3.1 Introduction

Aqueous electrolytes, used in metal finishing for electrodeposition of metal coatings, are principally solutions of metal salts, which, in solution, dissociate to form electrically charged anions and cations. These ions can be simple metal cations, Me^{z+}, positively charged complex ions or hydrogen ions, H^+. Also present will be ionised acid species, negatively charged complexes or hydroxyl anions, OH^-. Figure 3.1, which shows by way of illustration, the copper–sulfate ion system, also makes clear that the charged ions themselves are surround by an outer sheath of water molecules, held by electrostatic forces to the ions themselves. The orientation of these water molecules is seen to differ according to whether they surround a positively or a negatively charged ion. The reason for this lies in the dipole nature of water molecules. The same is also true for complex ions which, in comparison to simple ions, have a more complex structure. The reason for this is that complex species are higher-order compounds, built up from first-order species. In many of their properties, they differ markedly from the simple compounds of which they are formed.

The build-up of a complex can be described as follows. Around a central ion, in many cases, a heavy metal, are spatially arranged other ions or uncharged molecules (Fig. 3.2). These are often referred to as ligands. The central ion can coordinate, in this way, a greater number of outer ions or radicals than its normal valency would imply. This being the case, the conventional, simple means of formulating a chemical compound is no longer adequate.

The bonding between the central ion and the ligands is predominantly electrostatic or also non-polar bonding. The number of ligands is expressed as the so-called coordination number. There is no correlation between the valence number of the central ion and the coordination number, which is often 4, 6 or 8 in value. The reason for this lies in rules, which are an expression of steric ordering. Figure 3.3 shows the three most commonly found spatial configurations.

Since the ligand species are usually larger than the central ion, the latter is more or less completely shielded, with the result that its chemical properties are usually extensively modified.
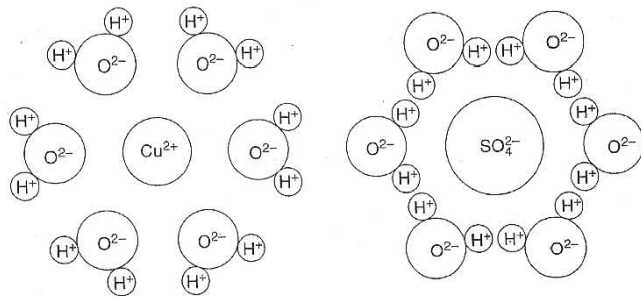
Figure 3.1   *Formation of hydration sheaths around a positively and a negatively charged ion, as illustrated by copper (cation) and sulfate (anion).*
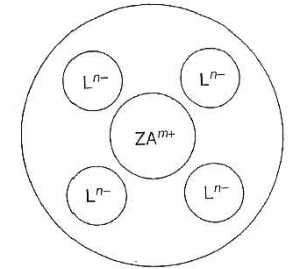
Figure 3.2   *Schematic arrangement of a complex. ZA^{m+} is the central ion, L^- the ligands (m, n are the charge numbers, k can be positive, negative or uncharged) [1].*

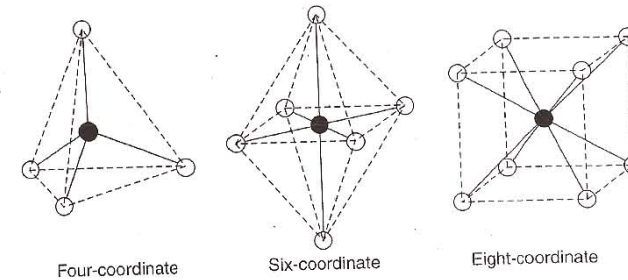Four-coordinate   Six-coordinate   Eight-coordinate

Figure 3.3   *The most commonly found coordination structures of metal complexes (● = central ion, ○ = ligands) [2].*

Many electrolytes used in Metal Finishing are based on complexes. A typical example would be potassium hexacyanoferrate(II), in which six CN ligands surround a central iron ion. The species dissociates as shown below:

$$K_4[Fe(CN)_6] \longrightarrow 4K^+ + \begin{bmatrix} & CN & \\ CN & & CN \\ & Fe & \\ CN & & CN \\ & CN & \end{bmatrix}^{4-} \tag{3.1}$$
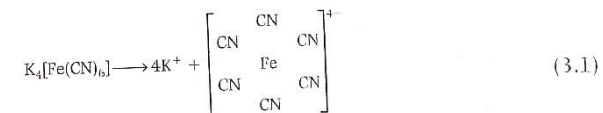
In addition to ligands which possess only one coordination site used in complex formation, there are other species with more than one coordination points allowing them to envelop the central ion. Complexes formed on this basis are known as 'chelated' and the ligands are known as 'chelating species' or 'chelants' (from the Latin, crab's pincers). Examples of these include ethylenediamine tetraacetic acid (EDTA) and ethylenediaminetetra-2-hydroxpropane (quadrol), with chemical formulae {(HOOC–CH$_2$)$_2$N–CH$_2$–CH$_2$–N(CH$_2$–COOH)$_2$}

or $\{CH_3CH(OH)CH_2\}_2-N-CH_2-CH_2-N(CH_2CH(OH)CH_3)_2\}$. The structural formulae of these are shown below:

EDTA

Quadrol
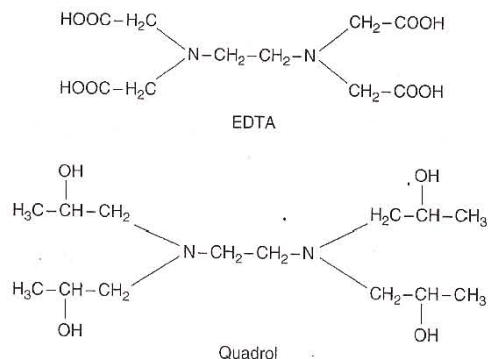
Using EDTA as example, it is seen that the two nitrogen atoms bond at two coordination sites, the four oxygen atoms of the acetate grouping bond at four coordination sites [3, 30].

3.2 Electrodeposition Electrolytes

The electrodeposition of metal coatings in industrial metal finishing is usually based on aqueous electrolytes, known in the industry as electrodeposition baths or simply, baths. Their primary constituent is the metal salt of the metal to be deposited, then in most cases an acid or alkali to promote conduction. In some cases the bath is buffered. In addition, there will be additives to promote the electrodeposition process or optimise the deposit properties.

The metal deposition is brought about either by current flow from an external power source, or by addition of a strong reducing agent, which sets up a coupled anodic and cathodic reaction. Depending on which of these is the case, the terms 'electrodeposition' or 'electroplating' or 'electroless deposition' are used (see Chapter 4). The term 'plating' usually refers to electroplating, but retains a degree of ambiguity.

3.2.1 Electroplating Electrolytes

Over the last few decades, hundreds of different plating baths have been developed to allow or optimise the deposition of metals or alloys. A useful means of characterising such baths is in terms of their operating pH. In terms of this, one has acid, neutral and alkaline baths, where the pH values are usually <3, ≈7 and >9, respectively. In the following, examples of each of these three are detailed. In all three cases, it is vital to avoid significant pH changes during the electrodeposition process. For this reason, all plating electrolytes have added acid, alkali or buffers.

3.2.1.1 Acid electrolytes

Acid electrolytes are usually based on simple metal salts such as sulfates or chlorides, less commonly are phosphates or sulfamates encountered. Also present is a high concentration of the parent acid, partly to optimise electrical conductivity, partly to minimise pH changes. The metal salts will dissociate as usual, into their constituent anions and cations. A typical example is the so-called 'acid copper' [4] typically constitutes as:

150–250 g/l copper(II) sulfate pentahydrate $CuSO_4 \cdot 5H_2O$
30–75 g/l sulfuric acid ($d = 1.84$ g/cm^3)
30–150 mg/l chloride (Cl$^-$ ion)

The copper salt is the source of the metal ions. From a copper sulfate solution alone, copper deposits will be mossy, coarse-crystalline and brittle. Only after the parent acid is added will a compact, fine-grained and ductile deposit be formed. In addition, by increasing electrolyte conductivity, the process can be carried out at a lower voltage, reflecting a smaller ohmic drop in solution.

To this acidified sulfate solution, brightening additives are usually added (see Section 3.2.1.4.1), whose function is self-evident. Addition of chloride ions is critical for the correct functioning of such brighteners, and the concentration of this is usually in the range 30–150 mg. At chloride concentrations <20 mg/l, striated and rough deposits are formed. Above the higher limit, matt deposits are found and the covering power falls off (see Section 3.2.1.5.2).

This type of electrolyte is usually operated in the temperature range 20–45°C and at current densities of 1–20 A/dm^2.

Another example of an acid deposition bath is the high-chloride nickel electrolyte, typically of composition:

200 g/l nickel(II) chloride hexahydrate $NiCl_2 \cdot 6H_2O$
up to 100 g/l nickel(II) sulfate heptahydrate $NiSO_4 \cdot 7H_2O$
30–50 g/l boric acid, H_3BO_3

The pH in this system lies in the range 2.5–4 [5] with the boric acid as buffer to maintain a constant pH. Operating conditions are 40–70°C and deposition current density of 3–10 A/dm^2. There are also electrodeposition baths using organic or inorganic complexes as source of the metal ions. Thus, fluroboric acid $H[BF_4]$ is the basis of well-know fluroborate electrolytes, while hexafluorosilicic acid $H_2[SiF_6]$ is likewise the parent acid of fluorosilicate baths [5]. In both cases, the metal is present in cationic form.

Equally, however, there are metal ion complexes where the metal is anionically charged [5]. These include hexavalent chromic acid (for chromium plating) and acid gold baths, based on the anion $[HCr_2O_7]^-$ and $[Au(CN)_2]^-$, respectively.

3.2.1.2 Neutral electrolytes

Under this heading are included systems which operate in the weakly-acid to weakly alkaline range. Since these are poorly conducting, they are not in common use. (hydrogen cations and hydroxyl anions have far the greatest electrolytic conductivity).

An important exception to this, however, are the neutral zinc plating baths, operating in the pH range 7.5–8.8. They contain two or more zinc-containing complexes, which must be maintained in a given concentration ratio. The first of these are complexes of ammonium chloride zincate, of composition $Zn[(NH_3)_2Cl_2]$ or $Zn[(NH_4)_2Cl_4]$, with the second category being zinc chelated with polyhydroxy-carboxylic acid.

Thus a typical composition of such an electrolyte would be [6]

26–52 g/l zinc (as the metal)
105–165 g/l chloride (as Cl^- ion)
45–90 g/l chelating agent

Another example of a neutral electrolyte is that used for electrodeposition of precious metals, which incorporate added salts to increase their conductivity. So a typical composition for a neutral (pH 6.8–7.5) gold bath might be [7]:

7 g/l gold (as the potassium dicyanoaurate(I), $K[Au(CN)_2])$
7 g/l copper (as potassium cyanocuprate(I) $K_2[Cu(CN)_3])$
28 g/l sodium dihydrogen phosphate NaH_2O_4

This bath is used at 65–75°C with a deposition current density of 0.5–1 A/dm^2. One final example of a neutral electrolyte is that for forming gold–palladium–nickel alloys in which both cationic and anionic metal ion complexes are present as $[Pd(NH_3)_4]^{2+}$ or $[Ni(NH_3)_6]^{2+}$ and $[Au(CN)_2]^-$ or $[Au(SO_3)_2]^{3-}$ [5].

3.2.1.3 Alkaline electrolytes

This category is best sub-divided as cyanide-containing and cyanide-free types. It might be noted here that in both cases, alkaline electrolytes react slowly with carbon dioxide in air to form alkaline metal or other metal carbonates. Anything that increases electrolyte-to-air contact, such as agitation or air-sparging, will accelerate the rate of carbonate formation. Above a certain concentration, carbonates in solution will adversely affect the metal deposition process and will have to be removed, using either a physical or chemical approach.

3.2.1.3.1 Cyanide-containing electrolytes

Electrolytes are designated as 'cyanide-containing' when they contain significant amounts of so-called 'free cyanide', that is, an excess of the simple KCN or NaCN. This will dissociate in solution, to form the constituent ions. It is vital that such solutions be at all times kept sufficiently alkaline, for if this is not so, HCN, the deadly hydrocyanic acid will form and be liberated in gaseous form (also known as 'Prussic acid gas'). In fact, accidents due to this are extremely rare. In spite of this, metal finishers are under on-going pressure to replace cyanide-based processes with those not containing this species.
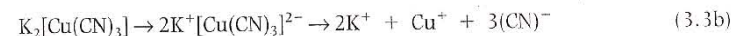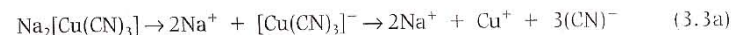
Citing an example, such as cyanide copper solution [4], is helpful.

The copper(I) cyanide, CuCN, which acts as the source of the metal, is not soluble in water, but can be made so by addition of an alkali metal cyanide (NaCN or KCN).

This leads to the formation of a cyanide complex, as:

$$CuCN + 2NaCN \rightarrow Na_2[Cu(CN)_3] \qquad (3.2a)$$

$$CuCN + 2KCN \rightarrow K_2[Cu(CN)_3] \qquad (3.2b)$$
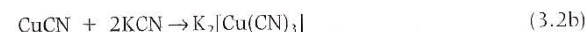
Dissociation of the complex salt sodium (or potassium) tricyanocuprate(I) takes place as shown:

$$Na_2[Cu(CN)_3] \rightarrow 2Na^+ + [Cu(CN)_3]^- \rightarrow 2Na^+ + Cu^+ + 3(CN)^- \qquad (3.3a)$$

$$K_2[Cu(CN)_3] \rightarrow 2K^+[Cu(CN)_3]^{2-} \rightarrow 2K^+ + Cu^+ + 3(CN)^- \qquad (3.3b)$$

It follows that the presence of a significant amount of 'free cyanide' (as the sodium or potassium salt) as well as free alkali are necessary for the functioning and safe operation of this system, not just to solubilize the copper cyanide, but also for the following reasons:

(a)   Cyanides will slowly break down, either by anodic oxidation or homogeneous or heterogeneous (catalysed) air oxidation. Alkali is removed, as explained above, by carbonate formation.

(b)   If there is insufficient free cyanide to solubilise the copper salt, the anodes will become encrusted with the insoluble metal cyanide, their rate of dissolution will be reduced and the electrolyte may become depleted of copper ions. In some cases, because the effective anode area is reduced, the current density will increase and polarisation or passivation may occur.

(c)   In the absence of sufficient cyanide in solution, the electrodeposited copper will be powdery rather than forming a dense adherent layer.

A typical cyanide copper electrolyte (low copper type) would have the following composition:

25 g/l copper(I) cyanide CuCN
30 g/l sodium cyanide NaCN
3 g/l sodium sulfite Na_2SO_3
6 g/l sodium carbonate Na_2CO_3

Such a bath operates at pH 12, at a temperature of 20–30°C and a current density of 2–2.5 A/dm^2. The particular characteristics of this electrolyte lend themselves to copper-plating of undercoats on zinc diecastings.

A similar copper electrolyte, but with higher copper content, is made up as [8]:

270 g/l potassium tricyanocuprate(I) $K_2[Cu(CN)_3]$
10–30 g/l sodium cyanide NaCN
10 g/l potassium cyanide KCN
5 g/l sodium sulfite Na_2SO_3
5 g/l sodium hydroxide NaOH

This electrolyte too, has pH 12, and will also include brightening additives. It would normally be operated at 65°C and at a current density of 1.5–4 A/dm^2.

Table 3.1   Composition of alkaline cyanide zinc plating baths [6, 9].

Constituents	Concentration [g/l]		
	High cyanide	Medium cyanide	Low cyanide
Zn	30–50	15	17–15
NaCN	75–150	40	10–30
NaOH	75–150	90	80–150

Other examples of alkaline cyanide baths are used for deposition of zinc, silver and gold. In the case of zinc, cyanide electrolytes are categorised as low, medium or high cyanide. Typical compositions for these are shown in Table 3.1.

In many cases, some 25–30 g/l of sodium carbonate is also added, to increase bath stability, and small quantities of sulfides may be added, in order to precipitate out, as the highly insoluble metal sulfide, any metallic impurities.

Of the greatest importance, when operating cyanide zinc solutions, is not only the zinc ion concentration, but also the ratio of NaCN and NaOH to the zinc ion concentration, in order to ensure uniform thickness distribution. In practice, one uses the so-called 'M-factors', which are defined as follows:

$$M_{CN} = \frac{NaCN}{Zn}$$

$$M_{OH} = \frac{NaOH}{Zn}$$

Such M-factors can be used to determine the trade-off between highest useable current density and optimum throwing power. Thus, a high M_{CN}^- factor, that is, high NaCN content, implies a lower useable current density but good throwing power (see Section 3.2.1.5.3). Thus, when zinc plating components of complex geometry or with pronounced profiles, a high M_{CN} factor is desirable. By contrast, a high M_{OH} factor, that is, high NaOH concentration, is preferred when high deposition rates are desired, even at the expense of covering power [9].

Being able to 'fine tune' such zinc electrolytes for a particular application is thus a useful attribute. In addition to examples of cyanide electrolytes cited above, one might also list those in use for deposition of a range of alloys, including copper–zinc, copper–tin, gold–copper–cadmium or gold–copper–zinc [5].

3.2.1.3.2 Non-cyanide alkaline electrolytes

Under this heading, one could list a range of zinc baths used for rack or barrel plating of small parts. Cited compositions for such electrolytes are 12–14 g/l zinc and 120–160 g/l NaOH, or 11–13 g/l zinc and 110–150 g/l NaOH [9]. The optimum ratios of NaOH to zinc are 8–10. The higher the zinc and NaOH concentrations, the higher the current efficiency, other things being equal.

These cyanide-free alkaline zinc electrolytes lack the stability of their cyanide-containing counterparts, and are mainly used where (for whatever reason) it is desired to avoid the use of cyanides, but without sacrificing the benefits of uniform

deposit thickness distribution. These systems are usually operated at 18–35°C and at a deposition current density of 0.5–6 A/dm² [9].

3.2.1.4 Electrolyte additives

In addition to metal salts, electrodeposition electrolytes usually contain various other species. Thus both inorganic and organic salts, acids or alkalis will be added to increase electrolyte conductivity. Other species, both organic or inorganic, may be added for specific purposes, for example, to increase bath stability, or improve levelling or metal distribution, or to optimise the chemical, physical or technological properties of the deposited metal (corrosion resistance, brightness or reflectivity, hardness, mechanical strength, ductility, internal stress, wear-resistance or solderability).

In working with such additives, it should be recognised that they are often effective over only a defined concentration range, and should their concentrations fall outside this range, all kinds of problem can arise either in the deposition process or the deposit properties. In the following sections, such addition agents are considered in greater detail.

3.2.1.4.1 Brightening agents

In metal finishing, bright or highly reflective surfaces (the terms are usually synonymous) can be of both decorative and functional importance, if for no other reason that bright surfaces require less mechanical finishing, after plating, if indeed any at all.

Defining brightness or reflectivity of a surface as the extent to which incident light is reflected, it follows that surface roughness and unevenness are antithetical to good reflectance. Reflective surfaces are characterised by a crystallite size at the surface of less than 0.3 μm². Thus, highly reflective deposits are found under conditions where fine-grained deposits are formed. To achieve this, it is long-established practice to add metallic or organic compounds, known as brighteners or brightening agents. Their use is based on empiricism, there being no certain means of predicting their effects. In the same way, selecting the most appropriate such compound(s) will usually be based on trial-and-error.
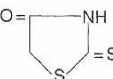
Two different types of brightener are recognised, the first being brightener carriers, the second, brightener additives [10–12].

Addition of brightener carriers, also known as primary brighteners or Class I brighteners, leads to a significant grain refining action in the deposited metal. While this greatly increases the brightness of the metal, it will not impart a mirror-finish or anything close to this. Among the best-known brighteners of this type are [13]

- sulfonamides
- sulfonimides
- benzenesulfonic acids (mono-, di- or trisulfonic acids)
- napthalenesulfonic acids (mono-, di- or trisulfonic acids)
- alkylsulfonic acids
- sulfinic acids
- arylsulfonesulfonates.

These primary brighteners are essential components of a complete brightening system, in that they reinforce the efficacy of Class II or secondary brighteners, the

Table 3.2   Some commonly used brighteners [14].

Designation	Structural formula
Thiourea	$H_2N - \overset{\overset{\textstyle S}{\|\|}}{C} - NH_2$
Acylthiourea	$R - \overset{\overset{\textstyle O}{\|\|}}{C} - NH - \overset{\overset{\textstyle S}{\|\|}}{C} - NH_2$
Mercaptoalkylsulfonic acid	$HS - C_nH_{2n} - SO_3H$
Bis-(sulfoalkyl)-disufide	$[S - C_nH_{2n} - SO_3H]_2$
Thiocarboxylic acid amide	$\overset{R}{\underset{R^1}{}}{>}N - \overset{\overset{\textstyle S}{\|\|}}{C} - S - C_nH_{2n} - SO_3$
Thiocarbazone	$H_2N - \overset{\overset{\textstyle S}{\|\|}}{C} - O$
Thiosemicarbazone	$\overset{R}{\underset{R^1}{}}{>}C = N - NH - \overset{\overset{\textstyle S}{\|\|}}{C} - NH_2$
Thiohydantoin	$O = \overset{NH}{\underset{S}{\bigcirc}} = S$

latter being rarely used without the former. Class II brighteners, even at very low concentrations, impart a near-mirror finish to the deposited metal. The most important of these are listed in Table 3.2.

Out of a very large number of potential Class II brighteners, only a few are used in practice, largely because – although many such species are highly effective in their brightening action, they can adversely affect process or deposit properties in other ways. In order to minimise this, secondary brighteners are usually employed with a primary brightener in a combination known for the compatibility and synergy of both.

A number of electrolytes form bright deposits only in a comparatively narrow temperature and current density operating window. Figure 3.4 shows this for chromium deposition.

As Fig. 3.4 shows, at any given temperature, a range of current densities exists, within which bright deposits can be formed. Alternatively, at any given current density, there is range of temperatures in which the same is true. Figure 3.4 is valid only for a particular chromium electrolyte system, and depending on concentrations of species used, and the catalyst, similar diagrams can be drawn, though the general shape of these is similar. At a given temperature, the widest possible range of operating current densities is desirable, especially when items of complex geometry or with deep profiles are involved, as in such cases, there will be marked variations in
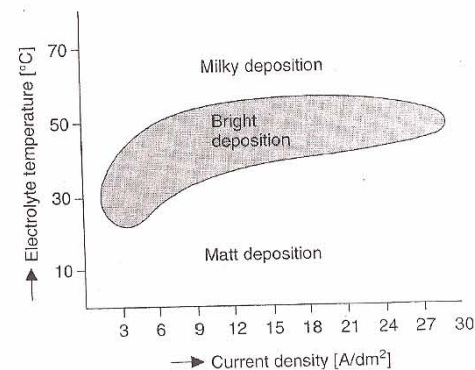
Figure 3.4   Operating window for bright chromium deposition as function of deposition temperature and current density [8, 15].

current density at different locations on the work. An approach such as that shown in Fig. 3.4 is essential in ensuring that bright deposits are formed over the entire surface, however complex this might be.

There are many theories to explain the brightening action of this class of additive. Most probably, the effect is due to a controlling effect, and perhaps a rate-limiting action, on the electrocrystallisation step. Such theories link with the accepted mechanism for metal electrodeposition, based on a nucleation and growth at a series of centres. From the growth nuclei, grains develop with a range of sizes and orientations. It is assumed that the brighteners are preferentially adsorbed on the developing growth peaks, thereby inhibiting further growth at these points. Having no alternative, the electrocrystallisation is forced to continue in the valleys rather than the peaks, whereby a levelling action results. The end result is a smooth and shiny surface. It follows that brightening is associated with a levelling action as well.

3.2.1.4.2 Levelling agents

Either before or after electroplating, it may be necessary for the work to be mechanically finished, using grinding, then polishing stages, and these can significantly add to the overall cost [16], especially when the deposited metal is hard, for example, hard chromium. Levelling agents can act to smooth pre-existing irregularities in the surface, such as pits or scratches and thus they compensate for poor surface quality of incoming work.

The levelling action of an electrolyte, that is to say its ability to form a smoother surface than that of the original substrate, is defined as 'levelling power' [11, 17–19]. By levelling action is implied the deposition of a greater thickness of metal in the depths of a groove than at its outer edge. This can be quantitatively expressed as:

$$E = \frac{d_t - d}{R_z} \cdot 100\% \qquad (3.4)$$

Figure 3.6   Dependence of bright nickel levelling action on deposition time. From top down, 7, 14 and 21 min V = 350:1 [5].
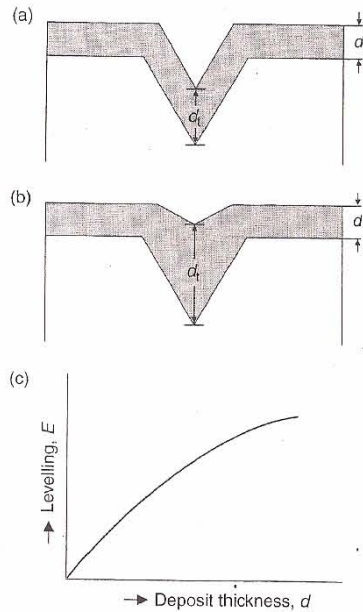
Figure 3.5   Illustration of levelling action: (a) geometric levelling; (b) true levelling; (c) levelling as function of deposit thickness.

In Eqn (3.4), E is the levelling effect, d_t the deposit thickness at the base of the groove, d the overall deposit thickness and R_z the roughness of the substrate.

A distinction is made between geometric and true levelling. In the former case, the key factor is that the deposit is thicker at the bottom of a groove than at the edge (Fig. 3.5a). The effect is measured in terms of the geometry and shape of the groove. The hallmark of true levelling is a higher metal deposition rate in the groove than at the adjacent areas (Fig. 3.5b) and this results when the so-called levelling agents or levellers are added to the electrolyte. The manner in which these additives work is by restricting the rate of metal deposition, but only at those locations where they are freely supplied, specifically at peaks and edges. The levelling action of such species can vary quite widely, apart from which it is usually temperature dependant and can often be enhanced by work movement or solution agitation. Levelling action is a function of deposit thickness and increases as thickness increases (Fig. 3.5c).

Certain electrodeposition electrolytes are specially effective in their levelling action. These include bright nickel, whose levelling action is shown in Fig. 3.6. On a polished surface of a copper–zinc alloy, grooves were formed using a scribing diamond with loading 0.5 N. Onto this scribed surface, bright nickel was deposited at 58°C, pH 4.0 and a cathodic current density of 4 A/dm².

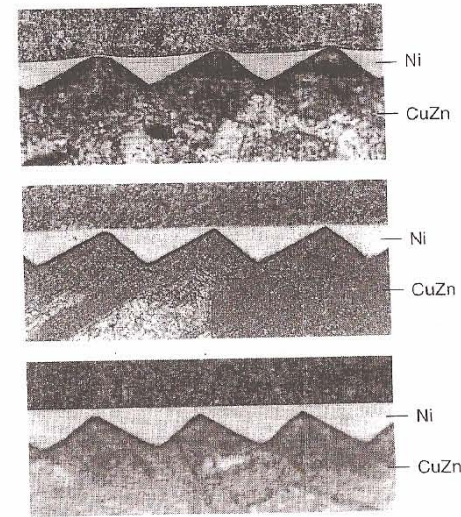From this sequence of cross-sections, it can be seen that as a result of the pronounced levelling action of the bright nickel, deposition occures initially in the grooves. The levelling effect increases as the deposit thickness grows so that, after sufficient time, the troughs and peaks have been effectively levelled.

A negative levelling action is defined as a situation where less metal is deposited in the depths of a groove than at the outer surfaces, that is to say that the electrodeposition enhances the surface roughness. This effect is observed with some cyanide electrolytes.

3.2.1.4.3 Surfactants (wetting agents)

Plating baths will usually contain wetting agents, also known as surfactants. These are characterised by their asymmetry and dipolar nature (●—). They have a hydrophilic ('water loving') 'head' (●) and a hydrophobic ('water-repellent') 'tail'⁻. Surfactants can be 'anionic', 'cationic' or 'non-ionic' depending on the charge at the hydrophilic end. The polar hydrophilic radicals are typically $-COO^-$ or $-SO_3^-$ groupings, while the hydrophobic part of the molecule might be a non-polar aliphatic long-chain hydrocarbon [20, 21]. Non-ionic surfactants are themselves uncharged, acquiring their charge from ions present in aqueous solution [17].

Wetting agents are surface-active species, that is, they act by accumulating at a surface or interface. At an air–electrolyte interface, they are oriented with hydrophilic head into solution, the hydrophobic tail to the air-side. In this way they reduce the surface tension of a liquid.

Chromium plating afford a good example of the working of such wetting agents. In this process, chromium deposition is accompanied by a substantial evolution of hydrogen gas at the cathode (work) surface. These bubbles rise to the electrolyte surface and there explode, thereby forming a mist of the chromic acid

Table 3.3 Classification of surface-active agents ($n = 10–20$; $m = 8–16$; $o = 5–20$) [20].

Type	Hydrophilic grouping	Example	Designation
Anionic	$-COO^{\ominus}$	$CH_3-(CH_2)_n-COO^{\ominus}$ with $Na^{\oplus}$; basic soap with K^+: lubricating soap	Soaps
	$-O-SO_2-O^{\ominus}$	$CH_3-(CH_2)_n-O-SO_2-O^{\ominus}$	Fatty alcohol sulfates
	$-SO_2-O^{\ominus}$	$CH_3-(CH_2)_n-SO_2-O^{\ominus}$	Alkyl sulfonates
		$CH_3-(CH_2)_m-\langle\bigcirc\rangle-SO_2-O^{\ominus}$	Alkylarylsulfonates
Cationic	$-N^{\oplus}-CH_3$ with CH_3 groups	$CH_3-(CH_2)_n-N^{\oplus}-CH_3$ $Cl^{\ominus}$	Alkyltrimethyl-ammoniumchloride
Amphoteric, zwitterionic	$-N^{\oplus}-CH_2-CO-O^{\oplus}$ with CH_3 groups	$CH_3-(CH_2)_n-N^{\oplus}-CH_2-CO-O^{\oplus}$	N-alkylbetain
Non-ionic	$-O-(CH_2-CH_2-O-)_L-H$	a) $CH_3-(CH_2)_m-O-(CH_3-CH_2-O-)_L-H$ b) $CH_3-(CH_2)_m-\langle\bigcirc\rangle-O-(CH_2-CH_2-O-)_L-H$ c) $CH_3-(CH_2)_n-C(=O)-O-(CH_2-CH_2-O-)_L-H$	Polyethyleneglycol adducts of $\bigtriangledown$ with (a) alkyl alcohols (b) alkyl phenols (c) fatty acids

electrolyte[1], which is extremely hazardous to health, and indeed to nearby equipment. As a result, powerful air-extraction facilities are essential. If, however, a wetting agent is added, usually a fluorinated type capable of withstanding the powerful oxidising action of chromic acid, the surface tension will be reduced from, typically 70 to 20 mN/m and the extent of chromic acid mist formation is greatly reduced [22]. At the same time, a thin and compact layer of foam is formed at the surface which substantially reduces evaporative losses from the electrolyte.

Wetting agents or surfactants also build up at the solid–liquid interface of the work, immersed in the electrolyte. The hydrophilic groups are hydrated and drawn towards the aqueous phase, with the hydrophobic end being weakly adsorbed onto the work surface. With this degree of ordering imposed at the interface, the interfacial tension is reduced, that is, the work surface becomes more easily wetted by the electrolyte, with several resulting benefits to the electrodeposition process.

In metal finishing, anionic or non-ionic surfactants are most often used. The lowering of surface tension facilitates the release of gas bubbles adhering to the work surface, whether these be cathodically evolved hydrogen or trapped air. Where such bubbles adhere to the surface, their shielding action results in little electrodeposition occurring and they can be the cause of pitting or deposit porosity. Table 3.3 gives a classification of surface-active agents.

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[1] Hexavalent chromium compounds are toxic and carcinogenic.

Addition of surface-active agents also results in the following:

- certain organic compounds, insoluble or poorly soluble in water can be solubilised or their distribution in solution made more uniform;
- coagulation and sedimentation of suspended solid matter as dirt in solution which would otherwise lead to rough or porous deposits, is reduced;
- crystal growth is inhibited and a brightening action of the deposit results;
- draining of adherent electrolyte, on withdrawing the work from solution is improved, drag-out losses are reduced.

It should be noted that the type of surface-active agent best used is very much linked to the particular electrolyte employed, and a poor choice can result in all manner of adverse consequences in process operation. Maintaining the optimum concentration is also critical. If too low, some or all of the benefits listed above may not come into play, while if too high, the deposit properties may be adversely affected. Finally, the choice of wetting agent may be influenced by the type of electrolyte agitation being used, whether air-sparging, work-movement or eductor.

3.2.1.5 Electrolyte properties
The aim of the electrodepositor will usually be to form dense, uniform and adherent metal coatings. Of the countless factors which are important for this, the electrolyte and its properties are vital, and this is discussed below.

3.2.1.5.1 Electrolytic conductance
Whereas, in a metal, electric current flows by means of free electrons, the passage of current in an aqueous solution of ionised species is due to the migration of ions, molecules or atoms bearing a positive or negative charge. In some important aspects, these two mechanisms behave differently, and conduction of the latter type is therefore known as electrolytic conductance, as opposed to electrical conductance found in a metal. Electronic conductors are sometimes known as Class I conductors, electrolytic conductors as Class II. Worth noting that under a wide range of conditions, both types of conductors obey Ohm's law. Arguably, the key feature of aqueous electrolytes is that the compounds dissolved in them, have partly or completely ionised. It is by the movement of such charged ions that electric current can be passed through the solution. For further details and data, see Refs. [8, 23]. The key issues are the degree of dissociation of the dissolved species in solution, and the so-called ionic mobility, reflecting the fact that under a given potential gradient, some ions travel faster than others, and are thus a more effective means of carrying charge.

In broad terms, it is usually assumed that inorganic acids, alkalis and metal salts are close to 100% dissociated (see Table 3.4), metal salts of organic acids, such as copper acetate, are partly dissociated, while, for example, organic acids range from being highly dissociated (formic, acetic) to being almost undissociated (butyric, oleic acids).

Ions formed by dissociation of the parent species travel across the electrolyte between anode and cathode, under the influence of the potential gradient established by application of a voltage. Cations (positively charged) travel to the cathode (the negative pole) and anions, negatively charged, move in the opposite direction to

Table 3.4   Degree of dissociation of selected acids and salts.

0,1 N solution of	Degree of dissociation [%]
H_2SO_4	96
HNO_3	92
HCl	91
H_3PO_4	81
NaOH	80
KOH	73
$ZnCl_2$	24
Na_2SO_4	13
NaCl	12
$ZnSO_4$	0.17
$CuSO_4$	0.01

Table 3.5   Ionic mobility values for selected ions.

Ion	v [cm/h]
H^+	11.34
OH^-	6.01
Cl^-	2.25
K^+	2.18
SO_4^{2-}	2.13
NO_3^-	2.09
Ag^+	1.76
Fe^+	1.73
Na^+	1.32
Cu^{2+}	1.04

the anode. Their ionic mobility is defined as rate of travel (in cm/s) under unit potential gradient (volt/cm = 1). It should be noted that since all ions in aqueous solution carry a hydration sheath, what is actually measured is the rate of travel of the hydrated ion. This explains why, for example, in the alkali metal series, the larger ions such as Rb^+ travel faster than the apparently smaller ions such as Li^+, the reason being that the latter carries a larger hydration sheath.

A selection of ionic mobility values is shown in Table 3.5. It will be noted that the hydrated proton and hydroxyl ions have the highest mobility values, and this is due to the fact that, for these two species, an additional charge transport mechanism operates. It should be emphasised that the foregoing description is greatly simplified. Factors such as solution viscosity (itself linked to temperature) and ionic activity (a measure of concentration, but corrected for other effects) are also important.

In terms of the simplified theory presented here, one might expect a solution undergoing electrolysis to become depleted, as ever more anions migrate in one direction to the anode, and cations to the cathode. In practice, such effects are only significant under very special conditions. Working against ionic depletion are effects such as solution agitation (including natural convection) and diffusion under the effect of a concentration gradient (Fick's law). Chapter 4 provides further insights.

Table 3.6   Specific conductivity of selected electrolytes [19].

Electrolyte	$\chi \times 10^{-5}$ [m/Ω mm^2]
Zinc, sulfuric acid	0.49 (at 25°C)
Nickel	1.04 (at 50°C)
Copper, sulfuric acid	1.10 (at 25°C)
Copper, cyanide	2.15 (at 60°C)
Zinc, cyanide	2.52 (at 25°C)
Chromium	6.57 (at 50°C)

These explain the apparent paradox that chromium can be electroplated (at a cathode) from hexavalent $Cr_2O_7^{2-}$ ions when in fact one might expect such ions to be repelled from a cathode.

For electrolytes, as for metallic or inorganic conductors, the concept of specific conductivity, χ or its reciprocal ρ, specific resistivity, is useful. These can be visualised as the conductivity (or resistivity) of a cube of the material or liquid, to which Ohm's law is applied, that is, current is measured across opposing faces of the cube under a voltage gradient of 1 V/cm. Conductance is thus expressed as (m/Ω mm^2) or (mS/cm) where S (the siemens) = [1/Ω]. Some examples of specific conductivity are given in Table 3.6.

It is seen that the electrical conductivity of metals, for example silver, with $\chi = 63$, and copper with $\chi = 60$ is of order 10^6 higher than the best conducting electrolytes. Thus, 30% sulfuric acid solution at 18°C has a conductivity 800,000 times lower than copper.

In order to increase the conductivity of electrodeposition baths, acids or alkalis or salts are often added, and these are known as 'supporting electrolytes'. In the case of acid electrolytes, chloride and acids are used for this purpose, with chlorides alone being used with neutral solutions and, for alkaline solutions, sodium hydroxide or cyanide.

In order to compare the conductance of several electrolytes, a rational basis for doing so must be established. In practice, this is done by comparing values for 1 M solutions (also known as c_{Mol}) or as c_{Ae} the molar equivalent concentration.[2] In the first case, molar conductivity is expressed as:

$$\Lambda_m = \frac{\chi}{c_{Mol}} [cm^2/\Omega \cdot mol] \tag{3.5}$$

and in the second case as the equivalent conductance χ_{Ae}

$$\Lambda_{Ae} = \frac{\chi}{c_{Ae}} [cm^2/\Omega \cdot val] \tag{3.6}$$

The conductivity of an electrolyte is a function of the degree of dissociation, the mobility of the individual ions, the temperature (and thus viscosity) and the electrolyte composition. It should be noted that not only the ionic mobility but also the charge carried by each ion, as well as their concentrations. The hydration sheaths on

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[2] The equivalent weight of an atom is its atomic weight divided by valence value.
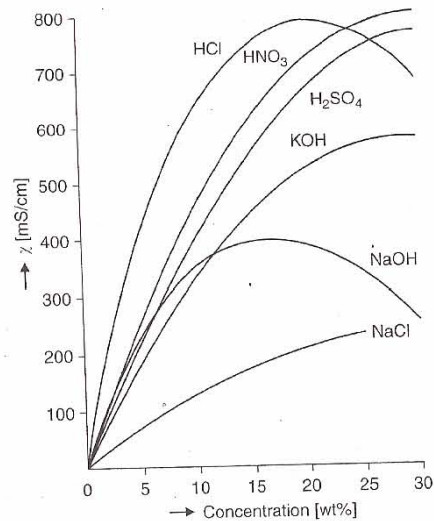
Figure 3.7   Conductivity of various electrolytes as functions of their concentration [24].

the ions play no part in the overall charge transport process. Some values for specific conductivity of selected electrolytes are plotted versus their concentrations in Fig. 3.7. It is seen that conductivity initially increases with concentration, after which a maximum value is reached. In the gradients of these plots and also the concentration values at which maximum conductivity is reached, there are significant differences between the various species shown.

The reason why, at higher concentrations, the linear relationship between conductivity and concentration breaks down, is ascribed to electrostatic interactions between neighbouring ions. These become more significant as concentration increases and this interaction decreases the effective rate of ionic mobility.

The marked decrease in conductivity at the highest concentrations is due to the greater coulombic forces acting between the ever-closer ions in solution. This can lead to a loose association of oppositely charged ions, which are effectively neutral and thus no longer contribute to the overall solution conductivity.

While, in principle, the electrolytic conductivity of a solution has no effect on the properties of the deposited metal, in cases where it is too low, certain adverse effects will appear. These include:

- Primary current distribution deteriorates, with the result that disproportionately heavy deposition occurs at leading edges and corners of the work. More generally, the outcome is less uniform metal distribution.
- Because the resistance is higher, more heat will be generated by the passage of the same current through the electrolyte (i^2R effect), the result being

increased electrical energy required, and perhaps more cooling of the solution being necessary.

High concentrations of alkali metal or alkaline earth metal cations, as well as cationic impurities in solution, all adversely affect solution conductivity.

3.2.1.5.2 Covering power

The term 'covering power' is used to describe the extent to which an electrodeposition electrolyte can cover the entire surface of an object being plated, with reasonably uniform thickness, including at least some deposition in recesses and cavities.

It is accepted that metal deposition begins only above a certain deposition potential, the value of which depends on the surface, and the metal being deposited. For an electrodeposition bath to exhibit covering power, the so-called minimum covering-power current density must be applied.

Estimation of covering power is frequently determined using the so-called Hull cell, named after its American inventor [DIN 50957, 5, 17]. As Fig. 3.8 shows, this is a miniature electrodeposition tank, but one in which the cathode is angled with respect to the anode. As a result, when a voltage is applied across the anode and cathode, the resulting current density will vary along the length of the cathode, being highest at the point it is closest to the anode. In this way, one can, within a single test run, assess the effect of varying current density. After such a run, the cathode is removed and inspected. At the highest current densities, the deposit may be burned. At the lowest current densities, no deposition may be observed. Thus the Hull cell allows the determination of the so-called 'operating window', the current density range over which acceptable deposition occurs. An electrolyte is said to have good covering power when satisfactory metal deposition extends into the lowest current density range.

Covering power is largely a reflection of the energy of nucleation at the work surface. Among the parameters affecting it, are the nature of the substrate surface, its composition and the operating conditions. Covering power usually increases with increasing current density and decreases with increasing temperature.

Covering power is specially important in the case of chromium plating, since it is generally poor for this metal anyway. A uniform deposit will result only when high
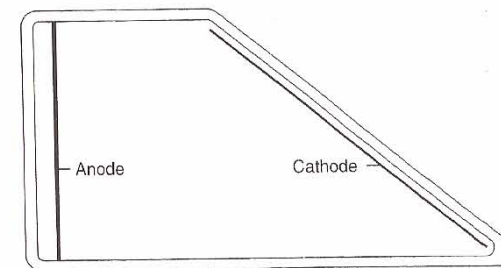

Figure 3.8   Hull cell for experimental determination of covering power of electroplating solutions.

current densities are used and total current densities can be up to 100% greater than the actual chromium deposition current density [19] with copious co-evolution of hydrogen. Typically, a uniform chromium deposit will form in 1–3 min. Further deposition is then carried out at reduced current density.

In general, alloy steels with high carbon content as well as cast iron and aluminium and its alloys all require relatively high current densities to achieve covering, as compared with unalloyed steel, copper and nickel [19].

3.2.1.5.3 Macro-throwing power

In the electrodeposition of metals, the depositing metal film does not grow uniformly at the same rate across the surface, reflecting the various factors which influence the rate of crystal growth.

Macro-throwing power is a term used to describe the ability of an electrolyte to lay down as nearly as possible, a uniformly thick deposit across the surface of an object. The more this is so, the better the throwing power, and thus throwing power can be used as a predictor for the uniformity of a deposit. It will be clear that good covering power is a pre-requisite for good macro-throwing power.

The macro-throwing power of an electrolyte is a manifestation of the extent of primary and secondary current density distribution in the system [17, 19].

Primary current distribution is the outcome of Ohm's law, applied to the dimensions and geometry of the spatial anode–cathode configuration and the shape of the electrolyte container. As seen in Figs. 3.9(a) and (b), there is a concentration of electrical lines of force at edges, points and corners. The result is a higher current density at these points and, in most cases, heavier deposition. The higher the electrolyte resistance, the greater such enhanced effects at edges, etc., will be. The parallel field lines shown in Fig. 3.9(c) are never achieved in practice.

Secondary current distribution reflects the electrochemical behaviour of the system, mainly in terms of the overvoltage at the cathode (polarisation). This is total overvoltage, and thus includes the various types of overvoltage which impede the rate of metal deposition. Overvoltage, or polarisation, is thus an expression of the difference between actual potential and the theoretical, reversible potential under conditions of current flow. The higher the overvoltage, the more uniform is metal distribution and anything that results in increased overvoltage will thus result in
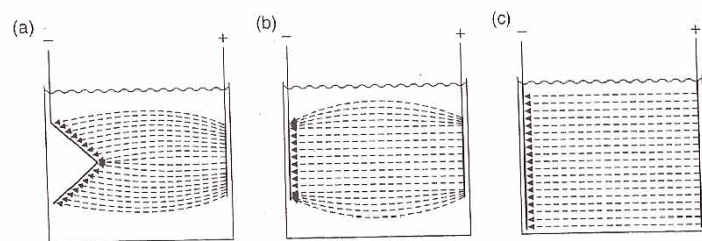

Figure 3.9   *Primary current density distribution as a function of the electrical field between anode and cathode.*
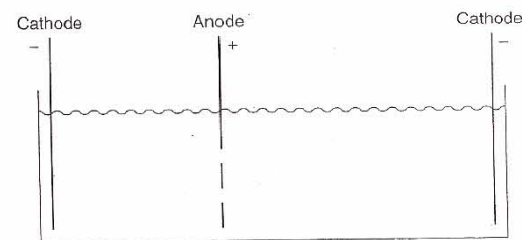
Figure 3.10   *Haring–Blum cell for experimental determination of throwing power of electrodeposition electrolytes [25].*

more uniform current density. Included in such effects are electrolyte composition, electrical conductivity and electrolyte agitation as well as deposition current density.

The experimental determination of macro-throwing power can be made either using a Hull cell or a Haring–Blum cell (Fig. 3.10).

A rectangular, open-topped electrolyte container is equipped with two cathodes, one at each end, of the same size, shape and material. Between these, is positioned an anode made of perforated mesh or similar construction. This anode is placed closer to one cathode than to the other, typically 1:5 in terms of the two anode–cathode spacings. The aim, though it is never completely achieved, as a result of edge-effects, is to replicate the uniform field shown in Fig. 3.9(c).

Assuming that the electrolyte resistances in the two compartments reflect the respective anode–cathode spacings, and are thus 1:5, one would expect, on the basis of primary current distribution effects, five times more metal distribution at the cathode of the shorter of the two compartments. In such a case, the macro-throwing power would be taken as zero. In practice, various electrolyte effects intervene and rather different values are obtained. These alter the amount of electrodeposited metal on the more distant cathode and result in positive values of macro-throwing power. Macro-throwing power is defined using the equation

$$S = \frac{L - M}{L + M - 2} \cdot 100\% \qquad (3.7)$$

where S is the throwing power, L the distance between anode and cathode and M the ratio of deposited metal on the nearer and farther cathodes.

It should be noted that two Haring–Blum cells, each with anode positioned in the ratio 1:5 vis-à-vis the two cathodes, but of different total length will give different results. Some authors, especially when using poorly conducting electrolytes, advise against perforated anodes, since current can flow through the perforations, creating spurious effects. Instead, a planar anode giving a seal between the two electrolyte compartments is suggested.

For cyanide- or sulfuric acid-based copper electrolytes, this method gives values of 25–30% and 2–5%, respectively [26] showing that cyanide copper electrolytes have a macro-throwing power far superior to that of acid copper. In general, it can be

asserted that complex-type electrolytes and those containing brightening additives have good macro-throwing power. Thus, in the case of copper plating components with complex geometry, cyanide copper or cyanide-free alkaline copper are the electrolytes of choice, where a uniform deposit is desired.

In practice, it is clear that the uniform electrical field which the Haring–Blum cell sets out to create, is rarely achieved. The electrical field is distorted by the shape of the work being plated, and by the means by which the work is attached to the racks, the configuration of anodes, etc. In practice, despite its poor performance in the Haring–Blum cell, a satisfactorily uniform deposit can be obtained using an acid copper electrolyte.

A far more challenging situation, in terms of macro-throwing power, is found with hexavalent chromium electrodeposition [25], which is inferior even to acid copper. In some cases, this requires that the chromium be electroplated from the trivalent electrolyte. In this case too, electrolyte agitation and increased temperature can lead to reduced macro-throwing power.

3.2.1.5.4 Micro-throwing power

Given that many components being electroplated have far from perfectly smooth surface, micro-throwing power is important. This is the extent to which metal electrodeposition occurs at the outer plane of the substrate or at the base of valleys or cracks. In principle, electrodeposition at these latter sites is hindered, in that access of fresh electrolyte and dispersal of exhausted electrolyte are hindered. Micro-throwing power becomes important in such situations, and is an expression of tertiary current distribution. The less metal that is deposited on peaks and outer planes, the better is the micro-throwing power. Micro-throwing action is achieved by preferentially activating the metal surfaces at the base of cracks or valleys, ensuring that those species which promote electrodeposition are concentrated there, while at the same time inducing inhibitors to adsorb at the outer surfaces [27]. In many cases it is found that micro-throwing power is inversely related to macro-throwing power. When the one is good, the other is not, and vice versa. Micro-throwing power thus acts to bring about a levelling (see also Section 3.1.4.2).

3.2.2 Electroless Deposition Electrolytes

Electroless deposition, also known as chemical deposition (see Chapter 4) is brought about when, to an electrolyte similar to those used in electroplating, a chemical reducing agent is added. Metal ions are thus reduced to metal at the surface of the work, not by externally applied current, but by the oxidation of the chemical reductant at the metal surface [31].

Examples of such systems include the widely used electroless nickel, where the deposited nickel includes a significant amount of phosphorus, when hypophosphite is the reducing agent used. Though such systems are used to deposit metallic coatings over metal substrates, they are also able to deposit a metal on non-conductors, such as plastics, once these have been activated. The basis of this hugely important activity, so-called 'metallising of plastics' is described in Chapter 4. In the case of electroless nickel, the deposits typically contain from 3 to 15 wt% phosphorus. After

heat-treatment, a range of Ni–P intermetallics are formed, whose hardness and corrosion resistance are superior to those of conventionally electroplated nickel.

The nickel salt used is usually the sulfate hexahydrate, $NiSO_4 \cdot 6H_2O$, with sodium hypophosphite as reductant. This is usually in the form of colourless hygroscopic crystals, molecular weight 107 and readily water soluble ($100\,g\ NaH_2PO_4 \cdot H_2O$ per $100\,g$ water at $25°C$).

Table 3.7 shows the composition of commonly used electroless nickel systems and the deposition conditions used. These so-called hypophosphite electrolytes have a pH of 4.6–5.6. Operated at 85–95°C, they deposit Ni–P coatings at a rate of 10–30 μm/h. Operating under the simplest conditions, they have a finite life, typically expressed as 2–10 MTO (metal turnover) [28] where 1 MTO implies a complete depletion of the nickel content of the bath. It is clear that to achieve this, the bath will need to be several times replenished with fresh nickel salts to make good the nickel removed from solution. In the past, accepted practice was to dispose of the bath after 30–80 g/l nickel had been deposited from it [28]. One can continue to use the bath for much longer, but the deposit properties will suffer. However, more recently, numerous processes for bath life extension have been published, many based on removal of the orthophosphite ions formed. The so-called EDEN (electrodialysis of electroless nickel) process claims that when used, the life of an electroless nickel bath is virtually infinite.

As Table 3.7 suggests, the Type III system is in many ways the best of the three. It uses lower nickel and hypophosphite concentrations, has higher stability, that is to say is less prone to spontaneous deposition. It has a high deposition rate and longer bath life. Bath life is here defined as the age of the bath before metal deposits exhibit properties inferior to those from a virgin bath. The Type III system can be operated at high pH and temperatures to give greater deposition rates. Against this, it must be noted that the lower phosphorus content gives a deposit with somewhat reduced corrosion resistance, as compared to that from Type I and Type II systems.

Table 3.7 Compositions and operating parameters for three proprietary electroless nickel systems.

Bath constituents and operating parameters	Type I	Type II	Type III
Nickel content [g/l]	7.3	7.3	6.3
Sodium hypophosphite [g/l]	40	40	30
pH	4.6–5.2	4.6–5.2	4.8–5.6
Bath temperature [°C]	86–92	86–92	88–95
Deposition rate [μm/h]	12–14	13–15	18–25
Bath life [MTO] (metal turn over)[1]	5–6	5–7	9–12
Bath life (g/l Ni)	37–44	37–50	57–63
Bath loading [dm²/l]	up to 2	up to 2	up to 3
Agitation/air sparging	Required	Required	Required
Filtration	Continuous	Continuous	Continuous
Bath stability	High	High	Very high
P content of deposit [%]	10–11	11–12	8–9

[1] MTO equates to the depletion of the entire nickel content of the bath.