and plating time = 15 minutes per sample (middle of bath) at constant potential.

FIGURE 76.3. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm² and plating time = 15 minutes per sample (bottom of bath) at constant potential.
FIGURE 77.1. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm² and plating time = 10 minutes per sample (top of bath) at constant potential.

FIGURE 77.2. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm² and plating time = 10 minutes per sample (middle of bath) at constant potential.

FIGURE 77.3. Effect of vibratory agitation on deposit thickness of copper in electroplating process in a 25 litre bath of 22 litres of electrolyte, sample area = 156 cm² and plating time = 10 minutes per sample (bottom of bath) at constant potential.
FIGURE 78. Limiting current density and metal deposit thickness distribution profiles from top to bottom of a 25 litre electroplating tank.
LCD – sensor method.
XRF – X-ray fluorescence analysis.
FIGURE 79. Limiting current density distribution along a tank diagonal for a vibratory agitated electrolyte: bottom position.

FIGURE 80. Limiting current density distribution along a tank diagonal for a vibratory agitated electrolyte: centre position.

FIGURE 81. Limiting current density distribution along a tank diagonal for vibratory agitated electrolyte: top position.
FIGURE 82. Distribution profile of limiting current density across the tank (side to side, breadthwise) for three vertical positions.

FIGURE 83. Distribution profile of limiting current density across the tank (side to side, lengthwise) for three vertical positions.

FIGURE 84. Limiting current density distribution profile determined by sensor, from top to bottom of a vertical flat sheet cathode at various air agitation rates.
FIGURE 85. Mass transfer correlation using modified Reynolds and modified Sherwood numbers incorporating data for electrodes in two positions near the perforated disc vibrator plate. Disc diameter 10cm, tank 5 litres of 19cm diameter.

FIGURE 86. Mass transfer correlation using modified Reynolds and modified Sherwood numbers incorporating data for electrodes in five positions in the tank. Disc diameter 10cm, tank 25 litres of 26cm diameter.
FIGURE 87. Evolution of a particle from bulk solution into metal via five steps after Johal.
FIGURE 88 Relationship between the air voidage fraction and the IR drop in an electroplating acid copper sulphate solution.

FIGURE 89 Graph showing results, using theoretical model and photo-micrograph data.

FIGURE 90 Variation of air voidage fraction with volume of air bubbles in the electroplating acid copper sulphate solution.
FIGURE 91 Graph showing experimental solution conductivities as a function of agitative air voidage, compared with five classical models.

FIGURE 92 Graph showing laboratory experimental solution conductivities as a function of agitative air voidage, based on the five classical models.
FIGURE 93: Alumina mapping X-ray micrograph showing distribution profile at vibratory agitation rate of 70 (a) Top of sample panel, (b) Middle of sample panel (c) Bottom of sample panel
FIGURE 94: Alumina mapping X-ray micrograph showing distribution profile at vibratory agitation rate of 140 (a) Top of sample panel, (b) Middle of sample panel and (c) Bottom of sample panel
FIGURE 95: Alumina mapping X-ray micrograph showing distribution profile at vibratory agitation rate of 210 (a) Top of sample panel, (b) Middle of sample panel and (c) Bottom of sample panel
FIGURE 96 Weight percentage (Wt %) of incorporated alumina with copper, limiting current density using vibratory agitation Vs. vibrational amplitude. Illustrating regions of laminar, transition and turbulence.