Nickel plating handbook

ABOUT THE NICKEL INSTITUTE

Nickel Institute (NI) is the global association of the world's primary nickel producers. Our mission is to promote and support the use of nickel in appropriate applications. NI grows and supports markets for new and existing nickel applications including stainless steel; and promotes science, risk management and socio-economic benefit as the basis for public policy and regulation. Through our science division NiPERA (www.nipera.org), we undertake leading edge scientific research relevant to human health and the environment. NI is the centre of excellence for information on nickel and nickel-containing products and has offices in Asia, Europe and North America.

TERMS IN THIS HANDBOOK

Terms used in this publication relate to industry practice and are commonly understood by plating professionals. The term decorative plating is used to describe practices, processes and outcomes for a broad range of applications, but the term decorative often masks the critical nature of the outcome required. Decorative plating processes often impart the technical and functional success of the products they are used on. Corrosion resistance, brightness and levelling, mechanical and physical properties are characteristics of these processes and cannot be discounted as cosmetic.

Contents

1. INTRODUCTION

The technology of electroplating of nickel has been extensively developed, particularly through the last five decades, to make possible the efficient production of a broad range of industrial coatings for both decorative and functional applications. Electroplated nickel is commercially important with upwards of 150,000 tonnes deposited annually worldwide. This widespread use reflects the useful properties of nickel as a coating and its versatility. A feature of electroplating is that, by modifying the composition of the electrolyte and the operating conditions, the properties and appearance of nickel can be customised to meet specific needs.

Electroplated nickel is used extensively to enhance the utility, value and sales appeal of consumer goods and manufactured products. Other nickel coatings are used to improve the physical properties such as wear resistance, heat resistance or corrosion resistance. In many important applications, the nickel coatings serve the dual role of providing a bright decorative coating and imparting improved corrosion resistance or other functional properties.

A further important use for electrodeposited nickel is electroforming. Nickel electroforming is the process by which nickel is built up by electrodeposition onto a suitable mandrel and subsequently removed to produce a nickel product which corresponds precisely to the shape and texture of the original substrate.

This handbook has been prepared to provide practical information on the operation and control of nickel plating processes. The basics of electroplating are addressed and it is focussed on the operation of the plating bath. Information is included on the composition of plating solutions, correct control of anodes, trouble-shooting and practical operation. Quality aspects and specifications are discussed to ensure that coatings meet the required performance standards. This handbook also includes important information on safety and environmental matters.

2. UNDERSTANDING THE ELECTROPLATING PROCESS

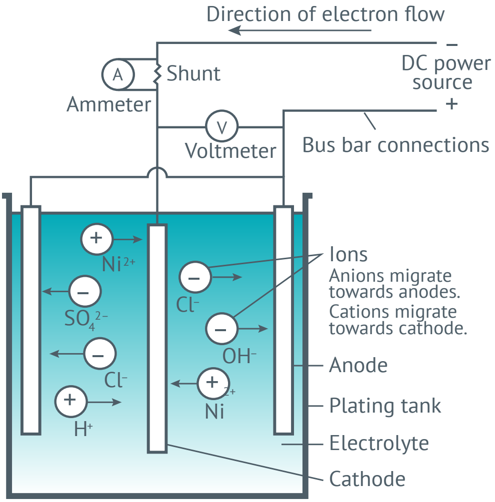
Electroplating is an electrolytic process for depositing a layer of metal upon a substrate to enhance the appearance or properties of the component. Electroplating is a form of electrodeposition. Although a wide range of metals can be electrodeposited, we will restrict our discussion to nickel plating.

BASIC PROCESS OF ELECTRODEPOSITION

The *electrodeposition* process essentially involves passing an electric current between two *electrodes* immersed in an *electrolyte*. The positively charged electrode is known as the *anode* while the negatively charged electrode is the *cathode*. The *electrolyte* contains electrically charged particles or *ions*. When an electrical potential or *voltage* is applied between the electrodes these ions migrate towards the electrode with the opposite charge – positively charged ions to the cathode and negatively charged ions to the anode. This results in the transfer of electrons, that is a current flow, between the electrodes – thus completing the electrical circuit. The electrical energy is supplied by a DC power source such as a rectifier. The basic electrical circuit is depicted in *Figure 1*.

Generally in electroplating, the anodes are composed of the metal being plated. These are referred to as *soluble* anodes.

Figure 1 Basic electrical circuit for electroplating



During electroplating, the positively charged metal ions discharge at the cathode (the component to be plated) depositing metal on the surface. The component being plated therefore receives a coating of metal. The reverse effect occurs at the anode and, with a soluble anode, metal ions are formed through dissolution.

For nickel plating, the electrolyte contains soluble nickel salts along with other constituents which will be discussed in the section on *Chemistry of nickel electroplating solutions*. When dissolved, the nickel salts dissociate into divalent, positively charged nickel ions (Ni2+) along with negatively charged ions. When current flows, the positive ions react with two electrons and are converted to metallic nickel at the cathode surface. At the anode, metallic nickel is dissolved to form divalent, positively charged ions which enter the solution. The nickel ions discharged at the cathode are thus replenished by those formed at the anode.

RATE OF DEPOSITION

In his classical work on electrodeposition, Michael Faraday showed that the ***amount of metal deposited at the cathode and the amount dissolved at the anode*** are directly proportional to the quantity of electricity passed – in other words to the ***current and time*** of electrodeposition.

Faraday also related the amount of a particular metal deposited or dissolved to its *atomic weight* and *the number of electrons involved in the electrochemical reaction*. The number of electrons involved is designated the *valency* of the metal. The atomic weight divided by the valency is referred to as the *chemical equivalent or equivalent weight* of the metal.

Faraday showed that the quantity of electricity required to deposit or dissolve 1 gram equivalent of a metal is a constant and has a value of 96,500 coulombs (ampere-seconds) or 26.799 ampere-hours. This is known as *Faraday's Constant.*

Using these relationships, it can be shown that the ***weight of nickel*** deposited at the cathode and the amount dissolved at the anode can be calculated from the following expression:

$$W = 1.095\ It$$

Where ***W*** is the amount of nickel deposited at the cathode (or dissolved at the anode) in grams, ***I*** is the current that flows through the plating tank in amperes and ***t*** is the time that the current flows in hours.

This assumes that all of the current is effectively used in the deposition or dissolution of nickel (i.e. the *current efficiency* is 100% – this will be explained further below).

The factor 1.095 in the above calculation is derived from Faraday's work discussed on the previous page. For nickel, the atomic weight is 58.70 and the valency is 2, giving an equivalent weight of 29.35. Therefore, 26.799 ampere-hours will deposit (or dissolve) 29.35 grams of nickel or 1.095 grams per ampere-hour.

It will be seen therefore that at 100% current efficiency 1 ampere-hour will deposit (or dissolve) 1.095 grams of nickel.

CURRENT EFFICIENCY

In practice, secondary electrochemical reactions may occur, which consume a small percentage of the current. Typically, a small amount of current is consumed in the discharge of hydrogen ions from water. The discharged hydrogen forms bubbles of hydrogen gas at the cathode surface.

The cathode current efficiency is expressed as the percentage of the current actually depositing nickel at the cathode to the total current applied. Similarly, the anode current efficiency refers to the percentage of current producing nickel ions at the anode.

The cathode current efficiency of different nickel solutions may vary from 90% to 97%. The lower values are characteristic of some bright nickel solutions which have been formulated to give maximum levelling and brilliance at low thicknesses.

Values of 96% are usually achieved on additive-free nickel solutions. A figure of 95.5% is commonly applied for estimating purposes in the absence of accurate figures.

Anode efficiency for nickel dissolution is almost always 100%, providing the pH and chloride levels are maintained within the normal operating ranges.

Because the cathode efficiency is generally lower than the anode efficiency, the nickel ion concentration and the pH of the solution will slowly rise during operation. However, in many cases, the rise in nickel concentration may be counterbalanced by solution losses through dragout or leakages.

AVERAGE COATING THICKNESS

The average coating thickness can be derived by dividing the weight deposited (in grams) by the product of the density of nickel (8.907 g cm^{-3}) and the surface area to be electroplated (in dm^2), then multiplying by 100 to obtain the thickness in micrometres (µm).

Alternatively, the average thickness can be computed directly from the current and time using the following calculation:

$$T = \frac{12.294\,It}{A}$$

Where ***T*** is the average thickness (µm) and ***A*** is the area being electroplated (dm^2), ***I*** is the current that flows through the plating tank in amperes and ***t*** is the time that the current flows in hours.

The above calculation is based on 100% cathode current efficiency.

The ratio of current to area ***I/A*** is known as the *current density*. It will be seen, therefore, that the average thickness depends on the *current density* and time, whereas the weight of nickel deposited (or dissolved at the anode) depends on the *current* and time. Usually in nickel plating, the current density will be expressed as amperes dm^{-2}.

In practice it will, of course, be convenient to refer to tables to estimate the ampere-hours or the current and time required to obtain a desired average thickness. Refer to *Table 1*.

Table 1 Time to electrodeposit nickel at various current densities

Time in minutes to deposit the indicated average thickness of nickel at various current densities

Current density (A dm^{-2})	5 µm	10 µm	15 µm	20 µm	25 µm	30 µm	40 µm	50 µm
1	26	51	77	100	128	154	200	255
1.5	17	34	51	68	85	102	140	170
2	13	26	39	51	65	78	100	130
2.5	11	22	32	42	53	64	84	105
3	8.5	17	26	34	43	52	68	85
4	6.5	13	20	26	33	40	51	65
5	5	10	15	20	25	30	41	50
6	4.5	8.5	13	17	22	26	34	43

Based on 95.5% cathode current efficiency.

DEPOSIT THICKNESS DISTRIBUTION

Particularly on shaped components, the deposit thickness will not normally be uniform. The actual thickness at any point on the surface is commonly referred to as the *local thickness*. A minimum local thickness for the coating is commonly specified to ensure that the desired performance requirements are achieved. It is therefore important to understand the factors which influence the deposit thickness distribution. These factors are the *current distribution* and the *throwing power* of the plating solution.

CURRENT DISTRIBUTION

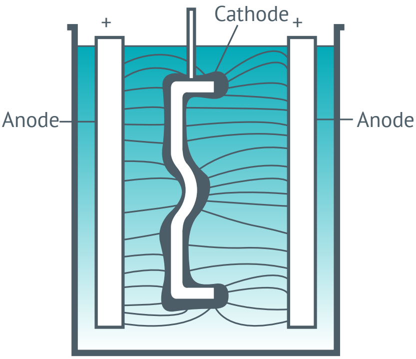
The actual thickness at any point on the surface depends primarily on the current density at that point. The current distribution is largely determined by geometric factors such as the shape of the part, the location of the part relative to the anodes and the placement of parts on the plating racks. The current density will be higher on prominences and areas closest to the anodes due to the lower resistance to current flow with the shorter anode-to-cathode distance. Conversely, the current will be lower in recesses and in areas shaded or facing away from the anodes because of the increased resistance to current flow. These variations in current density inevitably mean that prominences will receive a thicker coating than recessed areas.

Current distribution is the major factor affecting metal distribution in nickel plating. To some extent these effects can be controlled by appropriate racking of parts, positioning of anodes or by the use of shields or auxiliary anodes. Shields are fabricated from non-conductive materials and placed between the anode and cathode to control the current flow. Auxiliary anodes are placed closer to the cathode to direct the current to the area requiring increased thickness. Both soluble and insoluble anodes may be used.

THROWING POWER

In addition to the geometric factors, metal distribution is affected by cathode polarisation, the cathode efficiency – current density relationship and the electrical conductivity of

Figure 2 Thickness variation resulting from non-uniform current distribution



the solution. The complex relationship between these factors and metal distribution is termed the *throwing power.* Throwing power can be determined experimentally. Solutions exhibiting a positive value will be capable of reducing the variation in thickness between prominent and recessed areas. Conversely solutions with negative values, such as chromium plating solutions, may exhibit a greater thickness variation than would be expected based purely on geometric factors.

The throwing power of nickel plating solutions generally falls in the lower end of the positive range. Some bright nickel solutions, however, record small negative values. Generally, the current distribution, and consequently the metal distribution, will be primarily determined by geometric factors. However, the throwing power can be somewhat improved by lowering the current density, increasing the electrical conductivity of the solution, increasing the anode-to-cathode distance, and by raising the pH and temperature. A formulation containing a high concentration of sodium sulphate has been shown to have the best throwing power.

INTERNAL STRESS

During electrodeposition, stresses can develop within the deposit due to the effects of the electrocrystallisation process or the co-deposition of impurities, particularly hydrogen and sulphur. The stress can be either tensile or compressive. With tensile stress the deposit attempts to contract and under extreme conditions this may cause the coating to crack. Compressive stress has the opposite effect, with the deposit tending to expand.

Stress becomes an important consideration when thick coatings are produced, particularly in electroforming where the adhesion between the deposit and the mandrel is deliberately kept low to facilitate separation.

Stress in electrodeposited nickel can vary over a wide range depending on solution composition and operating conditions. Generally, Watts nickel solutions (see section 3) without additives will exhibit tensile stress in the range 125 to 185 MPa, under typical operating conditions. Lower stress levels can be achieved with sulphamate nickel solutions.

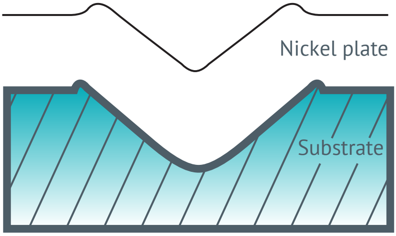
Compressively stressed nickel deposits can be produced by the use of sulphur-containing organic additives such as saccharin or compounds of the type incorporated in carriers of bright nickel solutions.

LEVELLING AND MICROTHROWING POWER

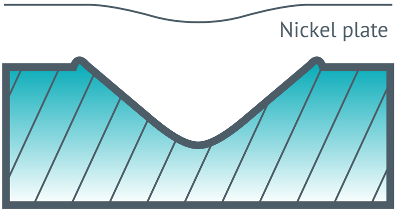
Levelling is the ability of an electroplating solution to preferentially fill in defects and scratches on the surface. Semi-bright and bright nickel processes generally have excellent levelling properties. These solutions incorporate organic additives which are absorbed preferentially at micropeaks. This results in limiting the current flow at the peaks and increasing the current density in microgrooves – thereby promoting levelling.

Microthrowing power refers to the ability of an electroplating solution to fill tiny crevices with deposits which follow the contour of a defect without any levelling. Additive-free nickel plating solutions exhibit excellent microthrowing power but little levelling ability. Microthrowing helps to produce sound, low-porosity deposits and, partly for this reason, additive-free nickel solutions are often used for depositing undercoats for subsequent plating with other metals such as gold.

Figure 3 Diagrammatical representation of levelling by nickel-plating solutions incorporating levelling agents



Absence of levelling (Watts deposit)



Levelling provided by levelling agents

3. CHEMISTRY OF NICKEL ELECTROPLATING SOLUTIONS

THE WATTS NICKEL PLATING SOLUTION

The majority of nickel plating solutions, particularly those used for decorative plating, are based on the 'Watts' formulation developed by Professor Oliver P. Watts in 1916. The Watts electrolyte combines nickel sulphate, nickel chloride and boric acid. While the proportions may vary according to the application, a typical formulation together with operating parameters is given in *Table 2*.

Table 2 Typical formula and operating conditions for Watts nickel electroplating solutions

Nickel sulphate ($NiSO_4.6\ H_2O$)	240 – 300 g L^{-1}
Nickel chloride ($NiCl_2.6\ H_2O$)	30 – 90 g L^{-1}
Boric acid (H_3BO_3)	30 – 45 g L^{-1}
Temperature	40 – 60 °C
pH	3.5 – 4.5
Cathode current density	2 – 7 A dm^{-2}
Deposition rate	25 – 85 µm h^{-1}

FUNCTION OF INGREDIENTS

The *nickel sulphate* is the primary source of nickel ions ($Ni2^+$) with nickel chloride a contributing source. *Nickel chloride* has two major functions – it appreciably increases solution conductivity thereby reducing voltage requirements and it is important in obtaining satisfactory dissolution of nickel anodes.

Boric acid is a buffer and has the major function of controlling the pH of the solution. As discussed in the previous section, due to the cathode efficiency being less than 100% there is a tendency for the pH to increase as some hydrogen ions (H^+) are discharged to liberate hydrogen gas. Regular additions of sulphuric acid are therefore required to adjust the pH. Boric acid limits the effect on the pH resulting from the discharge of hydrogen ions, thereby, simplifying pH control. The mechanism by which boric acid operates is complex, but it is generally understood that it exists in solution as a mixture of borate ions and non-ionised boric acid.

When hydrogen is discharged some boric acid will ionise to replace the hydrogen ions lost and so the pH change is limited. At the same time, borate ions form. When acid is added to adjust the pH, these borate ions combine with hydrogen ions to reform boric acid. Boric acid is therefore only lost through dragout or other solution losses.

THE ROLE OF ADDITION AGENTS

Watts nickel plating solutions are commonly used for functional applications as will be discussed in a later section. Deposits from Watts solutions without additives are soft and ductile but dull in appearance. The appearance and properties can however be dramatically changed by the use of addition agents. The addition agents consist of organic and certain metallic compounds selected to brighten and level the deposits. As will be discussed further in the section on decorative plating, addition agents may be used to produce semi-bright, bright or satin nickel coatings.

BRIGHT NICKEL PLATING

In bright nickel plating, four main classes of addition agents are used:

CARRIERS

(Confusingly these are sometimes also referred to as Brighteners of the First Class, Secondary Brighteners or Control Agents)

These are usually aromatic organic compounds containing sulphur. Examples are benzene sulphonic acid, 1, 3, 6-naphthalene sulphonic acid (sodium salt), *p*-toluene sulphonamide, saccharin and allyl sulphonic acid. The major function of carriers is to refine the grain structure and to provide some increased lustre compared with additive-free solutions. Many carriers, for example, saccharin, also have significant stress reducing properties. Carriers introduce sulphur into the deposit and the effect of this incorporated sulphur is discussed under decorative plating.

Consumption of carriers is largely by dragout as they are not consumed rapidly by electrolysis.

BRIGHTENERS

(Also referred to as Brighteners of the Second Class, Primary Brighteners, Levelling Agents)

In combination with carriers, brighteners produce brilliant deposits with good ductility and levelling properties over a broad current density range. There are a wide range of brighteners used (generally supplied as proprietary mixtures).

Compounds include formaldehyde chloral hydrate, o-sulpho benzaldehyde, allyl sulphonic acid, 2-butyne-1, 4-diol, thiourea, coumarin and many others. Brighteners are generally present in very low concentrations and are consumed by electrolysis. They therefore need to be replenished on a regular basis in order to maintain the desired brightness.

AUXILIARY BRIGHTENERS

These are sometimes incorporated to augment the luster attainable with carriers and brighteners or to produce the brightness and levelling with thinner deposits. Compounds employed include sodium allyl sulphonate, 2-butyne-1,4-diol, and sulphobetaines such as pyridinum propyl sulphonate. Metals such as zinc, cobalt and cadmium also act as auxiliary brighteners, but are not commonly used today.

ANTI-PITTING AGENTS (WETTING AGENTS)

Bubbles of hydrogen gas which are formed at the cathode may cause pitting if they cling to the surface. The role of anti-pitting agents is to lower the surface tension of the solution and to facilitate release of these bubbles. Anionic surfactants such as sodium lauryl sulphate are normally used.

SEMI-BRIGHT NICKEL PLATING SOLUTIONS

As semi-bright nickel is used in situations where resistance to corrosion is important, the deposits must be free from incorporated sulphur. Consequently additives which contribute sulphur to the coatings must be avoided. Levelling agents include coumarin, 2-butyne-1,4-diol and other acetylenics. Coumarin was widely used in the past but, as it produced undesirable reduction products which had to be removed by carbon treatments, it has now been largely superseded by alternative additives. The use of these additives yield smooth, ductile deposits which exhibit excellent levelling. The grain structure of semi-bright nickel deposits is usually columnar compared with the banded (lamina) structure of bright nickels.

SULPHAMATE NICKEL ELECTROPLATING SOLUTIONS

Nickel sulphamate solutions are chiefly used for the deposition of functional coatings or for electroforming. For such applications the low stress which can be achieved without the use of addition agents, the high deposition rates and desirable deposit properties offset their higher cost.

Typical composition and operating conditions are shown in *Table 3*.

Table 3 Typical composition and operating conditions for nickel sulphamate electroplating solutions

Nickel sulphamate [$Ni(NH_2SO_3)_2.4H_2O$)]	300 – 450 g L^{-1}
Nickel chloride ($NiCl_2.6H_2O$)	0 – 30 g L^{-1}
Boric acid (H_3BO_3)	30 g L^{-1}
Temperature	40 – 60 °C
pH	3.5 – 4.5
Cathode current density	2 – 15 A dm^{-2}
Deposition rate	25 – 180 µm h^{-1}

Chloride has a pronounced effect on stress and also influences anode behaviour. A low chloride concentration is desirable to achieve a low stress level. It is possible to operate with zero chloride if sulphur activated nickel anodes are used under appropriate operating conditions. However, a low concentration of nickel chloride (5 g L^{-1} minimum) is generally recommended to provide some insurance of satisfactory anode performance. Alternatively, nickel bromide may be substituted, and does not increase stress as much as chloride.

If the anode efficiency falls (as evidenced by a brown film on the nickel anodes), some breakdown of the sulphamate ion may occur. This can lead to disastrous effects on the deposit properties including undesirable tensile stress and brightness.

Another potential problem is hydrolysis of nickel sulphamate which produces sulphate and ammonium ions. These greatly increase the tensile stress of the deposit. To avoid hydrolysis of the nickel sulphamate it is important to maintain the temperature below 65 °C and the pH above 3.0.

One of the advantages of sulphamate solutions is the higher solubility of nickel sulphamate compared with nickel sulphate. It is therefore possible to use higher nickel concentrations and to operate at very high current densities.

OTHER NICKEL ELECTROPLATING PROCESSES

Several other formulations can be used for specific applications. These include fluoborate, hard nickel, all-chloride, all-sulphate, high sulphate and black nickel plating solutions. With the exception of black nickel, which is employed in decorative applications, these processes are generally only used in functional applications and are discussed in the section on *Engineering and functional nickel coatings*.

4. ANODES FOR NICKEL PLATING

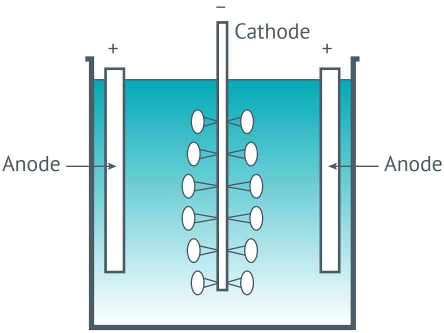
NICKEL ANODE REQUIREMENTS

The major functions of nickel anodes in electroplating are to:

- Conduct the electric current to the electrolyte
- Replace the nickel ions discharged at the cathode
- Distribute current as uniformly as possible over the cathode surface

To achieve these requirements, the anodes should be of a suitable size, shape and composition, and positioned to optimise uniform distribution of current. In a good installation, the anodes will be closely spaced along the anode bar and located opposite the plating racks. To avoid excessive current flow to the bottom of the plating racks, it is desirable to install anodes slightly shorter than the racks. Similarly, it is often helpful to position the anodes away from the edges of the plating racks (particularly the end rack in the tank), to reduce the current flow to the edge of the rack and to position parts in the middle of the rack, closer to the anode than at the top and bottom.

Figure 4 Positioning of anodes and racks to improve cathode current distribution



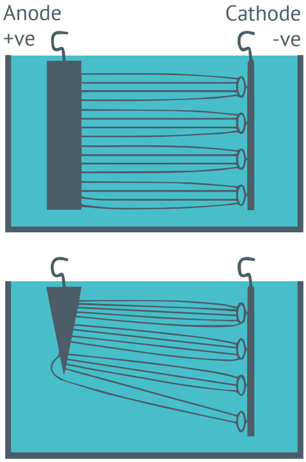
Good electrical contact with the anode barmust be maintained at all times. Anodes consisting of nickel metal are preferred in order to replenish the nickel ions and to simplify solution control. However, there are some occasions where insoluble anodes have to be employed. (see later section of this chapter)

TYPES OF NICKEL ANODE MATERIAL

Since the 1960s, fabricated oval section bar anodes such as cast carbon and depolarised types, have been superseded by titanium baskets containing refined primary nickel. These solid shapes include squares cut from electrolytic nickel cathode sheets, circular forms produced by electroforming onto metal mandrels, spherical carbonyl nickel pellets, and pellets flattened by mechanical working.

Electrolytic nickel is also available in strips of various sizes, e.g. 150 x 600 mm, which are suspended from the anode rod by a titanium hook bolted through a hole drilled in the strip. But, a characteristic of these is that the anode area decreases as it dissolves from the bottom upwards, due to high anodic current at the tip, as shown in *Figure 5*. This causes variable current distribution over the cathode, resulting in excessive deposit thickness at the top of the work piece or rack, and a thinner deposit at the bottom. Further, when the anode has reduced to a spear shape, anode polarisation at the tip can lead to low anode efficiency and, consequently, greater than expected consumption of nickel salts and organic addition agents (brighteners and levellers).

Figure 5 Problems with nickel strip



Primary nickel for plating has high purity of 99.95% Ni + Co. Apart from the pure grade, an activated grade is also available, which contains a small amount of sulphur to lower the anodic potential. For most nickel plating operations, both pure and activated grades dissolve satisfactorily under anodic conditions. In chloride-free or bromide-free nickel sulphamate plating solutions, sulphur activated nickel must be used.

TITANIUM ANODE BASKETS

Anode baskets for nickel plating are fabricated from titanium, which has excellent properties of lightness and strength. It is available in a wide range of sheet, mesh and rods. Typical basket designs are shown in *Figure 6*.

Figure 6 Typical titanium baskets

The thickness of the basket should be large enough to allow the nickel pieces to settle freely during anodic dissolution in a working basket. Ramming the nickel down is not recommended, as this may damage the basket.

As titanium has poor electrical conductivity, it is important the basket be appropriately designed to carry the desired current. Hooks must be fabricated from bar (not sheet) to maintain pressure contact with the anode rod and to ensure sufficient current carrying capacity and strength. Similarly, it is essential to have side members in sheet or bar section running the whole length of the basket. The tray at the bottom of the basket is designed to hold the final small pieces of nickel and nickel fines, maintain electrical contact and thus enable complete dissolution.

Baskets can be made in special shapes to meet specific needs, including curved baskets for use as conforming anodes in electroforming.

Titanium is an ideal choice for anode baskets as it conducts the electrical current to the nickel metal without acting as an anode itself. This is due to a protective oxide film formed on the titanium surface during electrolysis. Titanium baskets will have a long service life in all nickel plating solutions other than Woods nickel, providing nickel is maintained in pressure contact with the titanium. Then the nickel will take current preferentially and corrosion of the titanium will be avoided. However, under certain conditions, the protective film can break down. This breakdown only occurs when the applied potential or voltage exceeds the breakdown potential of the titanium in the solution concerned. This circumstance can arise when there is insufficient nickel in the basket, or the pieces of nickel being used are too large.

These problems can be avoided by ensuring that:

- The baskets are kept full of nickel pieces at all times
- Nickel is packed correctly into the baskets without bridging
- A large number of electrical contact points between the nickel and the titanium basket are provided by using small nickel pieces
- Anode bags are cleaned or replaced when needed

The great advantage of titanium baskets is the maintenance of a large and unchanging anode area. This ensures that:

- The current distribution over the cathode is not affected by changes in the anode area, as with strip anodes
- Optimum anode efficiency is maintained

POWER CONSUMPTION

Pure forms of primary nickel that do not liberate a non-conducting residue can operate under stable current and voltage conditions without regular cleaning.

The shape and size of pure nickel pieces affects power consumption and may lead to corrosion of titanium anode baskets.

Generally, smaller pieces require less power demand and provide the lowest risk to titanium baskets compared with larger pieces.

Sulphur activated nickel (containing 0.02% sulphur) dissolves initially at lower voltage than comparable shapes of pure nickel.

Power consumption is one of a number of variables discussed in this chapter that will determine anode choice. Contacting your reputable supplier will help determine the optimal anode choice for you.

PACKING DENSITY

Packing density governs the weight of nickel tied up as inventory in the titanium anode baskets, described as work-in-progress (WIP). The financial value of all nickel committed to WIP in the anodes has a significant impact on the application of working capital in the production process. Working capital is one of a number of variables that needs to be considered for the most efficient and best quality result.

Packing density determined with new nickel pieces is not representative of production conditions. Evaluation must be carried out on a 'working anode basket', filled with nickel pieces undergoing all stages of anodic dissolution.

ANODE FINES

When a working basket is examined under steady state conditions, a small percentage of fines will always be observed in and around the bottom tray or in the anode bag. The question is whether these fines will ultimately dissolve anodically, or leave an insoluble residue which must be periodically removed.

ANODE BAGS

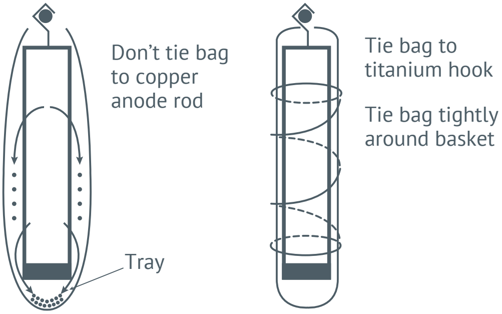
Nickel anodes and baskets must be fitted with bags to prevent nickel fines or nickel sulphide residues entering the plating solution. Polypropylene is widely used for anode bags because of its durability. However, other fabrics including cotton and other synthetics are used successfully. Care should be taken to avoid tearing or damage to the bags.

To ensure that nickel fines are kept within the electrical field of the titanium basket, anode bags should be tight fitting and tied so all fines receive anodic current and can dissolve. There should be no 'billowing' of the anode bags, which would allow nickel fines to fall outside the basket. They should be tied tightly around the basket, as illustrated in *Figure 7.*

Tie anode bags to the titanium hooks of the basket – not to an unprotected anode rod. Otherwise, moistening of the ties could lead to contamination by anodic dissolution of copper ions into the solution. Double bagging is desirable.

Clogging of anode bags is particularly troublesome when plating tubular steel and similar components which introduce large quantities of iron. This problem can be reduced by using iron control additives in the plating solution (see Chapter 9).

Figure 7 Titanium baskets and anode bags



DON’T
Nickel fines fall out of
electrical contact and
do not dissolve

DO
Nickel fines retained
within titanium basket and
dissolve anodically

PRACTICAL TIPS FOR MAINTENANCE OF NICKEL ANODE BASKETS

- Anode baskets filled with small nickel pieces should be left untouched for extended periods to allow the continuous process of dissolution to proceed under stable conditions.
- Ensure good electrical contact between the anode rod and the basket hooks at all times.
- Keep the basket full of nickel pieces.
- To ensure the long life of expensive titanium anode baskets, use small pieces of nickel. The packing density of these small pieces is adequate when loaded under natural conditions. It is unnecessary to ram them down; a practice that can cause physical damage to the baskets.
- Anode bags should only be removed from the baskets when they become so clogged (e.g. with precipitated ferric hydroxide) that free movement of solution through them has become severely restricted.
- Use close-fitting anode bags and tie tightly, to prevent nickel fines from falling outside the electrical field. Double bag if desired, and only tie the bag to the titanium anode hook, not to an unprotected copper anode rod.

ANODE MAINTENANCE – BEST PRACTICE

Whether in electroforming, rack, barrel or reel-to-reel electroplating plants:

1. Use of nickel products that leave little residue after anodic dissolution reduces cleaning of the titanium baskets and anode bags leading to:
    - Reduced down time for cleaning

- Elimination of waste – nickel fines, salts and addition agents, damage to anode bags and heat loss
- Reduced waste treatment for contaminated washing water

2. Anode bags should be tight fitting and tied as described above, to ensure nickel fines are kept within the electrical field of the titanium basket.

Additionally, OH&S risks to workers and environmental issues arising from nickel ions and boric acid in commercial plating solutions can be reduced.

Best industrial practice, embracing lower power consumption, higher materials utilisation and waste minimisation, will contribute significantly towards overall energy optimisation (for both the plating plant and raw materials production). The carbon footprint of the company can therefore be reduced.

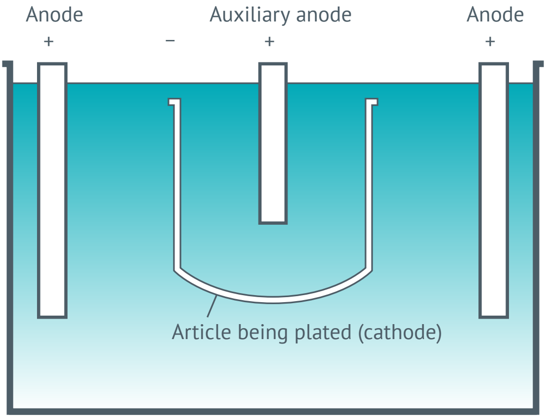
INSOLUBLE ANODES

Insoluble anodes are used for specific purposes where nickel anodes would not be practical. Applications include anodes for the internal plating of tubes, and as auxiliary anodes for plating into deep recesses. A further situation where insoluble anodes might be selected is when there is limited spacing between the components being plated (e.g. some electronic applications).

Insoluble anodes are commonly fabricated from platinised titanium, although other inert conductive materials such as graphite can be used.

When insoluble anodes are used, the pH of the solution in the vicinity of the anodes will fall due to the liberation of hydrogen ions from the oxidation of water at the anode surface. At the same time, oxygen and/or chlorine will be released. These can oxidise some organic additives in the solution. Chlorine can also lead to health concerns. These effects become significant when more than 20% of the total bath current passes through insoluble anodes.

Figure 8 Auxiliary anodes – example showing location of auxiliary anode to increase thickness deposited into recessed areas of work



5. DECORATIVE NICKEL PLATING

Nickel plating is extensively used in a range of decorative applications. These include components for the automotive, cycle and marine industries, household appliances, door furniture, hardware items, jewellery and a wide variety of consumer items.

The principle purpose of decorative plating is to enhance the appearance and decorative appeal of the articles, however the coatings may also be required to meet stringent performance criteria. The criteria may include adhesion, ductility, corrosion resistance, etc. depending on the application and the service conditions.

In the majority of cases the nickel-plated layer is top-coated with chromium or with alternative final finishes (e.g. gold, brass, etc.).

Copper plating is often applied as an undercoat. Copper is essential when plating zinc diecast alloys to avoid diffusion of the nickel. In other cases, copper may be specified to provide a ductile underlay, additional levelling or to assist in achieving a satisfactory bond on certain difficult-to-plate metals (e.g. lead containing alloys) and plating on plastics.

BRIGHT NICKEL PLATING

Nickel is most commonly applied as a bright coating. Highly lustrous coatings are achieved through the use of suitable addition agents in the plating solutions. Additionally, modern bright nickel plating solutions exhibit excellent ‘levelling’ properties (i.e. they have the ability to hide polishing lines and other surface imperfections). Bright nickel solutions are based on the ‘Watts’ formulation (refer to chapter 3, *Chemistry of nickel electroplating solutions*) with the addition of brightening and levelling additives, stress control agents and wetting agents. Commonly, the additives are supplied as proprietary products. These may also incorporate supplementary brighteners or additives to suppress the effects of impurities.

SATIN NICKEL PLATING

Satin nickel processes produce attractive satin or semi-lustrous finishes. These effects are produced through the use of selected soluble organic additives in the plating solution or by additions of finely divided insoluble particles. Another process involves the use of emulsified liquid additives to produce the desired texture in the plate.

Satin nickel finds widespread use on doors, furniture and other hardware items.

NICKEL-CHROMIUM COATINGS FOR EXTERIOR SERVICE

Decorative, single coatings of bright and satin nickel with topcoats of chromium generally perform poorly under exterior service conditions.

Bright nickel (and most satin nickel) solutions co-deposit a small percentage of sulphur in the deposit, the sulphur originating from the 'carriers' or stress control agents. The incorporated sulphur increases the electrochemical reactivity of the nickel and thereby reduces the corrosion resistance of the coatings. Indeed, when bright nickel was first introduced, many failures due to premature corrosion were reported. Problems particularly occurred on automotive components in areas where salt was used as an anti-freeze on roads. Poor performance was also noted in other external service applications.

To overcome these problems new techniques have been developed which provide excellent corrosion resistance and satisfactory service performance. Two approaches have been adopted. The first involves modifying the nickel by applying **multi-layer nickel** coatings. The second approach is to modify the chromium topcoat by using **microdiscontinuous chromium** processes.

MULTI-LAYER NICKEL

These coatings generally consist of a primary layer of semi-bright nickel that constitutes 30-60%* or ⩾60-70% of the total nickel thickness, respectively, for metal substrate and plastic substrate, followed by a bright nickel coating on top. These are commonly referred to as dual-layer or duplex nickel. Semi-bright nickel differs from bright nickel in that it has no co-deposited sulphur and has a columnar rather than a lamina grain structure. This sulphur-free nickel has a lower electrochemical reactivity than the bright nickel. A variation involves applying a thin intermediate layer of high-sulphur nickel of about 10% of total nickel thickness between the semi-bright and bright layers – referred to as triple-layer nickel, the remainder of the total coating thickness is usually made up of 50-70% of semi-bright nickel and 30-40% of bright nickel.

To understand how these coatings provide increased corrosion resistance, it is necessary to briefly examine the mechanism of corrosion. In the presence of moisture and atmospheric contaminants, corrosion initiates in cracks or pores in the chromium topcoat. As the chromium is electrochemically more noble than the nickel, corrosive attack takes place in the bright nickel with the formation of pits. As corrosion continues, the pitting becomes deeper and eventually reaches the substrate, resulting in rusting or other base metal corrosion. At the same time the thin chromium layer may become partly dislodged through undercutting. Because bright nickel is relatively electrochemically active, the rate of attack can be quite rapid under corrosive conditions.

With a dual-layer nickel, the primary (bottom) layer of semi-bright nickel is electrochemically noble compared with the bright nickel. Therefore corrosion will take place preferentially in the bright nickel layer. The result is that, when the attack reaches

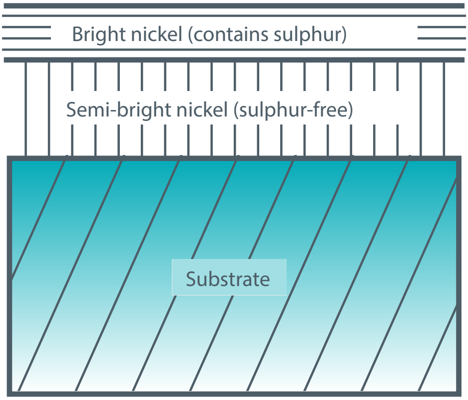
Note: updated thickness requirement as per the ISO 1456:2009 the interface between these two layers, corrosion will tend to spread laterally in the top layer rather than penetrate into the semi-bright coating. Microscopic examination shows typically flat bottomed pits in the bright nickel. This effectively retards the pitting attack because, before the pit can penetrate further, a considerable portion of the bright nickel layer must be removed.

Dual-layer nickel coatings show a marked improvement in corrosion performance compared with single layer coatings. They are therefore specified for severe service conditions.

As noted on the previous page, triple-layer nickel is sometimes substituted for dual layer nickel. However, providing there is a sufficient difference in electrochemical potentials between the semi-bright and the bright nickel deposits, the use of an intermediate high-sulphur layer offers little advantage and complicates process control. It should be noted that international standard ISO 1456 (refer to summary below), does not permit any reduction in total nickel thickness when triple-layer nickel is substituted for dual-layer nickel.

Additives in semi-bright nickel solutions are usually selected to be compatible with the bright nickel. As a result, work is generally transferred directly between the solutions without rinsing. Check with suppliers to ensure compatibility.

Figure 9 Dual-layer nickel



MICRODISCONTINUOUS CHROMIUM

As noted above, corrosion of the nickel begins at a crack or pore in the chromium top coating. Conventional electrodeposited chromium exhibits random cracks and has relatively few discontinuities. Any crack or pore is therefore surrounded by a large area of chromium which, in the presence of moisture, sets up a corrosion cell drawing an electrical current from a relatively small area of exposed nickel. This leads to quite rapid pit penetration through the nickel.

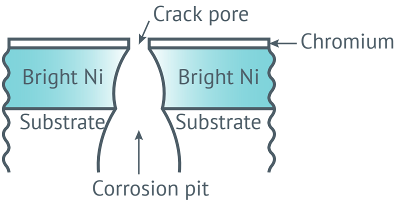
Chromium can be deposited in a crack-free condition and at one stage this was thought to be the solution to preventing corrosive attack. Unfortunately such coatings were found to later develop cracks or pores during service and consequently failed to provide long-term protection.

It was later established that improved results could be achieved by providing a large number of discontinuities in the chromium coating thus increasing the area of exposed nickel. This effectively increases the base metal protection by spreading the corrosion currents over a multitude of sites, thus reducing the size and depth of individual pits.

Figure 10 Corrosion of nickel/chromium coatings

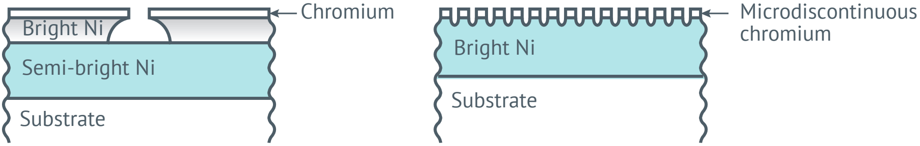
Nature of corrosion pitting on:
a. single-layer nickel plus chromium
b. dual-layer nickel plus chromium, and
c. microdiscontinuous chromium over nickel

(a) Bright nickel plus regular chromium



(b) Dual layer nickel plus regular chromium

(c) Bright nickel plus microdiscontinuous chromium



Microdiscontinuous chromium is the term applied to both microcracked and microporous chromium processes. **Microcracked chromium** can be achieved by modifying the formulation and/or the operating parameters of the chromium plating solution or, by using a highly-stressed nickel plating under the chromium, which induces microcracking in that chromium coating.

Microporous chromium is achieved by depositing the chromium over a thin bright nickel deposit containing insoluble, extremely fine, non-metallic particles dispersed throughout the solution. The resulting chromium deposit is completely microporous when plated over this special nickel layer. This is the most commonly used process.

ALTERNATIVE TOPCOATS

Although chromium is the most widely used topcoat for decorative nickel, a number of other finishes are finding increasing applications. These include gold, brass, copper and other metallic coatings, which are generally applied as thin 'flash' deposits and then protected by organic coatings or lacquers. Lacquer overlays may not be required over gold (particularly hard gold) if the coatings are of sufficient thickness to provide the necessary service performance.

The organic topcoats may be conventional air dry lacquers, clear baked enamels or electrophoretic coatings. The latter are increasingly being used because of their uniform coatings, reduction of drip problems and their environmental advantages.

A further approach is to tint the organic coating to simulate metallic finishes or to provide unusual decorative effects. Colours can be achieved either by incorporating dyes or pigments into the organic coating or by using post-dyeing techniques. Electrophoretic coatings are being widely used to apply these types of finishes over bright or satin nickel.

SPECIFICATIONS FOR DECORATIVE NICKEL/NICKEL-CHROMIUM PLATING

A number of international, national and commercial standards cover the specific requirements for decorative nickel electrodeposition, with or without a top coating of electrodeposited chromium as well as an optional copper undercoat, in order to achieve acceptable performance under different service conditions. In addition, these standards classify the various coating systems according to their resistance to corrosion. Coating designations that differ in thickness and type are specified and guidance is given in selecting the coating appropriate to the service conditions to which the coated product will be exposed.

The latest edition of ISO 1456:2009 international standard[1], with extended coverage incorporating ISO 1458:2002 *Metallic coatings – Electrodeposited coatings of nickel*, now specifies requirements for nickel electrodeposition with/without copper undercoats and with/without top coating of chromium electrodeposition that are applied to iron and steel, to zinc alloys, to copper and copper alloys, and to aluminum and aluminum alloys to provide an attractive appearance and corrosion resistance. The requirements of similar coatings for plastic materials are given in ISO 4525.[2]

The standards specify the test methods to be applied, covering thickness measurement, accelerated corrosion tests, ductility and adhesion. Examples of classifications and recommended coatings are given in *Tables 4a–4f*, adapted from ISO 1456:2009 and ISO 4525:2003.

It should be noted that single-layer bright nickel is not permitted in applications involving very severe corrosion service conditions. Double or triple-layer nickel coatings are almost universally used for these applications in order to provide the required resistance to corrosion. Although polished dull or semi-bright nickel is permitted, these are rarely used because of the cost of polishing.

Figure 11 Decorative nickel-plated parts

PLATING ON PLASTICS MATERIALS

The traditional method of preparing plastics for electroplating includes electrodeposition of a ductile acid copper layer, before electroplating with nickel plus chromium, to meet thermal cycle requirements. The thermal cycle test (refer to Chapter 8) assesses adhesion and monitors the effectiveness of the process. Although this traditional copper layer is still the most widely used, the substitution of a highly ductile nickel coating may be specified where it is necessary to facilitate the reclamation of electroplated plastics at the end of the product-life cycle.

Table 4a* Nickel on iron and steel, with or without copper undercoats
Nickel plus chromium on iron and steel, with or without copper undercoats

Service condition number	Nickel	Copper + Nickel	Nickel + Chromium	Copper + Nickel + Chromium
1	Fe/Ni10	Fe/Cu10a/Ni5	Fe/Ni10/Cr r mc mp or b	Fe/Cu10a/Ni5/Cr r mc mp or b
2	Fe/Ni20	Fe/Cu15a/Ni15	Fe/Ni20/Cr r Fe/Ni15/Cr mc mp or b	Fe/Cu15a/Ni15/Cr r Fe/Cu15a/Ni10/Cr mc mp or b
	Fe/Ni20d	Fe/Cu15a/Ni15d	Fe/Ni20d/Cr r Fe/Ni15d/Cr mc mp or b	Fe/Cu15a/Ni15d/Cr r Fe/Cu15a/Ni10d/Cr mc mp or b
3	Fe/Ni35	Fe/Cu15a/Ni25	Fe/Ni35/Cr r Fe/Ni30/Cr mc mp or b	Fe/Cu15a/Ni30/Cr r Fe/Cu15a/Ni25/Cr mc mp or b
	Fe/Ni30d	Fe/Cu15a/Ni20d	Fe/Ni30d/Cr r Fe/Ni25d/Cr mc mp or b	Fe/Cu15a/Ni25d/Cr r Fe/Cu15a/Ni20d/Cr mc mp or b
4			Fe/Ni40/Cr r Fe/Ni30/Cr mc mp or b	Fe/Cu20a/Ni35/Cr r Fe/Cu20a/Ni25/Cr mc mp or b
			Fe/Ni35d/Cr r Fe/Ni25d/Cr mc mp or b	Fe/Cu20a/Ni30d/Cr r Fe/Cu20a/Ni20d/Cr mc mp or b
5			Fe/Ni45d/Cr mc or mp	Fe/Cu25a/Ni35d/Cr mc or mp

Where only Ni is specified, Ni b, Ni p or Ni s may be substituted.
Where Cr r is specified, Cr mc or mp may be substituted.
** Adapted from ISO 1456.2009.*
ISO 1456:2009 also includes specifications for nickel coatings and copper plus nickel coatings without chromium topcoats plus specifications for black chromium.
Refer to page 39 for explanation of symbols.

Table 4b* Nickel / nickel plus chromium on copper and copper alloys

Service condition number	Nickel	Nickel + Chromium
1	Cu/Ni8b Cu/Ni8s	Cu/Ni8b/Cr r or b Cu/Ni8s/Cr r or b
2	Cu/Ni15	Cu/Ni12b/Cr r Cu/Ni10/Cr mc mp or b
3	Cu/Ni25	Cu/Ni20/Cr r Cu/Ni15/Cr mc mp or b
	Cu/Ni20d	Cu/Ni15d/Cr r Cu/Ni12d/Cr mc mp or b
4		Cu /Ni30/Cr r Cu /Ni25/Cr mc mp or b
		Cu /Ni25d/Cr r Cu/Ni20d/Cr mc mp or b
5		Cu/Ni45d/Cr mc or mp

Where only Ni is specified, Ni b, Ni p or Ni s may be substituted.
Where Cr r is specified, Cr mc or mp may be substituted.
**Adapted from ISO 1456:2009.*
ISO 1456:2009 also includes specifications for black chromium.
Refer to page 39 for explanation of symbols.

Table 4c* Nickel on zinc alloys with or without copper undercoats – nickel plus chromium on zinc alloys with or without copper undercoats

Service condition number	Nickel	Copper + Nickel	Nickel + Chromium	Copper + Nickel + Chromium
1	Zn/Ni10	Zn/Cu10a/Ni10	Zn/Ni10/Cr r mc mp or b	Zn/Cu8a/Ni10/Cr r mc mp or b
			Zn/Ni10d/Cr r mc mp or b	Zn/Cu8a/Ni10d/Cr r mc mp or b
2	Zn/Ni20	Zn/Cu15a/Ni15	Zn/Ni20/Cr r Zn/Ni15/Cr mc mp or b	Zn/Cu15a/Ni15/Cr r Zn/Cu15a/Ni10/Cr mc mp or b
	Zn/Ni15d	Zn/Cu15a/Ni10d	Zn/Ni20d/Cr r Zn/Ni15d/Cr mc mp b	Zn/Cu15a/Ni15d/Cr r Zn/Cu15a/Ni10d/Cr mc mp or b
3	Zn/Ni40	Zn/Cu20a/Ni30	Zn/Ni35/Cr r Zn/Ni30/Cr mc mp b	Zn/Cu20a/Ni30/Cr r Zn/Cu20a/Ni25/Cr mc mp b
	Zn/Ni30d	Zn/Cu20a/Ni25d	Zn/Ni30d/Cr r Zn/Ni25d/Cr mc mp or b	Zn/Cu20a/Ni25d/Cr r Zn/Cu20a/Ni20d/Cr mc mp or b
4			Zn/Ni40/Cr r Zn/Ni35/Cr mc mp or b	Zn/Cu20a/Ni35/Cr r Zn/Cu20a/Ni30/Cr mc mp or b
			Zn/Ni35d/Cr r Zn/Ni30d/Cr mc mp or b	Zn/Cu20a/Ni30d/Cr r Zn/Cu20a/Ni25d/Cr mc mp or b
5			Zn/Ni45d/Cr mc or mp	Zn/Cu25a/Ni35d/Cr mc or mp

An initial copper deposit is required to ensure adhesion of the nickel – refer to page 39 under Type of copper coatings.
Where only Ni is specified, Nib, Nip or Nis may be substituted.
Where Cr r is specified, Cr mc or mp may be substituted.
**Adapted from ISO 1456:2009.*
ISO 1456:2009 also includes specifications for nickel coatings and copper plus nickel coatings without chromium topcoats and specifications for black chromium.
Refer to page 39 for explanation of symbols.

Table 4d* Nickel / nickel plus chromium on aluminium or aluminium alloys

Service condition number	Nickel	Nickel + Chromium
1	Al/Ni10b	Al/Ni10b/Cr r
2	Al/Ni25	Al/Ni25/Cr r Al/Ni20b/Cr mc or mp
	Al/Ni20d	Al/Ni20d/Cr r Al/Ni15d/Cr mc or mp
3	Al/Ni35	Al/Ni35b /Cr r Al/Ni35p /Cr r Al/Ni30b/Cr mc or mp Al/Ni30p/Cr mc or mp
	Al/Ni30d	Al/Ni30d/Cr r Al/Ni25d/Cr mc or mp
4		Al/Ni45d/Cr r Al/Ni35d/Cr mc or mp
5		Al/Ni50d/Cr mc or mp

**Adapted from ISO 1456:2009.*
ISO 1456:2009 also includes specifications for nickel coatings without chromium topcoats.
The use of copper undercoat is permissible and may be desirable on certain alloys or for specific applications. The specified nickel thickness must not be reduced if copper is used.
Where only Ni is specified, Nib, Nip or Nis may be substituted.
Where Cr r is specified, Cr mc or mp may be substituted.
Refer to page 39 for explanation of symbols.

Table 4e* Plating on plastics materials – nickel plus chromium copper plus nickel plus chromium

Service condition number	Nickel + Chromium	Copper + Nickel + Chromium
1	PL/Ni20dp Ni7b/Cr r	PL/Cu15a Ni 7b/Cr r
2	PL/Ni20dp Ni10b/Cr r	PL/Cu15a Ni15b/Cr r PL/Cu15a Ni10b/Cr mc or mp
3	PL/Ni20dp Ni15b/Cr r	PL/Cu15a Ni25d/Cr r PL/Cu15a Ni20d/Cr mc or mp
4	PL/Ni20dp Ni20d/Cr r PL/Ni20dp Ni20b/Cr mc or mp	PL/Cu15a Ni30d/Cr r PL/Cu15a Ni25d/Cr mc or mp
5	PL/Ni20dp Ni20d/Cr mc or mp	PL/Cu15a Ni30d/Cr mc or mp
4	PL/Ni20dp Ni20d/Cr r	PL/Cu15a Ni30d/Cr r
5	PL/Ni20dp Ni20d/Cr mc or mp	PL/Cu15a Ni30d/Cr mc or mp

**Adapted from ISO 4525:2003 – Metallic and other inorganic coatings – Electroplated coatings of nickel plus chromium on plastics materials.*
Refer to page 39 for explanation of symbols.

SERVICE CONDITION NUMBER

The service condition number characterises the severity of the corrosion environment in accordance with the following scale:

1	*Mild*	Service indoors in warm dry atmospheres, e.g. offices
2	*Moderate*	Service indoors where condensation may occur, e.g. bathroom, kitchen
3	*Severe*	Service outdoors where occasional or frequent wetting by rain or dew may occur, e.g. outdoor furniture, bicycles, hospital goods
4	*Very severe*	Service outdoors in very severe conditions, e.g. components of automobiles, boat fittings
5	*Exceptionally severe*	Service outdoors in exceptionally severe conditions where long-time protection of the substrate is required, e.g. vehicle components: bumpers, wheels

CLASSIFICATION NUMBER

The classification number specifies details of the coating in an abbreviated fashion. For example: Fe/Ni35d/Cr r indicates that the coating is applied to iron or steel (Fe), and the coating consists of 35 μm of double-layer or triple-layer nickel (d) plus regular chromium (r). The designations for the types of nickel and chromium are shown in *Table 4f*.

Table 4f* Classification of types of nickel and chromium

Type of nickel	**Type of chromium**
b decorative, sulfur-containing bright, semi-bright, or satin nickel with a lamellar structure	r regular or conventional chromium having a minimum local thickness of 0.3 μm
d double or triple-layer nickel	mp microporous chromium having a minimum local thickness of 0.3 μm
p dull or semi-bright nickel mechanically polished	mc microcracked chromium a minimum local thickness of, 0.5 or 0.8 μm depends for metallic substrate (ISO 1456) and 0.3 or 0.5 μm for plastic substrate (ISO 4525), as well as the required crack pattern
s for sulfur-free dull or semi-bright nickel with a columnar structure which has not been polished	b black chromium thicknesses in the range 0.5 μm to 2 μm
dp refers to ductile, columnar nickel electrodeposited from special solutions	

**Adapted from ISO 1456:2009 and ISO 4525:2003*

TYPE OF COPPER COATING

The type of copper is designated by the symbol "a" for ductile, levelling copper electrodeposited from acid-type solutions. On iron and steel, an initial copper coating from a cyanide solution (5 μm to 10 μm thick) is normally applied to prevent immersion deposits and poorly adherent deposits. This initial copper coating may not be substituted for any portion of the ductile acid copper specified in *Table 4a*.

Zinc alloys are first electroplated with copper to ensure adhesion of the subsequent nickel coatings. The initial layer is usually electrodeposited from a copper cyanide solution, but cyanide-free alkaline copper solutions may also be used. The minimum thickness of the initial copper layer is 8 μm to 10 μm or increased to about 15 μm on articles of complex shape to ensure adequate coverage in low-current density areas outside the significant surfaces.

For aluminium and aluminium alloys, suitable immersion deposits of zinc or tin, plus electrodeposited copper or other undercoats are necessary prior to the nickel to ensure adhesion.

6. ENGINEERING AND FUNCTIONAL NICKEL COATINGS

This section covers the use of electroplated nickel coatings to modify or improve corrosion resistance, hardness, wear or magnetic and other properties.

COATING REQUIREMENTS FOR FUNCTIONAL APPLICATIONS

The corrosion resistance will depend on the thickness of the coating and on other factors, including the condition of the surface prior to plating. The minimum thickness requirements may vary from 5 μm, where the nickel is used as an undercoat prior to gold or other coatings, to 125 μm or more, for applications involving long-term protection or severe corrosive conditions.

Applications include processing equipment, drying cylinders or rolls, hydraulic rams and automotive cylinder liners. In many cases the nickel is applied to provide both corrosion and wear resistance. Nickel is also used to salvage worn components and in such cases the thickness will be determined by the extent of the repair required.

TYPES OF NICKEL PLATING SOLUTIONS FOR FUNCTIONAL APPLICATIONS

Watts nickel: Largely because of its relatively low cost and flexibility, the Watts nickel solution is widely used for functional applications. Typical compositions for Watts nickel are given in Chapter 3, Table 2.

The properties of the coating are affected by the operating conditions. Generally, conditions that increase the hardness will also increase the tensile strength and decrease the ductility (elongation).

Conditions which increase the hardness and tensile strength and decrease the ductility are:

- An increase in pH above 5.0
- A decrease in temperature
- An increase in the chloride content

It will be seen that close control of the operating parameters is vital, where these properties are important for the performance of the coating.

Sulphamate nickel: Nickel sulphamate solutions also find applications for functional coatings, particularly in electroforming which is discussed below. Typical compositions for sulphamate nickel solutions are given in Chapter 3, Table 3.

A major advantage of sulphamate nickel solutions is the low internal stress of the deposit. However, the chloride content should be kept low to achieve minimum stress, without the use of stress reducing additives. Alternatively, bromide can be substituted for chloride, to maintain low internal stress.

Other nickel plating solutions: A number of alternative formulations have been developed for specific applications, although they are not widely used. These include:

- *Fluoborate:* This may be operated at very high current densities. Mechanical properties are similar to the Watts nickel deposits. Disadvantages are high cost and highly corrosive solutions.
- *All-chloride:* This is an alternative process where high current densities are required. These solutions are also much more corrosive than Watts solutions and therefore equipment must be carefully selected. Deposits are fine-grained and generally harder than Watts nickel coatings.
- *All-sulphate:* The major use for these solutions is in applications involving the use of insoluble anodes (e.g. in the internal plating of pipes and fittings). The absence of chlorides eliminates the problem of toxic chlorine gas being liberated at the anode. Lead or graphite anodes are commonly employed. It is necessary to replenish the nickel ions and to control the pH through regular additions of nickel carbonate.
- *High sulphate:* The major feature of these solutions is their good throwing power. They have found limited use as a strike bath over zincate pre-treated aluminium.
- *Hard nickel:* This solution provides harder deposits and superior abrasion resistance without the use of organic additives. The higher hardness is achieved through the inclusion of ammonium ions. Close control of pH, temperature and current density is necessary for consistent performance.
- *Black nickel:* Apart from some limited use on optical equipment or for solar collectors, black nickel has chiefly been applied for decorative purposes. The coatings produced are only thin. Therefore, black nickel is usually applied over satin or bright nickel, and coated with a lacquer or other organic finish.

Typical compositions for these alternative nickel plating solutions are given in *Table 5*.

Table 5 Other nickel plating solutions – composition and operating conditions

Type	Composition g L^{-1}	pH	Temp. °C	Current density A dm^{-2}
Fluoborate	Nickel fluoborate, 225–300 Nickel chloride, 0–15 Boric acid, 15–30	2.5–4.0	38–70	3–30
All–chloride	Nickel chloride, 225–300 Boric acid, 30–35	1.0–4.0	50–70	2.5–10
All–sulphate	Nickel sulphate, 225–410 Boric acid, 30–45	1.5–4.0	38–70	1–10
High sulphate	Nickel sulphate, 75–100 Sodium sulphate, 75–100 Ammonium chloride, 15–35 Boric acid, 15	5.3–5.8	20–32	0.5–2.5
Hard nickel	Nickel sulphate, 180 Ammonium chloride, 25 Boric acid, 30	5.6–5.9	43–60	2–10
Black nickel	Nickel sulphate, 100 Ammonium chloride, 15 Zinc sulphate, 22 Sodium thiocyanate, 15	5.5–6.0	26–32	0.2

ELECTROFORMING

Electroforming is the process by which articles are manufactured through building up metal by electrodeposition onto a suitable mandrel, which is subsequently removed.

Electroforming has a number of features, which make it a viable production process for specific applications. These include:

- *Accurate reproduction of fine surface detail*
  (e.g. the electroforming of stampers for the production of compact discs)
- *Duplication of surface textures*
  (e.g. dies to reproduce wood grain or leather patterns)
- *High degree of dimensional accuracy*
  (e.g. precision components)
- *Ability to electroform shapes that are difficult and costly to produce by any other method of fabrication* (e.g. rotary printing screens)

Because of its excellent mechanical properties, fine grain structure and good corrosion resistance, nickel is the most widely used metal for electroforming. These properties make it particularly useful for the electroforming of dies and moulds for casting and moulding.

Figure 12 Electroformed nickel mould for reinforced plastic automotive body component

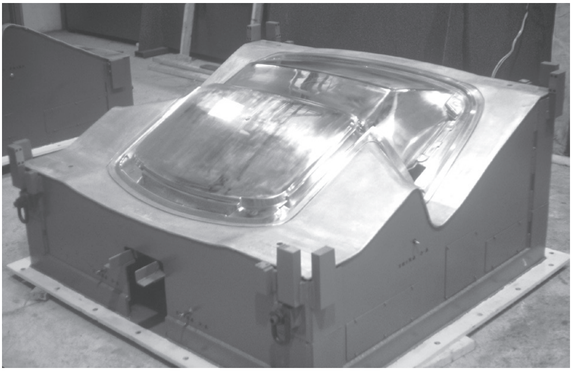


Photo courtesy of EMF Corporation.

Other important applications for nickel electroforming include tools, radar wave guides, spray masks and a wide range of components which would be difficult or more costly to fabricate by other means. Additionally, nickel electroforming is used in the production of foils and mesh products. This is a specialised procedure involving continuous deposition onto a rotating drum.

Because a wide range of articles can be produced by electroforming, the techniques will vary considerably according to the specific application. However, a general description of the electroforming process may be helpful.

MANDRELS

Mandrels may be either permanent or expendable.

Permanent mandrels are typically made from nickel, stainless steel, copper or brass. It is necessary to control the adhesion of the electrodeposited metal at a low level, to facilitate separation of the electroform. Nickel and stainless steel tend to be naturally passive but, the surfaces are usually chemically treated to ensure easy removal of the electroform.

Expendable mandrels include low melting point alloys (typically tin-zinc eutectic), or waxes, (which are melted at the completion of the electrodeposition process), or alternatively aluminium alloys (which are subsequently dissolved in sodium hydroxide).

Non-metallic mandrels must first be made conductive. A number of techniques may be used including silver reduction, application of fine silver powder or graphite, electroless deposition and metal sputtering.

ELECTROFORMING TECHNIQUES

The electrodeposition stage requires close control. While it is desirable to operate at high plating rates, it is important to consider metal distribution, nodular build-up and internal stress. Low stress is particularly important in electroforming as it is essential to prevent premature separation of the metal from the mandrel or warping of the electroform after removal.

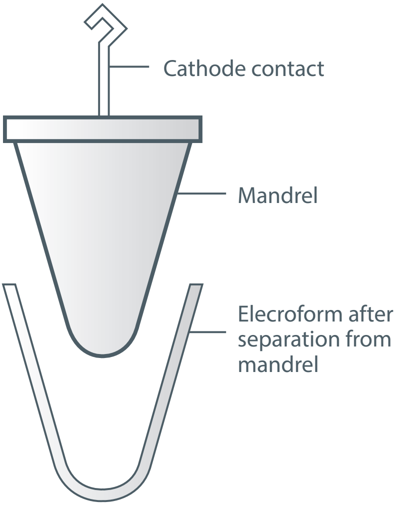
Low stress can be achieved by adding stress-reducing additives to Watts or sulphamate nickel solutions. However, a low tensile stress can also be maintained without the use of organic additives, using sulphamate baths with low chloride levels. It is important to carefully maintain the solutions and to continuously treat for impurities. Nodular build-up or treeing at edges may be troublesome. Fitting of shields is often helpful. In other cases the mandrel may be extended so that the treeing occurs on parts of the electroform that can be machined off at a later stage. In some cases, it may be necessary to machine off the trees part way through the electroforming operation and then return to the bath for further build-up. In such cases it is essential to re-activate the nickel to insure good nickel-nickel adhesion.

Agitation by air, eductors or mechanical, is important to minimise high current density burning or pitting. The choice of electroforming solution can also influence the degree of treeing. Certain addition agents similar to levelling agents can suppress the treeing tendency. Also, high chloride solutions are superior to Watts solutions in this respect.

For most applications, the electroformed shell will require some further processing, following electrodeposition and separation. This may involve trimming, machining or, particularly in the case of dies, backing up by a suitable material.

Electrodeposited copper can be electroplated as a back-up material but this is time consuming. Another possibility is to cast on a low melting point alloy, but this will limit the operating temperature of the mould or die. The most satisfactory procedure is to back-up by metal spraying with copper, aluminium or aluminium-silicon. Precautions must be taken to avoid overheating of the electroform and to ensure good bonding. Some dies and moulds will require cooling channels to be incorporated during the back-up operation in addition to the usual final machining steps.

Figure 13 Principle of electroforming showing electroform separated from the mandrel



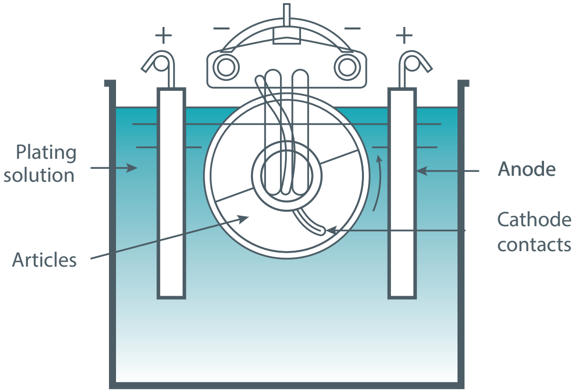
7. BARREL NICKEL PLATING

Both dull and bright nickel plating of small parts are commonly carried out using barrel plating techniques. In barrel plating the articles are tumbled in a revolving non-conducting container fitted with appropriate electrical contacts. The major advantage of barrel plating is that it eliminates the need for jigging or racking of the work. However, as discussed below, there are limitations on the size and type of work that can be successfully barrel plated.

DESIGN OF PLATING BARRELS

The most common type of production plating barrel is a round or hexagonal cylinder operated in a horizontal position and partly or fully immersed in the plating solution. The barrel cylinder is perforated with holes or slots to allow passage of current and solution circulation. It is fitted with doors for loading and unloading, and is fabricated from polypropylene or other suitable plastics. Cathode contact is usually provided by flexible danglers or, less commonly, studs at the ends of the barrel cylinder. Conventional anodes are positioned outside the barrel.

Figure 14 Immersed type plating barrel



This type of immersed barrel is commonly transported through the various stages of the pre-treatment and plating cycle. Alternatively the barrel may be operated for the plating stage alone with the pre and post operations carried out in baskets.

Another design is the open-ended oblique plating barrel. In its simplest form the plating solution is contained in the barrel, cathode contact is via studs and the anode is fitted through the open end. This type of barrel is generally only used for very small-scale production. A further type of open-ended oblique barrel is perforated and operated within a plating tank using conventional anodes. A mechanism allows for the barrels to be partially immersed for plating and then tipped into the discharge position. As it is not necessary to remove doors with this design they are sometimes used in fully automated systems.

TYPE OF WORK SUITABLE FOR BARREL PLATING

Components must be of a type that will tumble freely without nesting, locking together or becoming tangled. Flat parts which can stick together or onto the barrel surface may also cause problems which can sometimes be alleviated by mixing with other work. Care should also be taken with components which can 'peck' or damage themselves. Articles should not be too heavy (certainly not more than 500g), to avoid impingement problems or damage to the barrel. Otherwise, a wide variety of articles can be successfully barrel plated with their size largely being dictated by the barrel dimensions.

BARREL LOADING

For efficient operation the work load should be not more than 50% of the volume of the barrel. This is important to ensure that it is effectively mixed during the tumbling action, so all parts receive their full share of the current.

Two other aspects must be considered. First, the weight must be within the manufacturer's specification for the barrel. Second, the surface area of the load is important. It is not always realised that the surface area of a kilogram of parts can vary enormously, depending on the gauge or thickness of the metal from which the articles are fabricated. For most barrel nickel plating operations, the desirable current density range is 0.3 to 1.0 A dm^{-2}.

BARREL NICKEL PLATING SOLUTIONS

For applications where full brightness is not required, dull nickel solutions based on the Watts formulation or the high chloride type are used. A degree of burnishing takes place, particularly with longer plating cycles. The Watts solutions are sometimes modified by substituting ammonium chloride for the nickel chloride or by adding magnesium or sodium sulphate. Examples are given in *Table 6*.

Bright nickel plating solutions are widely used for decorative applications. These are similar to those used for rack plating. However, it is generally desirable to maintain the ‘carrier’ at a high level and to control the brightening and levelling additives as low as practicable. This reduces the tendency for the nickel to become passive during plating, which can result in an effect called ‘tinselling.’ This relates to the potential problem in barrel plating for the nickel plate to exfoliate or flake-off if the nickel is brittle or highly stressed.

VOLTAGE REQUIREMENTS

Because of the resistance to current flow through the perforations in immersed barrels, considerably higher voltages are needed compared with rack plating. The voltage required will depend on the solution composition, temperature, design of barrel, anode area, and nature and size of the work load. Generally, the required voltage will be in the range of 12–20 volts.

PLATING RATES AND METAL DISTRIBUTION

The restrictions on current flow dictated by the barrel design, and the consequent low current densities, means that barrel nickel plating rates are relatively low. For example, a 760 x 350 mm immersed barrel with a 500 dm^2 load will typically draw only 200 amperes at 15 volts – equating to 0.4 A dm^{-2}. This will give an average plating rate of around 4.8 $\mu m\ h^{-1}$.

Table 6 Typical dull nickel barrel plating solutions

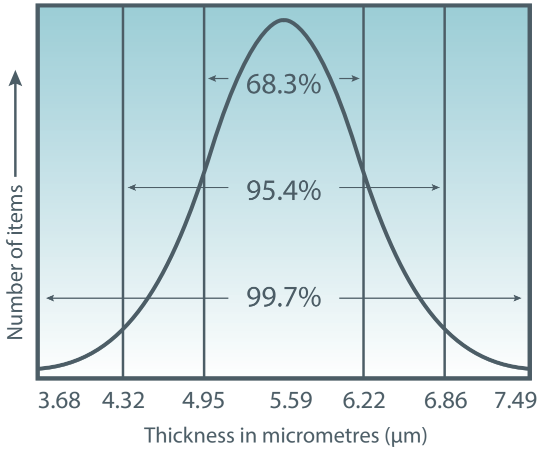
1. Nickel sulphate Ammonium chloride Boric acid pH Temperature	150 g L^{-1} 30 g L^{-1} 30 g L^{-1} 5.0–5.6 Ambient
2. Nickel sulphate Nickel chloride Boric acid Magnesium sulphate or Sodium sulphate pH Temperature	250 g L^{-1} 50 g L^{-1} 40 g L^{-1} 180 g L^{-1} 50 g L^{-1} 5.2–5.8 40–55 °C

However, due to the nature of barrel plating, there will be a variation in thickness from part to part. The degree of scatter likely to be experienced is shown in *Figure 15*. This also indicates the percentage of the whole batch falling within different thickness ranges.

If the plating specification nominates a *minimum* average thickness, it will be necessary to increase the plating time to allow for this variation.

The plating of fasteners requires particularly close control of thickness to avoid excessive build up, which could affect clearances.

Figure 15 Probable frequency distribution in a barrel load plated to a batch thickness of 5 µm



8. TESTING PROCEDURES FOR NICKEL ELECTRODEPOSITS

APPEARANCE AND SURFACE QUALITY

The normal procedure for establishing acceptable appearance standards is to prepare samples before production begins. Agreement should be obtained on critical areas where appearance and other surface conditions must be met.

Inspection should include examination of the coatings for roughness, pitting, burning, poor coverage and dark or streaked deposits as well as overall appearance.

For decorative plating the acceptance standards will include brightness, levelling, absence of haze and uniformity. However, for functional plating, brightness is not usually required and may possibly indicate a problem with the deposit. Uniform matte or satin deposits are typical of engineering coatings.

Where off-standard appearance is experienced, it is helpful to carefully record the areas of the work and the proportion of parts affected. This information greatly assists in identifying the cause of the problem. For example, it will be important to know whether pitting or roughness is occurring on upper or lower horizontal surfaces or perhaps only on particular positions on the plating racks. Refer also to Chapter 10 on trouble-shooting.

COATING THICKNESS

Thickness has a major influence on the performance of the plated coating, particularly in respect of corrosion resistance and wear resistance. The coating thickness may be specified as *local thickness* or *average thickness*. The specification may define the significant areas where the local thickness requirement must be met. Average thickness measurements are generally specified on small parts, particularly on barrel plated work.

Thickness testing methods fall into two categories – *destructive* and *non-destructive*.

DESTRUCTIVE METHODS

These include:

- Microscopic examination of cross-sections
- Coulometric method
- STEP test
- Scanning electron microscope method

The microscopic method specified in ISO 1463[3] involves sectioning the plated part, mounting, polishing and etching, using standard metallographic techniques and then measuring the coating thickness with the aid of an optical microscope. This method is time consuming, but capable of great accuracy and is often specified as a referee method in cases of dispute. It also enables readings to be taken of individual layers in composite coatings.

The coulometric method given in ISO 2177[4] involves equipment that isolates a small-defined area, applies current to anodically dissolve the coating and measuring the current and time before penetration to the substrate. A change in voltage is used to indicate penetration. Commercially available instruments provide a direct readout of the thickness. This type of equipment is commonly used on nickel and nickel-chromium coatings. Unlike most non-destructive instruments, they will measure nickel over most substrates.

A modification on the standard coulometric method is the STEP test – Simultaneous Thickness and Electrochemical Potential. This test enables the electrochemical potential difference between the nickel layers to be determined. This has significance with regard to corrosion performance. For dual-layer nickel, the potential difference between the semi-bright and bright nickel layers generally falls between 15 and 200 mV, with the semi-bright more electrochemically noble than the bright nickel. The STEP test is described in ASTM Standard B 764[5].

The scanning electron microscope specified in ISO 9220[6] may be used to measure individual layers in multiple layer coatings.

NON-DESTRUCTIVE METHODS

Where applicable, non-destructive tests have the advantage of generally being quicker, as well as avoiding the destruction of the parts. There are a number of non-destructive thickness testing procedures available. The ones most applicable to nickel coatings are based on:

- Magnetic attractive force
- Magnetic induction
- X-ray spectrometry
- Beta backscatter of particles

It should be noted that variations in the physical properties can cause inconsistencies in the results obtained with many non-destructive methods. For this reason it may be necessary to prepare calibration standards using the same nickel solution and on the same substrate. This is the case with instruments based on magnetic methods.

Non-destructive thickness testing measurement by X-ray fluorescence XRF, is a most valuable tool – although expensive.

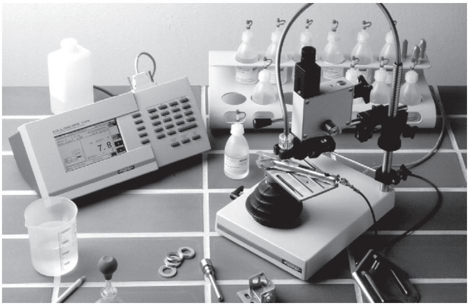
Instruments based on the backscatter of beta particles are only suitable for measuring nickel coatings on certain substrates. However they are also widely used for measuring gold deposits over nickel.

Reference may also be made to international standard ISO 1456:2009, which reviews methods of thickness measurement.

Table 7 Non-destructive thickness tests suitable for electroplated nickel coatings

Test	ISO
Magnetic	2361[7]
X-Ray spectrometry	3497[8]
Beta backscatter	3543[9]

Figure 16 Coulometric thickness testing equipment



ADHESION

Nickel electrodeposits are generally strongly bonded to the substrate. Indeed, except when the adhesion is abnormally poor, failure will occur almost invariably in either the substrate or in the coating. However, it is clearly essential to monitor adhesion in production operations. Despite the importance of adhesion testing, there are no quantitative methods which are suitable for regular quality control purposes. Adhesion is therefore generally evaluated by bending, twisting, filing or burnishing, in an attempt to detach the coating from the substrate. The file test is frequently employed for shop testing. In this test, a coarse file is applied to the cut edge in a manner to raise the coating.

On parts where such mechanical tests are not possible, thermal shock tests may be used. In the thermal shock test the plated parts are heated in an oven then quenched in water, thus promoting a rapid contraction of the metal, which will detach any poorly adhered coatings. The temperature specified depends on the substrate – 300°C for steel and 150°C for zinc alloy. Thermal shock tests are also usefully applied to nickel-plated aluminium and for plating on plastics.

ISO 1456 specifies testing procedures for a file test and a thermal shock test. ISO 2819[10] reviews methods available for testing adhesion.

DUCTILITY

Ductility is the term commonly used to describe the ability of a plated coating to undergo deformation without cracking. It is closely associated with the elongation value (expressed as a percentage).

The elongation of deposits from additive-free nickel plating is up to 30% under optimum conditions, but will be affected by the chloride content, operating conditions and effects of impurities. Semi-bright nickel coatings also exhibit good elongation values (typically over 8%), whilst generally bright nickel produces lower values. Deposits from sulphamate nickel solutions provide the highest elongation values.

For quality control purposes, simple tests are used to check the ductility of nickel deposits, particularly on bright nickel, which may become brittle due to impurities or an imbalance of brighteners. One such test involves plating a soft brass sheet 1 mm thick, with 25 µm nickel, then cutting from this a test strip 150 x 10 mm. The test strip is then bent through 180°, over a mandrel of 11.5 mm diameter, with the plated surface outermost. The plated coating is deemed to comply with the minimum requirement of 8%, if no cracks extend completely over the convex surface.

CORROSION RESISTANCE

Resistance to corrosion is critically important for many applications including decorative coatings, particularly nickel-chromium coatings, which are subjected to outdoor exposure.

Outdoor exposure tests have played an important role in evaluating different coatings and plating systems. These have included static tests in various environments and also service trials with plated parts attached to vehicles or ships. However, accelerated corrosion tests are widely used for quality control purposes and for the preliminary evaluation of new plating systems.

The main accelerated corrosion tests for nickel-chromium coatings accepted internationally are:

COPPER ACCELERATED ACETIC ACID SALT SPRAY TEST (CASS)

This is a modification of the neutral salt spray test which is used to evaluate zinc and other coatings. The plated parts are subjected to a salt spray inside a fog chamber, under closely controlled conditions. In the CASS test, the test solution is modified by the addition of copper and acetic acid, to appreciably increase the rate of attack on nickel. The CASS solution consists of 50 g L^{-1} sodium chloride, 0.2 g L^{-1} cupric chloride and is acidified to pH 3.2 using acetic acid. The solution is operated at 50°C.

The design of the test cabinet has a pronounced effect on the results, and therefore, must comply with the standard specifications.

ACETIC ACID SALT SPRAY TEST

This is similar to the CASS test but, as the test solution does not contain copper, it is much milder. The solution contains 50 g L^{-1} sodium chloride and is acidified with acetic acid to pH 3.2. Operating temperature is 35°C.

This test is preferred for thinner coatings, where it will give more reproducible results than the more aggressive CASS test.

CORRODKOTE TEST

The Corrodkote test is different to the above tests in that the corrosive medium is applied as a slurry. It was developed in an attempt to simulate the corrosive attack that is produced by road mud containing corrosive salts – typical of conditions where salt is applied to roads for de-icing.

The slurry or paste contains cupric nitrate, ferric chloride and ammonium chloride mixed with kaolin. This slurry is brushed onto the plated parts and allowed to dry. The parts are then placed in a cabinet under controlled temperature and humidity. Corrosion may be indicated by coloured stains on the paste, or by examination of the plated surface for pitting and/or blisters after removal of the paste.

Refer to *Table 8* for standard specifications covering accelerated corrosion test procedures.

Table 8* Standard specifications covering accelerated corrosion tests

Basis metal	**Service condition number**	**Duration of corrosion test hours (h)**		
		CASS ISO 9227[11] **ASTM B368**[12]	**Corrodkote ISO 4541**[13] **ASTM B 380**[14]	**Salt spray test ISO 9227 ASTM B 117**[15]
Steel, copper or copper alloys, zinc or zinc alloys, aluminium or aluminium alloys	1	No test requirement	No test requirement	8
	2	8	8	48
	3	16	16	96
	4	24	2 x 16	144
	5	64	No test requirement	No test requirement

**Adapted from ISO 1456:2009 – Metallic and other inorganic coatings – Electrodeposited coatings of nickel, nickel plus chromium, copper plus nickel and copper plus nickel plus chromium.*

THERMAL CYCLE TEST

The thermal cycle test is applied to plated plastics materials to assess adhesion and monitor the effectiveness of the process. The test should be carried out 24 h ± 2 h after completion of the electroplating operation.

TEST PROCEDURE

One full thermal cycle shall consist of the following steps:

1. Expose the parts for 1 h at the high temperature limit
2. Allow parts to return to 20°C ± 3°C and maintain at this temperature for 1 h
3. Expose the parts at the low temperature limit
4. Allow parts to return to 20°C ± 3°C and maintain at this temperature for 30 minutes

After being subject to three cycles, the coated article shall show no defects visible to the naked eye, such as cracking, blistering, peeling, sink marks or distortion.

Table 9* Thermal cycle temperature limits

Service condition number	Temperature limits °C	Temperature limits °C
	High	Low
1	60	-30
2	75	-30
3	80	-30
4	80	-40
5	85	-40

**Adapted from ISO 4525:2003 Metallic coatings – Electrodeposited coatings of nickel plus chromium on plastics materials.*

ACCELERATED CORROSION TESTING OF PLATED PLASTICS MATERIALS

Coated articles shall be subjected to the CASS corrosion test specified in ISO 9227[11], no earlier than 24 h after electroplating, for the duration as stated in *Table 10.*

Note: The duration of the corrosion test provides a means of controlling the continuity and quality of the coatings and does not necessarily relate to the life or performance of the finished article in actual service.

The duration shall either be continuous or consist of an appropriate number of 8 h or 16 h periods separated by rest periods of 1 to 16 h, as agreed between the purchaser and the electroplater.

A protection rating shall be assigned in accordance with ISO 10289[16] to each article tested, representing the extent to which the nickel plus chromium coating prevents corrosion of the copper or nickel undercoat, and exposure to the plastic substrate. Alternatively, a one-number rating based solely on appearance after testing may be assigned. The appearance rating shall be carried out no less than 8 h after corrosion testing.

COMBINED THERMAL CYCLE AND CORROSION TESTING FOR PLATED PLASTICS MATERIALS

Corrosion testing may be combined with thermal cycle testing for components that are electroplated to service conditions 3, 4 and 5.

For articles plated to service condition 3, two cycles are required: for conditions 4 and 5, three cycles are required.

Each cycle of combined thermal and corrosion testing consists of the following steps:

1. One 16 h cycle CASS test
2. Rinse with demineralised water only, after each CASS cycle
3. One cycle of thermal cycle procedure, as given in the section on thermal cycling on page 55

Table 10* Corrosion tests appropriate for plated plastics materials, according to each service condition number

Service condition number	Duration of CASS test (h)
1	See note
2	8
3	16
4	32
5	48

**Adapted from ISO 4525:2003 Metallic coatings – Electrodeposited coatings of nickel plus chromium on plastics materials.*

Note: Although no test duration is given for service condition 1, such coatings may be subjected to the acetic acid salt spray test specified in ISO 9227 for an agreed time not exceeding 8 h.

9. CONTROLLING THE ELECTROPLATING PROCESS

MONITORING THE OPERATING CONDITIONS

CURRENT DENSITY

Current density management is important for two main reasons. Firstly, the current density controls the rate of deposition. Secondly, the current density must be controlled within the correct operating range in order to obtain sound deposits having uniform appearance and free from burning or treeing.

For optimum productivity, it will be desirable to operate with the maximum surface area of work consistent with the desired current density and the available current. In practice, the size, shape or weight of the work may limit the surface area that can be loaded. In such cases, the current may need to be reduced to achieve the desired current density. The control of current density is particularly critical where work is being plated to a specified thickness and where the equipment operates on a fixed time cycle.

As it is sometimes difficult to establish the surface area of the work, and consequently to compute the required current, it is common practice to control the process by voltage rather than current. This may be reasonable where the work consists of components of similar characteristics and where other operating parameters are unchanged. It should however be recognised that the current density is the controlling factor.

The use of electronic controls can assist in controlling the current density. These include automatic current density devices on rectifiers and computer-aided controls. The latter compute and adjust the current for each load, based on the parts loaded.

TEMPERATURE

Changes in temperature can affect the performance of nickel plating and other process solutions. Specifically, temperature can influence the brightness range, throwing power, ductility, hardness, internal stress and burning characteristics.

The use of automatic temperature controls is highly recommended, together with regular monitoring to ensure the temperature is maintained within the optimum operating range.

PH

pH is a measure of the hydrogen ion concentration, or more simply the acidity, of a solution. In the case of nickel solutions the pH has an important influence on bath performance. The pH can affect the bright plating range, cathode efficiency, effects of impurities, throwing power, stress, as well as the physical properties of the deposit.

Despite the use of boric acid as a buffer, the pH continually changes. Under normal operating conditions the pH tends to rise and this must be counteracted by the addition of dilute sulphuric or hydrochloric acid. If the pH falls this will indicate either drag-in of an acid (e.g. from an acid dip), abnormal anode behaviour, or the use of insoluble anodes. The pH can be increased by stirring in a slurry of nickel carbonate or, less preferably, sodium hydroxide.

The pH is easily determined using a pH meter or colourmetrically using indicators or pH papers. pH meters provide the most accurate measurements, but should be properly maintained and regularly calibrated. Generally, the pH of nickel solutions should be maintained within ± 0.3 units of the optimum. As the pH changes rapidly, checks should be made at least once per shift.

AGITATION

Agitation is important to dislodge bubbles of hydrogen or air from the cathode surface, which might otherwise cause pitting. Agitation also overcomes stratification and assists in maintaining a uniform temperature throughout the solution. The agitation may be provided mechanically – as in cathode movement, air agitation, or eductors.

It is essential to monitor air agitation to ensure the effect is uniformly distributed over the work. Problems can occur due to blocking of the air holes in the submerged pipes with calcium salts or crystallised boric acid. Occasionally, problems can arise through accidental movement of the agitation lines.

FILTRATION

Continuous filtration is needed to maintain the plating solutions free of insoluble particles. These may be introduced through solid particles adhering to the work, drag-in, additions of impure chemicals, corrosion of dropped components, airborne particles, faulty anode bags, etc. Clearly, it is important to eliminate as many of the sources of insoluble particles as possible. Nevertheless, the filtration process must be properly maintained and controlled.

The flow rate and/or pressure readings can provide guidance on the performance of the filters and the need for cleaning or replacement of the filter media.

The required rate of filtration partly depends on the input of contamination and also on other factors such as the thickness of nickel being plated and the type of work. For example, components with significant upward facing areas will be more susceptible to roughness than other items. Air agitated baths generally require more filtration than non-agitated or cathode agitated solutions. As a guide, most air agitated baths should be filtered at a rate that will turn the solution volume over at least once per hour and preferably 2–3 times per hour.

The operation and servicing of the filters depends to some extent on the design of the equipment. Some filters use replaceable cartridges or filter pads, which can be obtained in a range of micron ratings. For most purposes, filter media designed to remove 5 to 15 micron particles are satisfactory. In other cases such as cloth type units, it is essential to use a suitable filter aid to achieve satisfactory filtration. Filter aids are based either on diatomaceous earth or fibrous materials such as cellulose. Both types are often used to form a filter bed that will adhere to the filter cloths.

MAINTAINING THE OPTIMUM SOLUTION COMPOSITION

CHEMICAL ANALYSIS

Analytical control of the main components of nickel-plating solutions is important to assist in maintaining the solution within the optimum operating range.

Analysis of nickel, chloride and boric acid can be carried out using relatively simple titration methods, although modern instrumental methods are also available. Any change in the concentration of these major constituents is generally very slow and therefore they need only to be checked infrequently.

Analysis for organic additives is more complex and generally requires the use of UV spectrophotometers or one or two other laboratory instruments. The concentration of carriers and stress reducing additives can be measured using these types of laboratory facilities. However, it is more difficult to effectively control brighteners by analysis. While most suppliers can provide analytical procedures for such additives, the results have only limited value for production control. This is because their concentration in a production solution can change very rapidly. Also, the effect of brighteners is affected by other factors such as agitation rate, pH, purity of solution, etc. For these reasons, the concentration of brighteners is usually controlled by observation of the brightness of the plated articles or by controlled plating tests – refer to the following notes. Where required, the level of anti-pitting agents can be controlled through surface tension measurements.

Analytical control can also be applied for metallic impurities. These are commonly analysed spectrographically, by atomic absorption or inductively coupled plasma. Organic impurities pose greater difficulties for the analyst, although some recent developments in instrumental analysis have been used to determine total organic carbon. Plating tests, discussed below, can provide useful information on the effects of impurities.

Care must be exercised in taking samples for analysis. *The only acceptable sample is one that is truly representative of the bulk of the solution*. Misleading results may be obtained if samples are not drawn correctly. The solution should be at the normal operating level and well mixed before the sample is taken, particularly in non-agitated baths where considerable stratification can occur. In the rare situations where it is not practicable to stir the solution, samples may be taken using a sampling tube.

PLATING TESTS

As the performance of plating solutions can be influenced by many factors, analytical results alone may not adequately indicate the condition of the solution. It is therefore very useful to periodically carry out performance tests on production baths. Such tests enable the operator to evaluate the plate appearance, brightness range in the case of bright baths, ductility and various defects including roughness, burning, treeing, pitting, low current density darkness, etc. It is also possible, using appropriate procedures, to evaluate throwing power or covering power.

The essential requirement of any plating test is to standardise conditions so that results will be reproducible. Simple beaker or small tank tests can be useful providing operating conditions are standardised, including type of test piece, temperature, agitation, size and type of anode, and the anode-cathode spacing. Methods of preparing the test piece should also be closely controlled. Bent panels of various types that incorporate high and low current density areas are often used with these beaker tests.

Small-scale plating tests enable the operator to test possible changes and to evaluate their effect before committing to action on the production bath. For example, the effectiveness of a projected activated carbon treatment could be quickly tested.

A particularly valuable test is the *Hull Cell* which is illustrated in *Figure 17*. The Hull Cell is designed so that the current density varies from one end of the panel to the other. A single test panel can therefore demonstrate the bath performance over a wide range of current densities. This makes it particularly useful for checking the brightness range of

Figure 17 Hull Cell

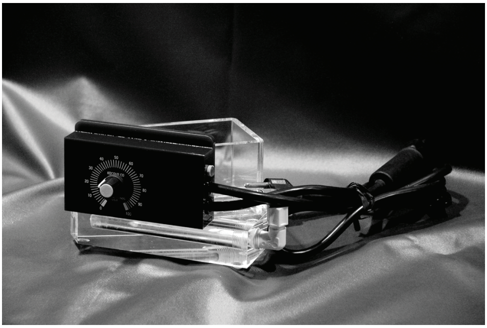


Photo courtesy of Kocour Company.

bright nickel baths. At the same time the panel can be examined for low current density darkness, brittleness or other defects. As the current density range on the Hull Cell panel is often broader than that on production components, the test may give early warning of potential problems, for example, the effects of impurities or a brightener imbalance. Measurements of throwing power are also possible using the Hull Cell.

Typically the Hull Cell is plated at 2 amperes for 10 minutes, but this can be altered to check particular aspects. Polished brass panels are commonly used but lightly abraded steel or brass panels can be useful to evaluate levelling.

MAKING ADDITIONS

The nickel and chloride concentrations are replenished by adding the appropriate nickel salts. *Table 11* lists conversion factors for nickel sulphate and nickel chloride. Boric acid will also require periodic additions based on analysis results.

It is preferable to pre-dissolve all solids in a separate mixing tank and to filter this solution into the main plating tank to avoid roughness problems. If this is not possible, additions can be made directly into the plating tank in small increments when the bath is not loaded. The solution will then require thorough stirring and filtering before recommencing production. Liquid additions can be added directly to the plating tank, but should be distributed as evenly as possible – avoiding contact with the articles being plated. Sulphuric acid (for pH adjustment) should be diluted before addition, to assist in dispersion and to prevent possible oxidation of organic addition agents.

Table 11 Nickel content of nickel salts

Nickel sulphate	$NiSO_4.6H_2O$	Contains 22.3% nickel
Nickel chloride	$NiCl_2.6H_2O$	Contains 24.7% nickel
Nickel sulphamate	$Ni(NH_2SO_3)_2$	Contains 23.2% nickel
Nickel carbonate	$NiCO_3$	Contains about 46% nickel

REPLENISHING BRIGHTENERS AND ADDITION AGENTS

Carriers and similar organic additives are chiefly consumed through drag-out and consequently their concentrations do not change rapidly. They can therefore be replenished periodically (typically weekly or monthly, depending on production), based on analysis or on a regular schedule which has been established by experience.

In contrast, the concentrations of brighteners and levelling additives can fall quite rapidly during plating. Continuous replenishment by drip feeding or by means of dosing pumps is recommended for high production installations. For lower production rates, additions should be made once or twice a shift. Dosing pumps may also be linked to ampere-hour meters. This will ensure effective control, providing the overall mix of the work being plated remains the same or similar. It should be understood that brightener consumption is partly controlled by the surface area of work being plated and will vary according to the current density and type of work. The consumption per ampere-hour will generally increase at lower current densities. Therefore, replenishment based on ampere-hours may need to be adjusted if the type of work or current density changes.

CONTROL OF IMPURITIES

Impurities introduced into nickel-plating solutions can affect both the physical properties and the appearance of the coatings. Effective control of impurities is therefore a vital part of quality management. Measures to prevent or minimise the entry of impurities should be the first priority. While this is largely a case of good housekeeping, a knowledge of the types of impurities, their effects and sources will assist in developing an effective control program.

TYPES OF IMPURITIES

Insoluble impurities: Insolubles may cause roughness – particularly on shelf areas. These may derive from a number of sources including airborne dust, abrasives, anode fines (introduced through torn or faulty anode bags), and impure chemicals. They may also result from precipitation of metallic impurities. For example, iron if oxidised to the ferric state (as will usually occur in air agitated baths) may precipitate as ferric hydroxide at pH values above 4.5.

Metallic impurities: Metallic impurities are frequently introduced through corrosive attack on unplated areas of the work or from articles accidentally allowed to fall to the bottom of the plating tank and not promptly removed. Metallics can also be introduced through drag-in from preceding processes (particularly if rack coatings are not properly maintained or if the rinsing is inadequate) or from impure chemical additions. Typical effects of common metallic impurities are summarised below.

Iron: Soluble iron may cause hazes or pitting and a reduction in ductility. As mentioned above, iron may also precipitate as ferric hydroxide, causing fine roughness.

Aluminium and silicon: May cause high current density haze or very fine roughness, often described as stardust or salt and pepper.

Calcium: Calcium, which may build up through the use of hard water, causes needle-like roughness due to precipitation of calcium sulphate when the calcium content exceeds the saturation point of 0.5 g L^{-1} at 60°C.

Copper, cadmium, lead, tin and zinc: These metals tend to preferentially deposit in low current density areas, causing haze and dark or black deposits.

Chromium: When introduced as hexavalent chromium (often through carry-over of chromic acid by damaged rack coatings), chromium will cause high current density gassing, dark streaks or prevent deposition at low current density. However, hexavalent chromium may be reduced to the trivalent state by reacting with organic additives. The reduced chromium produces similar effects to iron, aluminium and silicon.

Manganese: May cause a reduction in levelling of bright deposits.

Organic impurities: Organic impurities may result from contamination of the solution with oils or greases. These can enter through dripping from overhead equipment or carried over on the work due to poor cleaning. Other common sources are buffing compounds, lubricants/sizing from anode bags and unsuitable tank linings or hoses, etc. Additionally, organics can originate from oxidation or breakdown of organic additives. It might be noted that some earlier levelling agents (for example, coumarin) produced undesirable reduction products, which adversely affected the deposit properties. However, this is usually not a problem with modern systems.

Oils, greases, waxes being dispersed as droplets or surface oil slicks, can cause pitting.

Organics (soluble) may produce hazes or cloudiness in bright deposits or degrade mechanical properties of the coatings.

Dissolved air or gases: Dissolved air or carbon dioxide can cause a type of pitting characterised by a teardrop pattern. The usual source of dissolved air is entrapment in the filter system due to faulty pumps or valves or to the suction hose being too close to the air agitation pipes. Carbon dioxide can be introduced from additions of nickel carbonate to raise the pH. In both cases, the gases can be purged by heating above the operating temperature for several hours, preferably with the air agitation operating.

PURIFICATION PROCEDURES

Even when solution contamination is minimised through good operating practices, most nickel solutions will require either continuous or periodic batch treatments to remove impurities. Continuous filtration will generally remove suspended matter, but batch filtration into a separate tank may be necessary from time to time. During such pump-out the bottom of the plating tank and any submerged fittings should be thoroughly cleaned. Generally, anode bags would be serviced at the same time.

REMOVAL OF METALLIC IMPURITIES

The two most common purification procedures for removing metallic impurities are *low current density electrolysis or "plating out" and high pH treatments.*

Plating out consists of plating onto sheets or scrap at current densities appreciably below the normal operating range. It will be noted from the earlier discussion that a number of common metallic impurities, including copper, zinc, lead and tin, produce dark deposits at lower current densities. This effect is due to the higher proportion of contaminant being co-deposited with the nickel at these low current densities. By plating at current densities around 0.2 to 0.5 A dm^{-2}, it is therefore possible to remove the impurities with a minimum loss of nickel. The plating out sheets are often corrugated (say 75 mm corrugations) to provide a large surface area together with a range of low current densities.

Although the removal of impurities is most efficient on an ampere-hour basis at these low current densities, the overall current is restricted by the area of sheets that can be accommodated. If the level of contamination is particularly high, it may therefore be necessary to employ somewhat higher currents and sacrifice more nickel to achieve faster removal of the impurity. To be effective, it is essential to provide adequate solution movement over the plate-out sheets.

Continuous plating out is beneficial in plants subject to high rates of contamination, such as, for example, where large volumes. This is achieved by continuously circulating the solution through a plate-out cell attached to the plating tank.

High pH treatments: Iron, aluminium and silicon can be precipitated as their hydroxides at a pH of 5.0 to 5.5, and subsequently removed by filtration. The procedure involves transferring the solution to a treatment tank, heating to 66°C and stirring in a slurry of nickel carbonate until the required pH is achieved. The solution should then be allowed to settle for 8 to 16 hours before filtering back into the plating tank. Iron is most effectively removed if it is in the ferric state. Hydrogen peroxide may be added, if desired, to oxidise any ferrous iron. Peroxide can also assist in destroying organics, but its use should be first approved by the brightener supplier. However in air agitated baths, the oxygen in the air is usually sufficient to oxidise the iron. The precipitated hydroxides often absorb or occlude other contaminants which makes a high pH treatment particularly effective as a general purification procedure.

Other methods for controlling metallic impurities: As an alternative to removal, it is possible in some cases to complex or sequester the unwanted metals. Various organic products based on citrates, gluconates or benzene sulphonates are available as proprietary products which will assist in overcoming the effects of metals such as iron and zinc. Sodium fluoborate has also been used to control the effects of iron.

Another approach is to apply an insoluble powder, nickel dithiocarbamate, to the filter. This material is claimed to remove some common metallic contaminants through an ion-exchange mechanism.

REMOVAL OF ORGANIC IMPURITIES

A wide range of organics can be removed by using activated carbon (charcoal). Since the organics are absorbed onto the surface of the carbon, best results will be achieved with finely powdered grades which offer the largest surface area. Only grades specifically recommended for electroplating should be used.

For batch treatments, the solution should be transferred to a separate treatment tank and the activated carbon stirred in. The quantity required is best determined by a laboratory test, but is typically 4 to 8 g L^{-1}. The temperature is normally raised to around 66°C. The solution should be agitated for one hour and then allowed to settle for 8 to 16 hours before being filtered back into the plating tank. Care should be taken to ensure that the fine particles of carbon are fully retained on the filter, as any entering the plating solution will cause roughness. It is usually helpful to draw off from just below the surface, to avoid disturbing the settled carbon.

Not all organics are readily absorbed by activated carbon. In some cases the organic impurities can be converted to a form more easily removed by carbon through first oxidising with hydrogen peroxide or potassium permanganate. Before using either of these oxidation procedures, advice should be sought from the brightener supplier as these can react with the additives. Permanganate is now rarely used with bright nickel solutions. In difficult cases it is usually preferable to avoid permanganate and, if necessary, carry out two carbon treatments which can sometimes be more effective than one heavy treatment.

Activated carbon will also remove some addition agents, which must be replenished before plating is recommenced. The loss will vary considerably with the type of addition agents. Some modern brighteners are not appreciably removed by carbon absorption. Anti-pitting agents are generally rapidly absorbed.

With many bright nickel processes, it is useful to circulate the solution continuously over a bed of activated carbon on the filter. Provided the carbon is renewed regularly at fairly frequent intervals, this continuous treatment will maintain the solution in good condition with respect to organic impurities. Filter cartridges containing activated carbon may also be used for continuous purification where this type of filtration equipment is installed. However, the cost may be higher.

10. TROUBLE-SHOOTING

As with any electroplating operation, nickel plating processes may experience problems from time to time. The difficulty may directly involve the nickel plating bath or may be caused by the pre- or post-treatment stages, racking, electrical problems or equipment faults. It is essential that the plating supervisor develops skills in isolating the fault and taking appropriate corrective action.

This section covers the identification of defects and guidance on trouble-shooting techniques.

COMMON TYPES OF DEFECTS IN NICKEL PLATING AND THEIR CAUSES

ROUGHNESS

Roughness occurs when suspended particles co-deposit with the nickel. It will tend to be most pronounced on upward facing horizontal surfaces or "shelf " areas of the work.

The suspended matter may be introduced from various sources including airborne dusts, undissolved chemicals (particularly boric acid), abrasive particles adhering to the work as a result of poor cleaning, impure chemicals or from anode fines (from torn or unsatisfactory anode bags). Additionally, suspended matter may form in the nickel solution through precipitation due to drag-in of incompatible solutions or introduction of metallic impurities, which can form insoluble hydroxides (for example, iron), or by crystallisation (for example, calcium sulphate). Another potential source is oxidation of organic additives by chlorine liberated at insoluble anodes.

PITTING

Pitting is generally caused by either oil-like globules or gas bubbles (air or hydrogen) adhering to the surface during deposition. In the former case, the contaminant may be dispersed in the plating solution or alternatively be present on the work surface due to problems in the pre-treatment cycle. Adherent hydrogen bubbles can result from too low a pH, solution imbalance, contamination or low concentration of non-pitting additives (wetting agents). Dissolved air introduced through the filter system can also cause pitting. Pits in the nickel deposit may also be the result of pitting or porosity in the substrate or in underlying electrodeposits.

Occasionally pits will be formed by insoluble particles initially adhering to the work surface and subsequently washing off as the plating proceeds.

STAR DUST

(Also referred to as salt and pepper)
These terms refer to extremely fine forms of roughness. Star dust is commonly caused by contamination of the nickel solution with aluminium or silicon. The problem has also been associated with impurities in the rinse water.

BURNING

Burning may occur on edges and extremities of the work (high current density areas) if the applied current is too high for the size and type of load. Burning on the bottom parts of a rack may occur if the full current load is applied as the rack is lowered into the plating tank. This can be prevented by applying a reduced voltage to the rack during immersion or by re-positioning anodes away from the entry point.

Burning may be aggravated by low temperatures or solution imbalance.

POOR ADHESION / BLISTERING

Lack of adhesion may be indicated by blistering, or by peeling when the plated component is subjected to mechanical deformation, heating or through failure to pass standard adhesion tests. In some cases the problem may only manifest itself after chromium plating. This is due to the forces induced by the highly stressed chromium deposit.

Adhesion problems are nearly always caused by deficiencies in the pre-treatment operations, such as incomplete removal of greases, oils, dirt or oxides. Other pre-treatment problems include the formation of metal soaps from polishing compounds, silicic acid films from acids reacting with silicated cleaning solutions and immersion copper deposits from contaminated acid dips or pickling solutions.

It should be noted that adhesion failures do not necessarily occur between the substrate and the nickel plate. With composite coatings failure may be between the substrate and undercoat or between an undercoat and the nickel. Possible adhesion problems between nickel layers is discussed in Chapter 11.

LACK OF BRIGHTNESS / POOR LEVELLING / DARK STREAKING /UNEVEN APPEARANCE

Appearance problems apply particularly to bright or decorative plating but, even for purely functional applications, non-uniform colour or texture may be a cause for rejection. Further, the abnormality may be an indication of solution imbalance, incorrect operating parameters or solution contamination. Refer to Chapter 5 Decorative nickel plating, and Chapter 8 Testing procedures for nickel electrodeposits.

BRITTLENESS

Poor ductility or brittleness can occur due to solution imbalance (particularly high chloride levels), effects of impurities or, in the case of bright baths, excess brighteners.

TROUBLE-SHOOTING TECHNIQUES

Before discussing specific techniques, it is worth noting that experience is by far the most valuable tool a trouble-shooter can possess. It is therefore vital to become fully familiar with every aspect of the operation when the line is working smoothly. By 'walking the line' and taking note of instrument settings, agitation rates, filter operation, solution levels, appearance of work at each stage, etc., you can readily build experience. Having an intimate knowledge of the plating line will expedite solutions to future problems, by highlighting any changes from normal operation.

When a problem does arise, a great deal of time and frustration can be saved by applying a systematic approach to the investigation. The essential steps in trouble-shooting are:

DEFINE EXACTLY WHAT THE FAULT IS

To give a few simple examples:

- Is the speckled effect a problem of roughness or pitting?
- Is the work being rejected due to a general lack of brightness, inadequate levelling, presence of a haze or bloom, or perhaps due to dull patches which might indicate a pre-treatment problem?
- Or, in the case of an adhesion problem, is the nickel coating peeling from the substrate or from a copper undercoat?

INVESTIGATE THE FREQUENCY AND DISTRIBUTION OF THE DEFECT

What percentage of the work exhibits the defect? If less than 100%, look for any *pattern of distribution*. For example, are the defects found – only on some specific components, on all types of work, only on certain batches of work, at certain times during the day, on every load, on every second (third, etc.) load, on certain positions on a rack, on particular parts of the component, or on some other specific pattern?

This type of investigation can provide valuable clues as to the source of the difficulty. Just one example will suffice. Assume you are investigating a roughness problem in a plating line that has two cells for copper plating and three cells for nickel plating. You note that all types of work are affected but only on every second flight bar. This would immediately suggest that the roughness is originating in one of the two copper cells rather than in the nickel. The roughness might not have been easily seen at the copper stage due to the lower level of brightness.

CHECK OUT POSSIBLE FACTORS

- Process solutions operating outside their specific ranges of concentration or operating parameters
- Contamination of process solutions or rinses
- Anode problems – torn anode bags, poor contacts, low nickel level in baskets, solution level over top of baskets
- Any recent changes in nature of work or operating procedures
- Equipment problems – racks, barrels, electrical contacts, ancillary equipment

ISOLATE THE CAUSE

Use the information gathered to establish possible causes and, when necessary, run trials.

TAKE CORRECTIVE ACTION

Take the appropriate action to overcome the problem and to prevent it from recurring.

11. PRACTICAL TIPS

EFFECTIVE RACKING FOR ELECTROPLATING

Although components are sometimes wired for electroplating (suspended on copper wires), this method has several drawbacks. It is difficult to ensure that the components are correctly positioned in relation to the anodes, it is wasteful of nickel and the wires may tend to swing due to the agitation. Additionally, wire marks are often a problem. If wiring is selected, it is much preferred to attach the wires across a support frame. This allows the total cathode area (and hence, the current density) to be accurately controlled and also eliminates the problem of swinging.

The preferred approach is to employ suitably designed plating racks. There are a number of essential aspects to consider in the design of plating racks.

- The rack must be capable of carrying the maximum current without overheating. For nickel/chromium plating, the chromium plating stage will require considerably more current than the nickel, and this must be taken into account when designing the rack.

Figure 18 Plating rack specifically designed for automotive wheels

Photo courtesy of Associated Rack Corporation.

- The contacts with the cathode rod or flight bar must be designed to provide good electrical contact. V-type contacts are generally preferred.
- The rack tips or prongs must be designed to provide positive suspension of the components and good electrical contact. Special consideration is required when designing the tips for plating on plastics to avoid burning off the thin metallised film.
- Wherever possible, the rack tips should be positioned in recessed areas of the work to avoid nodular build up on the tips.
- Consideration should also be given to avoiding contact marks on significant surfaces of the work.
- The rack tips are commonly fabricated from stainless steel to facilitate stripping.
- Rack coatings (typically plastisols) should be continuous and free of pores with only the contact points exposed.

CARE AND MAINTENANCE OF PLATING RACKS

It is vital that plating racks are maintained in good condition if they are to perform satisfactorily. Appropriate storage of racks is important to avoid accidental damage – racks should be hung from rails rather than placed on the floor.

Racks should be inspected regularly. Damaged coatings can cause considerable problems including entrapment and carry-over of process solutions and/or metal build up on the racks. Rack tips may become loose, leading to poor or intermittent contact. Any such damage should be attended to without delay.

Excessive build-up of metal on the rack tips or prongs must be prevented by regular stripping. Mechanical removal should be avoided because of the likely damage to the racks. Nickel can be stripped either by chemical immersion using nitric acid-based strippers or anodically in proprietary electrolytic rack strippers. These anodic strippers are particularly effective if applied after each process cycle. It should be emphasised that proper attention to rack stripping is an essential part of process control.

REDUCING SOLUTION LOSSES

For both economic and environmental reasons, it makes sense to reduce solution losses. Losses can result from various causes including:

- *Leakage* from defective valves, pumps or other equipment
- *Spillage* due to careless handling, unsupported hoses, overflowing of tanks, etc.
- *Filter cleaning and servicing* – where applicable, the use of suitable drip trays below the filters can be helpful in recovering solutions that have drained from the filters during filter maintenance.
- *Carry over of process solutions*. This can be a major source of solution losses but carry over losses can be reduced in various ways:
  - First, ensure that parts are racked to allow free drainage, avoiding retention of solutions in cup-shaped or similar areas of the work
  - Next, increase the drain time if possible
  - In the case of barrel plating, use cylinders with the largest acceptable size of holes and/or, where possible, rotate the cylinder during the lift transfer.
- *Purification procedures*. Many purification procedures for nickel plating involve pumping to a treatment tank for high pH or carbon treatment followed by settling and finally filtering back into the plating tank. Unless care is taken, significant solution losses can occur during these operations. In particular, nickel solution can be retained in the sludge. Good practice involves drawing off the clear solution without disturbing the settled solids. Depending on the equipment available, various techniques can be used including gradually lowering the suction hose as the level falls to disturb the sludge as little as possible. Even so, the remaining sludge will contain valuable plating solution. One way to recover much of this solution is to transfer the sludge to a suitable drum where it can be allowed to settle further, thus permitting more solution to be drawn off. If available, the solids can also be removed by centrifuging or filtering.

AVOIDING ADHESION PROBLEMS BETWEEN THE SEMI-BRIGHT AND BRIGHT NICKEL COATINGS WHEN PROCESSING DUAL-LAYER NICKEL

Under normal operating conditions the adhesion between the semi-bright and bright nickel coatings will be excellent.

However the problem can occur if the semi-bright nickel deposit is allowed to become passive. Passivity can result if the nickel is exposed to the air or immersed in a rinse bath for extended periods. Passivity can also be caused by part of the nickel coating becoming anodic (even for a second or so) due to some “bi-polar” effect.

For example, (particularly in conveyor type plants), the work rack can be affected by bi-polar conditions as it exits the semi-bright tank or as it enters the bright nickel tank (i.e. when contact has been broken).

Several approaches may be made to eliminate this bi-polar effect (e.g. use a "live" exit and/or entry or re-position the anodes to avoid the possibility of current flowing between the rack and anode before the rack is fully immersed and contact has been effected).

HOW TO AVOID CHROMIUM PROBLEMS IN DECORATIVE NICKEL/CHROMIUM PLATING

Chrome blows and **misplates**. A common problem with chromium plating is poor coverage of the chromium, particularly around holes (although it may also be experienced in recesses and rough areas). This is generally due to the formation of hydrogen gas pockets and the upward sweep or "blow" of the gas from these areas. The problem can be overcome by suspending the articles in such a manner that gas pockets are avoided. It is often also necessary to plug all holes and seams. The chromium coverage into difficult areas can sometimes be improved by briefly "striking" the work at a higher voltage, before reducing to the normal voltage for the balance of the plating time.

Whitewashing and **false burns**. These terms refer to irregular white patches or streaks, which are sometimes experienced when plating bright chromium over nickel. The problem is caused by passivity in the nickel. The passivity can result from various conditions, but is most frequently the result of a portion of the nickel surface becoming anodic even for an extremely short period. This can occur if the component or rack becomes bi-polar. A typical situation, in a conveyor type automatic machine, is where a section of the rack load becomes briefly bi-polar, either as the work exits the nickel or enters the chromium bath. The false burn may appear on the *lower trailing corner of the rack*, when the bi-polarity occurs during exit from the nickel and on the *lower leading corner of the rack* if the bi-polarity is present on entry to the chromium. Where this is the problem, live leads on exit and/or entry should be fitted. Passivity can also arise due to excessive dwell time in the chromium solution before current is applied. Not surprisingly, any condition which makes the nickel more prone to passivity can contribute to the problem, for example, high brightener concentration or high pH.

PREVENTIVE MAINTENANCE

As in any production operation, close attention to the maintenance of equipment and process solutions will pay dividends in avoiding future problems.

In electroplating, particular care should be given to the condition of all electrical connections including V-blocks, bus-bar connectors and anode contacts. Plating racks and jigs also require regular inspection and maintenance. Instruments and other control equipment should be regularly checked.

Splashing or spray from chemical tanks can lead to corrosion, so regular cleaning to remove dried-on salts is essential. All spillages should be cleaned up immediately.

Most items of equipment will require routine maintenance including barrels, pumps, filters, air blowers, valves, exhaust fans, exhaust ducts, fume scrubbers, heating equipment, effluent treatment probes, conveyor systems, etc. Tank linings should be inspected and repairs arranged when necessary.

On the chemical side, it is important to implement a regular maintenance schedule covering all process solutions. This would include routine additions, replacement of cleaners and other pre-treatment solutions and regular purification procedures.

12. LOOKING AFTER THE ENVIRONMENT

Throughout the world, there is a growing recognition of the serious effects of pollutants on the environment and the need for industry to take a responsible role in controlling the discharge of hazardous and toxic wastes. Indeed there is now considerable public, political and regulatory attention being applied to ensure that industry reduces the level of pollutants released to the environment.

The electroplating industry is often considered chemically intensive and therefore must commit considerable resources to waste management and pollution control in order to meet its environmental responsibilities. It is becoming increasingly important for waste management to encompass waste minimisation and recovery techniques, as well as the treatment and disposal of wastes.

WASTE MINIMISATION

In electroplating plants, waste products are chiefly generated through chemical leakages, floor spills, disposal of spent or contaminated solutions and by drag-over of process solutions. In the previous chapter we discussed how solution losses and drag-over could be reduced. Attention to these aspects can significantly lower the amount of wastes being produced.

The disposal of spent or contaminated process solutions, particularly cleaners and other pre-treatment solutions, can also represent a significant waste load. Attention should therefore be directed towards extending the life of these solutions. For example, the buildup of contaminants can be reduced by simple means such as the skimming of cleaners to remove oils and the immediate removal of dropped articles from acid dips.

Chemical control and good housekeeping can also contribute to minimising the need to dispose of process solutions.

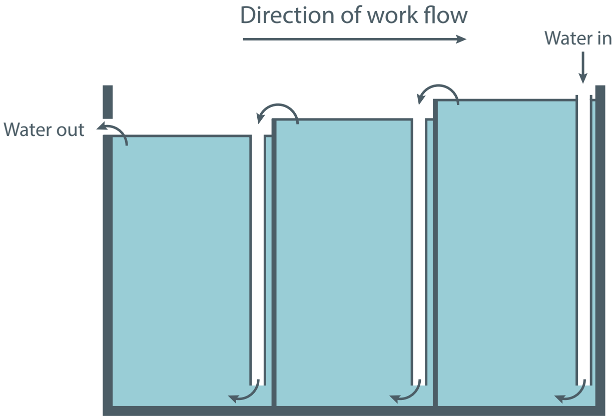
RECOVERY TECHNIQUES

CONCENTRATE RETURN METHODS

One approach for recovering nickel in an electroplating operation is to concentrate the rinse water and to return the concentrated solution back into the plating tank.

The use of multiple counterflow rinses significantly reduces the required flow of water and means that the first rinse following the plating bath is relatively concentrated. This may be fed back into the plating tank to replace evaporation losses. However, as the rate of evaporation from nickel solutions is not particularly high, some additional form of concentration is generally needed. The most interesting techniques for electroplating include evaporation, reverse osmosis and electrodialysis.

Figure 19 Multi-station counterflow rinse tank



Before discussing these techniques, it is important to note that any concentration process inevitably returns impurities and brightener reduction products to the plating solution as well as the nickel salts. This may necessitate additional purification procedures which, in some cases, may result in some losses of nickel or generate additional waste.

The return of concentrates can also lead to a build-up of nickel in the solution. This is the result of the anode efficiency being 100% while the cathode efficiency is somewhat lower. In the normal course of events, the gain in nickel concentration may be offset by dragout. The return of concentrate causes the nickel content to rise.

Another potential problem is a build up of sodium in the nickel solution. This can occur where the carriers or stress control additives are based on sodium compounds such as sodium saccharin. These limitations need to be considered when implementing a recovery system based on the return of concentrates.

Of the concentration techniques available, evaporation is perhaps the simplest and has been applied widely in electroplating operations, particularly to chromium plating. Energy costs need to be considered.

Reverse osmosis has also been available for many years. The main limitation is it cannot produce highly concentrated streams and there may be insufficient loss through normal evaporation, to accommodate the direct return of the concentrate.

Electrodialysis has low energy consumption and can produce concentrated streams. Against this is a relatively high maintenance cost. An interesting feature of this technology is that it may be applied for the continuous removal of impurities from bright nickel solutions by circulating the nickel solution slowly through the unit.

NON-RETURN METHODS

There are also recovery techniques which do not involve the return of concentrates. These non-return methods obviate any concern as to the accumulation of impurities or primary metal in the bath. Essentially, these techniques involve recovering metal from the rinse waters without return to the plating bath. The outflow from counterflow rinses is directed to a recovery unit and finally discharged to the waste treatment plant after the valuable metal has been removed.

The recovery method is generally based on electrowinning or electrolytic metal recovery. In order to produce a saleable product, the recovered metal should be in the form of a solid slab or sheet. Equipment capable of recovering metal in this form generally utilises some form of rotating cathode or other means of achieving high agitation rates.

WASTE TREATMENT

The conventional treatment of nickel-containing rinse waters, consists of pH adjustment to 9.3–10.0 to precipitate the nickel as nickel hydroxide. This is followed by flocculation, clarification and the production of a wet sludge. Some form of sludge dewatering is generally employed to facilitate handling and to reduce shipment and disposal costs.

Close monitoring of the pH is essential to obtain satisfactory flocculation and to meet the acceptance limits for discharge of the treated effluent.

The presence of complexing or chelating agents can inhibit the removal of nickel from the waste stream. These can originate from pre-treatment solutions and to meet the stringent discharge requirements for nickel, it may be necessary to segregate the nickel rinse waters or to modify the formulation of cleaners to remove the effects of these complexants.

Nickel plating facilities often incorporate cyanide-based solutions such as copper plating, and chromium plating solutions, which contain hexavalent chromium. Rinse waters from such solutions must be segregated and treated separately before being mixed with the nickel waste stream. Cyanides must be oxidised, usually by chlorination, and hexavalent chromium reduced to trivalent using sulphur dioxide or metabisulphites.

The disposal of spent or contaminated solutions can be expensive and troublesome. A common approach is to slowly feed the concentrated solution into the effluent stream. Care should however be exercised to ensure that this does not affect the flocculation process.

The design of waste treatment plants is critical to their ability to consistently meet the regulated discharge limits. Equally important is the need to provide ongoing maintenance and monitoring of the operation.

DISPOSAL OF SLUDGES AND SOLID WASTES

Increasingly stringent regulations covering the disposal of waste products to landfill are being enforced by local authorities. Generally, metal-bearing sludges including nickel are treated as regulated wastes and their disposal is strictly controlled.

Concern is based on the possibility of leaching toxic metals into the landfill. Recent investigations have shown that nickel sludges can be stabilised against leaching by using a dual-alkali treatment in which liquid magnesium hydroxide is used in conjunction with liquid sodium hydroxide.

In some cases, nickel-bearing sludges can be recycled. To be accepted for recycling, sludges must meet certain requirements, including nickel and moisture content and impurity level. The economics obviously will depend on volumes and transport costs.

13. HEALTH AND SAFETY

Nickel and nickel salts used in electroplating can pose health hazards*[1], and precautions should be taken to minimise exposure of operators, technicians and other people in areas surrounding plating plants and ancillary facilities.

Soluble nickel can cause dermatitis through contact with the skin, may cause lung cancer after repeated exposure through inhalation, and can possibly affect the unborn child. Therefore, steps should be taken to avoid contact with nickel plating solutions, by minimising batch treatment of the electrolyte, the cleaning of anodes and other activities that generate aerosol mist. Particular care must be taken when changing filters and working on other process equipment such as pumps and air agitation lines, or when manually cleaning anode rods.

Workers should avoid prolonged exposure to nickel solutions to prevent skin irritation or dermatitis. People who have become skin *sensitised* should take particular care to avoid contact with nickel and its compounds, by always wearing work gloves and immediately washing one's hands in the event of accidental contact. This applies as much in onsite or outside laboratories testing nickel plating solutions, as in the plating plant itself.

For some individuals, contact dermatitis can be caused through the wearing of jewellery which leaches nickel upon contact with sweat in amounts above 0.5 µg Ni cm^{-2} (item)/week (e.g. REACH*[2] regulation [item 27 of Annex XVII]). For this reason, nickel plating or nickel undercoats under gold plate should not be used in costume jewellery and other items normally worn next to the skin. In the occupational setting, the Nickel Institute (September 2014) recommends keeping daily dermal exposures to soluble Ni compounds below 0.44 µg Ni cm^{-2} (skin) unless other local regulatory dermal standards apply.

**Note:*

[1] *Nickel salts (e.g., Ni sulphate, Ni sulphamate) carry the following human health hazard classifications under GHS: (Global Harmonized System): Acute Tox. 4 (H302: Harmful if swallowed and H332: Harmful if inhaled), Skin Irrit. 2 (H315: Causes skin irritation), Resp. Sens. 1 (H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled), Skin Sens. 1 (H317: May cause an allergic skin reaction), Repr. 1B (H360: May damage fertility or the unborn child, developmental effects), Muta. 2 (H341: Suspected of causing genetic defects), Carc. 1A (H350: May cause cancer by inhalation route only), and STOT Rep. Exp. 1 (H372: Causes damage to respiratory tract through prolonged or repeated inhalation exposure). Nickel metal carries the following human health hazard classifications under GHS: Skin Sens. 1 (H317: May cause an allergic skin reaction), Carc. 2 (H350: May cause cancer by inhalation route only), and STOT Rep. Exp. 1 (H372: Causes damage to respiratory tract through prolonged or repeated inhalation exposure).*

[2] *A framework of chemical regulation in the European Community.*

AEROSOL NICKEL

To limit exposures to nickel through inhalation, compliance with national occupational exposure limits (OELs) is recommended. In cases where OELs have not been updated within the last decade, the Nickel Institute recommended values correspond to the OELVs for nickel compounds recently adopted in the EU:

- 50 µg Ni m^{-3} (as inhalable aerosol fraction)
- 10 µg Ni m^{-3} (as respirable aerosol fraction)

The above values are protective of possible respiratory effects such as respiratory toxicity and carcinogenicity as well as possible reproductive and mutagenic effects associated with inhalation exposure to Ni salts and Ni metal.

Needless to say, inhalation and skin contact should be minimised or avoided completely by good work practices, including:

Risk management for operators and technicians

- Mandatory use of protective clothing, eye protection and gloves
- Local exhaust ventilation
- Special care during bath make-up, maintenance and batch treatment
- Wearing of respirators with filters for any situation that risks high inhalation exposure (above OELs) to aspirated nickel solution

Works management

- Provision of highly visible safety and warning signs
- Separation and protection of clean areas from the nickel plating work zones, such as food preparation and eating facilities, offices and first-aid room
- Train operators and technicians on matters of good hygiene and the importance of washing hands frequently. Prevent smoking, eating and drinking near the nickel plating line

It should also be noted that a number of hazardous or corrosive chemicals are used in the pre-treatment and other operations associated with nickel plating. These must be handled and stored in accordance with substance-specific guidance, regulations and good operating practice.

NICKEL ALLERGY

Nickel is one of the most common causes of allergic contact dermatitis (ACD). Nickel sensitisation is the condition of becoming allergic to nickel. Nickel ACD (NACD) is the skin reaction that occurs in individuals once they are nickel-sensitised (or nickel allergic). Nickel sensitisation and NACD may occur when a sufficient amount of nickel ions (above the threshold for the immune reaction) is released from nickel-containing articles when they are in prolonged and direct contact with skin, as a result of corrosion of elemental nickel in the articles. The amount of nickel release depends on the type of material of which the article is made, its susceptibility to corrosion (in sweat especially), and the contact time with the skin. After release of nickel from the article, sufficient amounts of nickel ions must be absorbed through skin to cause the nickel sensitisation or NACD reactions.

NACD can occur as a rash, itch, redness, or dry skin in nickel-sensitised persons. Nickel Allergy is not an inherited condition and thresholds and symptoms may vary from one individual to another. Once sensitised, sufficient further exposure to sufficient amounts of nickel ions can cause NACD. While the symptoms will dissipate after removal of the source, NACD can reoccur with further exposure to sufficient amounts of nickel ions.

Regulation of nickel allergy

Non-occupational nickel allergic reactions sometimes occur when skin is in direct and prolonged contact with nickel-plated fasteners such as clothing hooks, clasps, zippers and may also arise from costume jewellery and body piercing, if these articles release sufficient amounts of nickel ions. In 1994, the EU issued the so called ‘Nickel Directive’ that limited the amount of nickel release from articles intended to come into direct and prolonged contact with the skin. This was subsumed into the EU Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), Annex XV11, Entry 27 in 2007, the relevant part of which states:

Nickel

1. *Shall not be used:*
   - a. *in all post assemblies which are inserted into pierced ears and other pierced parts of the human body, unless the rate of nickel release from such post assemblies is less than 0.2 μg cm^{-2} $week^{-1}$ (migration limit).*
   - b. *in articles intended to come into direct and prolonged contact with the skin such as:*
     - *earrings,*
     - *necklaces, bracelets and chains, anklets, finger rings,*
     - *wrist-watch cases, watch straps and tighteners,*
     - *rivet buttons, tighteners, rivets, zippers and metal marks, when used in garments,*

   if the rate of nickel release from the parts of these articles coming into direct and prolonged contact with the skin is greater than 0.5 μg cm^{-2} $week^{-1}$; and
   - c. *in articles such as those listed in point (b) where these have a non-nickel coating, unless such coating is sufficient to ensure that the rate of nickel release from those parts of such articles coming into direct and prolonged contact with the skin will not exceed 0.5 μg cm^{-2} $week^{-1}$ for a period of at least two years of normal use of the article.*
2. *Articles which are the subject of paragraph 1, shall not be placed on the market unless they conform to the requirements set out in those points.*
3. *The standards adopted by the European Committee for Standardisation (CEN) shall be used as the test methods for demonstrating the conformity of articles to paragraphs 1 and 2.*

Two CEN test methods are applicable for coated articles to determine nickel release rates. EN 1811:2011+A1:2015[17], is the reference test method used to measure the amount of nickel released due to corrosion in a simulated sweat environment, for a fixed period of time. For articles with a non-nickel containing top coating, the EN 1811 test is preceded by test method EN 12472:2020[18] that simulates two years of wear and corrosion.

Additionally, there is a European Standard EN 16128:2015[19] for determining nickel release from spectacle frames, sunglasses and other eyewear or articles for face protection.

LABORATORY TEST METHOD FOR NICKEL RELEASE

EN 1811 TEST METHOD FOR NICKEL RELEASE AND CALCULATION OF NICKEL RELEASE RATE FOR CONFORMITY ASSESSMENT[17]

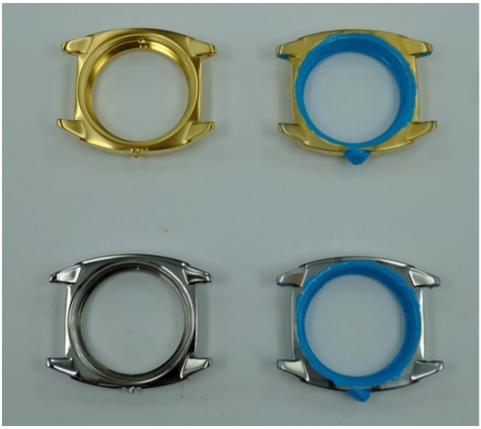
The laboratory test method for the conformity assessment of nickel release is provided by the CEN standard EN 1811 – Reference test method for release of nickel from all post assemblies which are inserted into pierced parts of the human body and articles intended to come into direct and prolonged contact with the skin.

The article to be tested for nickel release is placed in the artificial sweat test solution*[3] for one week. The concentration of dissolved nickel in the solution is determined by an appropriate analytical method, for example, inductively-coupled plasma spectrometry. The nickel release is expressed in micrograms per square centimetre per week (µg/cm^2/week). A summary of the following key steps involved in the nickel release test are included below.

MASKING

Non-significant (applicable) surfaces of the articles, which do not come into direct and prolonged skin contact, are masked off with a lacquer or similar protective coating to prevent nickel release, in according to Clause 7.1.3 of EN 1811, leaving only surfaces likely to come into prolonged skin contact exposed to the nickel release test (*Figure 20*).

Figure 20 Non-significant surface masked with paint



**Note:*

[3] *Artificial sweat solution containing 0.5 % by weight sodium chloride; 0.1 % by weight lactic acid and 0.1 % by weight urea; pH adjustment to 6.5 ± 0.05 by sodium hydroxide*

NICKEL RELEASE PROCEDURE

1. The article should be suspended in the appropriately sized and enclosed vessel of a non-metallic, nickel-free and nitric-acid-resistant material, so that the unmasked surface(s) of the article is/are totally immersed in the artificial sweat solution of about 1 ml per cm^2 of the article's area.
2. The article is removed after immersion at (30 ± 2)°C for (168 ± 2) h without agitation, the final release solution should then be made up with the artificial sweat solution to the volume (V in ml), including addition of nitric acid to a concentration of 1% in this diluted release solution.

DETERMINE THE AMOUNT OF NICKEL

1. Carry out nickel release tests, measured in micrograms per square centimetre per week ($\mu g/cm^2$/week), on 3 test articles from the same batch and on duplicated blank tests at the same time.
2. Make duplicate measurements of each release solution by analytical spectrometer, for example, inductively-coupled plasma spectrometry, capable to detect 0.01 mg nickel per litre in the release solution.

CALCULATION OF NICKEL RELEASE

Nickel release of a sample, d, expressed in $\mu g/cm^2$/week

$$d = \frac{V(C_1 - C_2)}{1000\ a}$$

where

a is the sample area of the test article, in cm^2;

V is the release solution volume after dilution, in ml;

C_1 is the mean nickel concentration in the diluted release solution after 1 week, in $\mu g/L^{-1}$;

C_2 is the mean value of the nickel concentration in the blank solutions after 1 week, in $\mu g/L^{-1}$

CONFORMITY ASSESSMENT

Non-conformity is determined if nickel release value significantly exceeds its limit when the lower confidence interval boundary of the measured release exceeds the legally prescribed limit

$d_{meas} \geqslant d_{lim} (1+ku)$

where

k is the coverage factor for the chosen significance level (0.05) which gives a corresponding value of 1.65 for the one-sided t-test assuming a large number of degrees of freedom for the combined uncertainty;

d_{lim} is the legal 0.2 $\mu g/cm^2$ /week or 0.5 $\mu g/cm^2$/week limit, respectively;

d_{meas} is the determined mean nickel release value from replicate concentration measurements;

u is the combined expanded measurement uncertainty (46% per EN 1811 determination).

As a result, an article is non-compliant only when the nickel release is $\geq$0.88 $\mu g/cm^2$/week and $\geq$ 0.35 $\mu g/cm^2$/week for the EU migration limit of 0.5 $\mu g/cm^2$/week and 0.2 $\mu g/cm^2$/week, respectively, after considering the measurement uncertainty of 46% in EN 1811 test standard.

EN 12472 SIMULATION OF WEAR AND CORROSION FOR THE DETECTION OF NICKEL RELEASE FROM COATED ARTICLES[18]

Nickel-containing articles with a non-nickel containing top coating are subject to simulation of 2 years of wear and corrosion in accordance with CEN standard EN 12472 before detection of nickel release by EN1811.

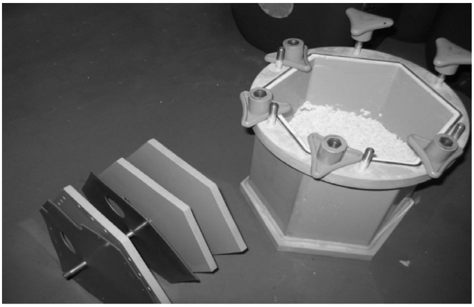
CORROSION PROCEDURE

1. The articles (opened to reveal critical surfaces) are suspended a few centimeters above the corrosive medium of (50 g/L^{-1} DL-lactic acid and 100 g/L^{-1} sodium chloride in de-ionized water) in a closed container for 2 h at 50± 2 °C.
2. The articles are then rinsed with de-ionized water and allow to dry at room temperature on absorbent paper for about 1 h.

WEAR PROCEDURE

1. Test articles are hung inside the retaining assembly to prevent damage by collision with barrel walls or other parts.
2. The retaining assembly is inserted into the tumbling barrel of hexagonal cross-section with an internal diameter of 19 cm (*Figure 21*), which is then half-filled with the premix wear medium*[4].
3. The enclosed tumbling barrel is rotated at a horizontal speed of (30 ± 2) rotations per minute for a total of 5 h ± 5 min, and reverse rotational direction after 2.5 h ± 5 min.

Figure 21 Typical hexagonal tumbling barrel (right) used in the wearing of coated articles suspended between 2 plates of the retaining assembly (left).



**Note:*

[4] *Preparation of the wear medium*
Homogenize the wear medium mixture (7.5g of abrasive paste for every kg of the total amount of granules) by rotating it in the tumbling barrel for 5 h
Abrasive paste – 6%-8% Ester wax of montanic acids-Wax E, 3% Octadecanoic acid, 30%-35% Petroleum Distillates, hydrotreated light paraffinic, 2% Polyethylene glycol cetyl/oleyl ether or triethanolamine, 48% Silicon dioxide 200 micron mesh size, and 6%-9% De-ionized water
Granules – outer shells of coconuts, which were grounded and sieved, to give a mixture of particles having dimensions between 0.8mm to 1.3mm

EN 16128:2015 for determining nickel release from spectacle frames, sunglasses and other eyewear or articles for face protection[19]

Following the simulation of wear and corrosion according to EN 12472, this reference method[19] comprises:

1. Coating test: For parts with an organic coating, using Electrochemical Impedance Spectroscopy to decide whether the coating is of sufficient quality to prevent nickel release. The impedance in $\Omega\ cm^2$ of the test part at 1 Hz in the specified saline solution is determined by using a specialized equipment, potentiostat. The determination should be greater or equal to the threshold limit ($3 \times 10^5\ \Omega\ cm^2$) for the all separated test parts of front, both left and right side of the spectacle frame, in order to pass the nickel release test for coated parts.
2. Migration test: For parts without an organic coating, to determine nickel released by an artificial sweat solution onto a test paper, followed by quantitative analytical detection. The nickel content of the extract solutions (2% nitric acid) of the test papers, separately tested on specific test area of front, side, bridge and trim of the spectacle frame, were determined by a suitable analytical instrument. The nickel release determinations should be less than or equal to the 0.76 $\mu g/cm^2$/week (legal 0.5 $\mu g/cm^2$/week limit plus the measurement uncertainty 31%) in order to pass the migration test.

14. PREVENTION OF NICKEL RELEASE FROM DECORATIVE NICKEL PLATED AND ALLOYED ARTICLES

In 1998, G. Norman Flint[20] of the Nickel Development Institute summarised metallurgical factors in the context of allergic contact dermatitis, including nickel-containing surface coatings and alloys.

However, there was no direct comparison of nickel release on various nickel containing materials subjected to the up-to-date the CEN test methods. Recently, C. M. Whittington and W. Y. Lo evaluated the nickel release of a number of surface finishing with nickel containing plating layer or alloy in their peer-reviewed papers and an article published in 2015[21], 2018[22] and 2019[23, 24], respectively.

C. M. Whittington and W. Y. Lo's recent studies demonstrated that electrodeposits of sulphur-containing bright nickel will more nickel than the EU limits, when evaluated by the CEN test methods. However, a range of decorative non-nickel surface coatings can prevent nickel release from nickel plated articles under the test conditions of the CEN standardised tests, rendering them compliant with EU nickel restrictions and suitable for placement on the EU market. The results from testing of these materials in accordance with EN 12472:2005+A1:2009[25] and EN 1811:2011+A1:2015 (for non-nickel coatings) and, EN 1811:2011+A1:2015 (for non-coated) are presented in *Tables 12a* and *12b*. Using test criteria, per EN 1811:2011+A1:2015, of ⩾ 0.88 µg/cm2/week is used for prolonged contact articles for common consumer products, their study demonstrates that appropriate selection of materials and surface finishes for the manufacture of articles which are likely to come into direct and prolonged contact with skin, can prevent corrosion of elemental nickel and nickel release by sweat in service[26] which enable nickel-containing consumer products to be safely placed on the market without concern for nickel release. Although the latest EN 12472:2020 standard has some minor changes in the technical part including the amendment on the requirement of the abrasive material in a quantitative manner and the clarification on the purity of the stock solution in the corrosive medium, the results of these earlier studies should give comparable trends for articles with various non-nickel top coatings on nickel release when tested with the latest EN 12472:2020 standard. The findings and conclusions in the references[21-24, 26] are limited to the materials tested and the test standards used.

SUMMARY OF PREVENTING NICKEL RELEASE FROM DECORATIVE SURFACE COATINGS

CHROMIUM

- Regular (conventional) chromium deposited from a hexavalent electrolyte with controlled thickness, forms an effective barrier layer.
- Microporous chromium deposited from a chloride trivalent electrolyte, with controlled thickness and pore count, produces a deposit that impedes nickel release when tested in accordance with the CEN standard test methods, within the EU limits. The development of microporosity inhibits microcracking of trivalent chromium, with 10,000-20,000 pores cm^{-2} being optimum.
- In both cases, excessive deposit thickness should be avoided. The minimum local thickness of 0.30 µm required under ISO standards[1,2] for decorative deposits is sufficient.

ELECTROPHORETIC COATINGS

Pore-free electrophoretic coatings over electrodeposited bright nickel will provide a barrier layer to prevent nickel release and pass the CEN tests (being within the EU limits). Such organic non-nickel topcoats may be dyed to produce a variety of coloured surface finishes.

PRECIOUS METAL COATINGS

Articles with precious metal surface coatings over bright nickel are particularly prone to higher rates of nickel release. Typically this acceleration occurs when a thin, porous flash topcoat of more noble gold is applied (<0.1 µm thickness), which is common for wearable articles such as costume jewellery and watch cases. However, an electrodeposited palladium barrier coating used either as a topcoat or an intermediate layer over bright nickel is effective in passing the CEN nickel release tests and meeting the EU nickel release limits.

NICKEL-CONTAINING DECORATIVE ALLOYS

The reaction of alloys with sweat may be quite different from that of the individual constituent metals, especially with alloys containing metals which form a protective oxide film such as stainless steels. Thus, the concentration of nickel in an alloy bears no relation to its potential for nickel release in the context of allergic contact dermatitis[20]. Following are common examples of wearable articles routinely manufactured from nickel-containing alloys, which pass the CEN nickel release tests:

- A gold alloy containing 6% nickel, used in the manufacture of costume jewellery
- Watch cases made of nickel-containing stainless steel Grades 304 (UNS S30400) and 316 (UNS S31600)

To prevent nickel allergy[26] at source for articles intended for direct and prolonged skin contact, product designers, manufacturers and merchandisers should specify:

1. Nickel-containing decorative alloys such as austenitic stainless steel or gold alloys that pass the CEN tests for nickel release, or
2. Bright nickel plated articles with a non-nickel barrier layer of electrodeposited chromium (regular hexavalent chromium or trivalent microporous chromium), palladium or electrophoretic coatings. This could ensure the rate of nickel release does not exceed 0.5 $\mu g\ cm^{-2}\ week^{-1}$ for a period of at least 2 years of normal use under the test conditions of the CEN standardised tests, rendering them compliant with EU nickel restrictions and suitable for placement on the EU market.

Table 12

Table 12a Nickel release from various nickel/ nickel-chromium plated ABS plastics specimens, some with additional top coats*						
Specimen	Article	Base materials	Plating on surface & thickness (µm)	Test	Nickel release rate (µg cm^{-2} week^{-1})	Result*
1	Bright nickel-regular hexavalent chromium plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ Cr^{6+}(0.16)	1	<0.01	Pass
				2	<0.01	
				3	<0.01	
2	Bright nickel-regular hexavalent chromium plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ Cr^{6+}(0.27)/ Electrophoretic	1	<0.01	Pass
				2	0.01	
				3	0.01	
3	Bright nickel-regular hexavalent chromium plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ Cr^{6+}(0.18)/ sol-gel	1	0.01	Pass
				2	<0.01	
				3	<0.01	
4	Bright nickel-microporous hexavalent chromium plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ mpCr^{6+}(0.40)	1	0.13	Pass
				2	0.01	
				3	0.23	
5	Bright nickel-microporous hexavalent chromium plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ mpCr^{6+}(0.28)/ Electrophoretic	1	<0.01	Pass
				2	0.01	
				3	0.01	
6	Bright nickel-microporous hexavalent chromium plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ Cr^{6+}(0.16)/ sol-gel	1	<0.01	Pass
				2	0.07	
				3	<0.01	
7	Bright nickel-regular chloride trivalent chromium plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ Cr^{3+}(0.41)	1	2.82	Fail
				2	4.19	
				3	1.74	

Specimen	Article	Base materials	Plating on surface & thickness (μm)	Test	Nickel release rate ($\mu g\ cm^{-2}\ week^{-1}$)	Result*
8	Pearl nickel-regular hexavalent chromium plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ Cr^{6+}(0.10)	1	<0.01	Pass
				2	0.25	
				3	0.01	
9	Bright nickel-black chloride trivalent chromium plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ Cr^{3+}(0.18)	1	9.00	Fail
				2	9.89	
				3	6.72	
10	Bright nickel-plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ UV cured cathodic PU e-coat	1	<0.01	Pass
				2	<0.01	
				3	<0.01	
11	Bright nickel-regular sulphate trivalent chromium plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ Cr^{3+}(0.41)	1	20.5	Fail
				2	18.8	
				3	7.95	
12	Bright nickel-microporous-sulphate trivalent chromium (uncontrolled pores) plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ mpCr^{3+}(uncontrolled) (0.21)	1	3.59	Fail
				2	4.5	
				3	3.28	
13	Bright nickel-microporous-sulphate trivalent chromium (uncontrolled pores) plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ mpCr^{3+}(uncontrolled) (0.35)/ UV cured cathodic PU e-coat	1	0.08	Pass
				2	<0.01	
				3	<0.01	
14	Bright nickel-microporous-chloride trivalent chromium (uncontrolled pores) plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ mpCr^{3+}(uncontrolled) (0.09)	1	0.48	Fail
				2	1.56	
				3	0.58	

Specimen	Article	Base materials	Plating on surface & thickness (µm)	Test	Nickel release rate (µg cm^{-2} $week^{-1}$)	Result*
15	Bright nickel-microporous-chloride trivalent chromium (10k-20k pores) plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ mpCr^{3+}(10k-20k pores) (0.37)	1	0.11	Pass
				2	0.25	
				3	0.36	
16	Bright nickel-microporous-chloride trivalent chromium (50k pores) plated ABS plastic	ABS plastic	Cu(25)/Ni(10)/ mpCr^{3+}(50k pores) (0.31)	1	0.02	Pass
				2	0.40	
				3	0.01	

MpCr: Microporous chromium plating

** In accordance with EN 12472:2005+A1:2009 and EN 1811:2011+A1:2015*

Table 12b Nickel release from steel / stainless steel and bright nickel / precious metal plated articles*

Specimen	Article	Base alloy	Surface & thickness (µm)	Test	Nickel release rate (µg cm^{-2} $week^{-1}$)	Result*
1	Rose gold bangle	60/40 brass	Cu undercoating/ flash plating 61% Au, 38% Cu flash containing 0.4% Ni	1	0.01	Pass
				2	0.01	
				3	0.01	
2	Golden tag	Zn base die casting	Cu(25)/Ni(10)/ Pd(0.3)/ TiN(0.2)/Au flash(<1)	1	< 0.01	Pass
				2	< 0.01	
				3	< 0.01	

Specimen	Article	Base alloy	Surface & thickness (µm)	Test	Nickel release rate (µg cm^{-2} week^{-1})	Result*
3	Golden link	Zn base die casting	Cu(25)/Ni(10)/ Pd(0.3)/ TiN(0.2)/Au flash(<1)	1	< 0.01	Pass
				2	0.17	
				3	0.02	
4	Golden bangle	Zn base die casting	Cu(56)/Ni(8)/Au flash(<1)	1	1.86	Fail
				2	0.01	Pass
				3	1.36	Fail
5	Half disc	Zn base die casting	Cu(25)/Ni(5)/Pd(0.3)/ TiN(0.2)/Au flash(<1)	1	0.04	Pass
				2	0.41	
				2	0.04	
6	Half disc	Zn base die casting	Cu(25)/Ni(10)/ Pd(0.3)/ TiN(0.2)/Au flash(<1)	1	0.05	Pass
				2	0.05	
				3	0.05	
7	Half disc	Zn base die casting	Cu(25)/NiP(10)/ Pd(0.3)/ TiN(0.2)/Au flash(<1)	1	0.05	Pass
				2	0.05	
				3	0.03	
8	Half disc	Zn base die casting	Cu(25)/Ni(10)/ Pd(0.3)/ Au flash(<1)	1	0.02	Pass
				2	0.02	
				3	0.02	
9	Gold alloy disc	Au76Cu16Ni6Zn2 Alloy	Not plated	1	0.24	Pass
				2	0.32	
				3	0.32	
10	Pendant	Zn base die casting	Cu(25)/Ni(10)/Pd(0.3)	1	0.05	Pass
				2	0.01	
				3	0.03	

Specimen	Article	Base alloy	Surface & thickness (µm)	Test	Nickel release rate (µg cm^{-2} week^{-1})	Result*
11	Pendant	Zn base die casting	Cu(25)/NiP(10)/ Pd(0.3)/ TiN(0.2)/Au flash(<1)	1	0.01	Pass
				2	0.01	
				3	0.01	
12	Watch case	304 Stainless steel	Not plated	1	0.01	Pass
				2	<0.01	
				3	<0.01	
13	Watch case	304 Stainless steel	TiN(0.2)	1	0.01	Pass
				2	<0.01	
				3	0.01	
14	Watch case	316 Stainless steel	Not plated	1	<0.01	Pass
				2	<0.01	
				3	<0.01	
15	Watch case	316 Stainless steel	TiN(0.2)	1	<0.01	Pass
				2	<0.01	
				3	0.01	
16	Bright nickel-tin cobalt plated steel clip	Steel	Ni/SnCo (SnCo 45:55) (0.07)	1	6.35	Fail
				2	4.68	
				3	6.25	
17	Bright nickel-tin cobalt plated steel clip	Steel	Ni/SnCo (SnCo 40:60) (0.1)	1	2.35	Fail
				2	7.02	
				3	5.20	
18	Bright nickel-tin cobalt plated steel clip	Steel	Ni/SnCo (SnCo 39:61) (0.1)	1	0.75	Pass
				2	0.90	Fail
				3	0.62	Pass

NiP: Nickel Phosphorus Plating
**In accordance with EN 12472:2005+A1:2009 and EN 1811:2011+A1:2015 (Specimens 9, 12 and 14, without top coating, were tested in accordance with EN 1811:2011+A1:2015)*

15. ABOUT THE AUTHORS

Original written 2014 by Clive Whittington† and Ian Rose
Revised 2022 by Dr. William Lo

Ian Rose is a graduate in Industrial Chemistry and has spent all of his career in the electroplating and metal finishing industries, both in the U.K. and Australia.

He worked in electroforming R&D at EMI in London, followed by successive roles as Technical Manager with three major plating supply houses – W. Canning, then Harshaw, and finally Enthone-OMI (now MacDermid, Atotech and Enthone respectively). In these positions he was responsible for all technical matters related to customer service, process control, plus the design and specification of plating installations. He has been closely involved with major facilities in the automotive, appliance and printed circuit industries.

Ian has authored a number of technical papers presented at national and international metal finishing conferences, as well as being Technical Chairman for two Interfinish Congresses. He is an Honorary Member of the Australasian Institute of Surface Finishing.

Clive Whittington was a graduate metallurgist, a Chartered Professional Engineer, a Fellow of the Institute of Materials Finishing (UK), and an Honorary Member of the Australasian Institute of Surface Finishing.

He worked with M&T Products (now Atotech) in Australia, and then Inco (now Vale) throughout Asia, serving nickel plating installations in the automotive and other decorative plating applications. Subsequently, he worked for Alcoa in the aluminium industry, and was based in Hong Kong for many years. Then he formed his own company and acted as Agent for OMG (now Norilsk Nickel).

Clive continued to provide independent technical support to the nickel plating industry throughout the Asia-Pacific region and has authored papers on the analysis of metallic impurities in nickel plating solutions and their effects on the process. With co-workers at the Hong Kong Productivity Council, he conducted independent studies into industrial best practice.

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Dr. Lo Wai-yin William, is a graduate and Ph.D. in Chemistry, a Fellow of the Institute of Materials Finishing (UK), and the Vice-Chairman of Hong Kong Surface Finishing Society. He works as the technical adviser and industrial consultant in surface finishing industry for more than 25 years. He focuses in industrial surface finishing, especially applied R&D, technology transfer in production and waste minimization technology, as well as its related materials technology and testing. He is based in Hong Kong that enabled him to complete numerous surface finishing projects and trainings both in Hong Kong and China, covering a wide spectrum of surface finishing technologies including electroplating, anodizing and vacuum plating. As an industrial consultant, he also published technical papers and best practice guidelines. Furthermore, he and his team received a number of awards in industrial technologies and research related to various surface finishing processes.

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