

Substitution issues related to the use of nickel in electrolytic and electroless surface engineering processes

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General considerations

There has been a considerable amount of legislation enacted during the past few years related to the safer use of chemicals. This covers products used in industrial processes, those that come into intimate contact with the public and those that might be discharged into the environment. Stricter limits have been imposed on the use of the more hazardous materials and more highly controlled legislation has been introduced. The European Union has enacted a number of pieces of critical legislation in this area including the SEVESO Directive, which relates to major accident hazards and the Integrated Pollution and Prevention Control Directive. Most recently, the Registration, Evaluation, Authorisation of Chemicals (REACH) Regulation which closely controls the use of chemicals came into force in 2007.

One of the objectives of this recent legislation has been actively to encourage the substitution of some of the most hazardous substances currently in industrial and general use with alternatives that are seen to present a lesser hazard.

In principle, the policy of substitution is obviously a desirable one and has proved effective in eliminating some of the more aggressive chemical compounds from domestic and industrial situations. Some of the substitute materials may not be as effective as the ones they are replacing, but this is often an acceptable trade off when considered in terms of health and safety, or alternatively worker comfort.

Many of the smells familiar to older people, such as chlorine in toilet cleaners or ammonia in cleaning

solutions, have disappeared from the domestic scene. Some of the more aggressive domestic alkaline cleaning preparations have also been replaced by less harmful preparations.

However, when the practicalities of implementing such a policy are considered carefully and logically in a wider commercial and industrial context, substitution presents much more complex problems. One of the principal difficulties is that it is not inevitable that every hazardous material can be substituted by a suitable alternative. Any substitute must not only be effective but it is also essential that it is free from its own innate, if different, hazards.

In the perception of both the general public and many legislative bodies, there is frequently an assumption that, with respect to substitution, all chemicals can be considered similarly. This is an unfortunate and inaccurate misconception that can lead to an over-optimistic view of the potential success of any substitution programme.

There are millions of chemicals that are either available in nature or that can be synthesised in small or large quantities. All of these chemicals cannot be considered in an identical fashion in relation to substitution issues. In order to develop a realistic view, it is necessary to take a step back and look more closely at the general properties of chemicals and in this respect it is useful to consider 'chemicals' in three distinctive categories.

Organic chemicals

To say that there are a lot of organic chemicals, including naturally occurring and synthetic ones, is a gross understatement. Because of the specific and unique chemical properties of carbon, according to reliable sources, it is estimated that there are between 9.8 million and 18 million such materials.

If it therefore becomes necessary to substitute one particular organic chemical with another, for whatever reason, then this leaves a lot of scope to find something that exhibits similar, if not identical, properties to those of the material that is required to be substituted.

In addition, the structure of many organic chemicals can very frequently be altered to form another, somewhat different or even very different, compound that shows similar properties. It is often possible to synthesise totally new substances that have never existed before, often producing molecules purposely designed for a specific application. This situation occurs frequently within the most innovative branch of the organic chemical industry, the manufacture of pharmaceuticals.

Inorganic chemicals

Although there are thousands of inorganic chemicals, both naturally occurring and synthetic, the number falls short by several orders of magnitude of the number of organic compounds. Carbon has the remarkable ability to form chains of atoms often of incredible length and complexity; the only other element that exhibits this property is silicon. Consequently, the ability to synthesise new inorganic molecules is much more limited than the almost limitless scope for manufacturing novel organic ones.

It therefore follows that if a particular inorganic chemical has been selected by reason of its properties and performance for a specific application the chance of finding an acceptable substitute is much less than it would be with an organic material.

Chemical elements

There are only 92 naturally occurring elements. Up to 26 transuranic elements have been created by nuclear

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technology but these are not products that could be considered for practical applications and many, indeed, have only a transitory existence.

The laws of chemistry and physics do not allow for the possibility of creating other elements with designer properties in the way that novel organic chemicals can be synthesised. Neither is there any way in which the basic properties of an element can be changed either by chemical processes or by techniques governed by the laws of physics. Any attempt to alter elements by processes which change the structure of the nucleus results in the formation, not of a novel element, but of one that already exists.

Of the 92 naturally occurring elements around 78 find either major or minor applications in early twenty-first century technology. The elements that currently find no practical applications are obviously ones that up until now have not been shown to exhibit any useful properties. (That is not to say, of course, that their properties may not prove useful, or even essential, in new technologies or applications, as these evolve in the future). Alternatively they may be scarce and therefore very expensive or basically unstable due to radioactive decay.

Many of the most useful elements in the periodic table are defined as metals and their physical and chemical properties – as with all other elements – are fixed and unchangeable. Metallic elements are, of course, frequently mixed together with other metallic elements, as well as with non-metals, to form alloys, the number of which currently available runs into many thousands. In terms of health and safety legislation alloys are considered to retain some of the hazardous properties of elemental constituents present in amounts exceeding 0.5%.

Therefore, when working with inorganic or elemental materials, and particularly metals, in order to identify substitute materials there is very limited choice of available alternatives and very little possibility of synthesising suitable replacement products.

The use of nickel plating in surface engineering and coating

Surface engineering and coating processes involve modification of the surface of a substance in order to convey the superior properties of the modified surface to the article that is

being treated. It is rarely appreciated even by specialists in industry – let alone the general public – that somewhere in the region of 90% of all finished goods are subjected to one or even many surface engineering processes.

There is a very wide range of technologies and chemical substances that are used in the surface engineering and coating industry. These may employ organic chemicals, inorganic materials, elements including metals, as well as alloys. Very frequently combinations of all of these types of material are employed.

One of the most important metals used in the plating industry is nickel which has a history within the surface engineering industry going back almost to the time when Michael Faraday discovered the laws governing electrolysis. The original electrolytic nickel deposition processes were discovered, or invented, during the 1840s, with almost simultaneous claims for the 'first' – and obviously patentable process – being made in Russia, France and Birmingham, England. Electroless nickel plating processes were not invented until over a century later in the 1940s.

The fundamental technologies of both electrolytic and electroless plating have remained basically the same since the inception of both of these processes. The degree of refinement and improvement during the intervening years has, however, been tremendous. This has enabled these systems to be used in an increasingly varied range of applications that could not possibly have been envisaged when they were originally discovered.

The initial use of nickel metal deposition was to produce a corrosion resistant coating, on substrates such as steel, brass and copper, which fortuitously also turned out to be visually attractive. The resulting nickel plated coatings were eagerly accepted by the rapidly expanding automotive industry in the early years of the twentieth century and their utilisation grew in parallel with growing automotive manufacture. The use of the nickel-based coatings took a major leap forward in the mid-1920s when chromium plating was invented. Chromium was found to be capable of providing a tarnish free layer on top of plated nickel which, on its own, needed frequent polishing to retain its bright finish. (The resulting composite deposit system became known, in general

parlance, as 'chrome plating'. This is an unfortunate misnomer since 99% of the thickness of these coatings is nickel.).

Since that time the many excellent properties, both physical and chemical, of electroplated or electroless plated nickel combined with the versatility of the processes used to deposit the metal have spawned a very wide range of applications. Many of these depend upon the excellent corrosion resistance of nickel-based coatings but in other situations nickel is chosen for one of its other useful properties such as wear resistance and hardness. In most instances where plated nickel is used its application relies not upon one particular physical or chemical property of the metal but upon the unique combination of properties found in plated nickel. Of course, the attractive appearance of nickel plated coatings with chromium, brass, silver or gold top-coats is another highly important advantage.

Health, safety and environmental considerations of nickel

The use of all industrial processes proliferated during the early twentieth century and accelerated rapidly during the two World Wars and also in the late 1940s and 1950s as the world recovered from the Second World War. As a result consideration of the effects that these processes – and of the chemicals used in them – have on the environment and on human health became increasingly important in all industrialised countries and also, more recently, in developing countries.

Nickel metal and other nickel-containing materials, such as stainless steel, have been responsible for the positive development of a massive number of technologies. Many of these developments have, without doubt, conferred enormous benefits to the human condition. Wide recognition of this situation has meant that the use of the nickel and associated materials has proliferated since the end of Second World War.

As a result it has been responsibly decided by many authorities that the environmental and human health consequences of the uses of nickel should be examined in a detailed and systematic way. Consequently, the properties of nickel metal and associated chemicals have recently been examined with respect to the

hazards they present both in terms of human health and their impact on the environment.

A comprehensive Risk Assessment programme related to the use of nickel and its salts was initiated within the European Union in 1996 and reached completion in 2007. The programme concluded that nickel-based materials are not without risk either to human health or to the environment. The conclusion most affecting nickel plating was that the water soluble salts used in both electrolytic and electroless processes should be classified as Category 1A carcinogens, Category 1B reprotoxicants and Category 2 mutagens.

The question is therefore being asked if it is not time that these salts should be substituted by those that are less potentially hazardous or, failing that, should the use of nickel plating itself be substituted by some more benign coating process. Indeed, the existing EU Directives on the use of carcinogens and chemicals in the workplace require that substitution should be looked on as the major risk-management option.

Could the salts conventionally used in nickel plating be successfully substituted with less hazardous materials?

In order to address this question it is necessary to consider the range of nickel salts that have been used in nickel plating processes and in particular those that find the most widespread use due to their favourable performance characteristics.

There are three water-soluble salts used predominantly in electrolytic and electroless nickel plating that account for probably 95%, or more, of the nickel compounds employed.

A number of other nickel salts have

<i>Nickel sulphate</i>	NiSO ₄ .6H ₂ O
<i>Nickel chloride</i>	NiCl ₂ .6H ₂ O
<i>Nickel sulphamate</i>	Ni(SO ₃ .NH ₂) ₂ .4H ₂ O

been used in specialised applications – more generally in electroless processes rather than electrolytic ones – but these are less common.

(Nickel nitrate, although highly

Nickel acetate	Nickel fluoborate
Nickel hypophosphite	Nickel methanesulphonate

soluble, is not used for nickel plating because of the undesirable reactions of the nitrate anion – particularly in

electrolytic processes where it produces nitrous oxide fumes).

When dissolved in water all of the seven soluble nickel compounds listed produce highly dissociated solution of the divalent nickel cation and the appropriate anion. Salts in which the Ni²⁺ ion is strongly complexed cannot be used in nickel plating in the way that complexed cyanide salts of copper and zinc are used in their respective technologies. Nickel cyanide, for example, has an extremely low dissociation constant and is almost completely insoluble in water.

The precise chemical structure of Ni²⁺ ions in aqueous solution has never been fully defined despite the widespread use of solutions containing these ions not only in nickel plating but in other technologies. A new study is, however, currently in progress at Loughborough University in the UK which will, hopefully, eventually shed light on the situation.

It seems reasonable, however, to hypothesise that the positive charge on the Ni²⁺ cation attracts the negative dipole of water molecules forming a hydration sheath. Consequently, in aqueous solutions of these compounds nickel can reasonably be considered to be present as some form of hydrated cation. What is unknown, at present, is the effect that the different anionic species in solution might have upon the structure of the Ni²⁺ cation.

Nickel plating processes

There are two basic processes by which nickel metal can be deposited from aqueous solutions containing Ni²⁺ cations.

- Electrolytic deposition by the imposition of a direct electrical current
- Electroless deposition where the nickelous Ni²⁺ ions are reduced to the zero valent metallic state by chemical agents added to the solution.

Electrolytic deposition

The deposition process is bought about by the application of direct current flowing between an anode and a cathode which are immersed in a solution containing the appropriate nickel salts.

Watts nickel solution

The basic electrolyte composition most widely used in industrial nickel plating is the Watts Bath, invented in 1916. A typical composition, where nickel

sulphate provides the main reservoir of Ni²⁺ ions, is shown below.

Nickel sulphate	NiSO ₄ .6H ₂ O	300 g L ⁻¹
Nickel chloride	NiCl ₂ .6H ₂ O	30 g L ⁻¹
Boric acid	H ₃ BO ₃	40 g L ⁻¹

The main reason for the addition of nickel chloride to the solution is to facilitate the dissolution of the nickel anodes since chloride ions destroy the passive film that forms on the nickel surface. A further benefit of chloride additions is that this increases the electrolytic conductivity of the solution which allows higher deposition rates to be achieved.

Ensuring good and uniform dissolution of the anode material in nickel electrodeposition processes is an inherent problem caused by the excellent corrosion resistance of the metal. A number of methods have been devised for reducing the corrosion resistance of nickel anode materials so that they dissolve more readily during the plating process. One commonly used in current commercial practice is to incorporate a small quantity of sulphur (typically 0.025%) into the anode nickel during manufacture. This can reduce or eliminate the need for the addition of nickel chloride to the solution which can in a number of circumstances be advantageous.

The use of boric acid, which has been found to be essential for the production of sound nickel deposits, is one of the key factors that have led to the widespread adoption of the Watts type solution over a period of almost 100 years. There is, even after this time, still some debate regarding the way in which boric acid additions affect the performance of these solutions. One of the major functions is still, however, recognised to be as a pH buffer at the immediate interface between the solution and the cathode. This effectively stabilises the solution pH at the interface during the reduction of the Ni²⁺ ions to nickel metal.

This Watts formulation is extremely versatile and will accept considerable variations from the optimum composition whilst continuing to produce sound nickel deposits. The basic solution can also accept a wide range of addition agents some of which are used to produce deposits that are fully bright and lustrous whilst others give rise to semi-bright deposits. Other classes of addition agents can be used to produce deposits that are much harder than those deposited by the basic solution.

There are also variations on the basic Watts composition that have been widely used in industrial applications. For example, high chloride baths have been employed specifically in decorative nickel plating to allow the use of increased deposition rates. All-sulphate and all-chloride variants can be used in specialised applications.

Nickel sulphamate solutions

The nearest equivalent to the Watts bath that is used extensively in nickel electrodeposition is the nickel sulphamate solution where the nickel sulphate content of the solution is substituted by nickel sulphamate, usually in similar concentrations. Like the sulphate-based solution the sulphamate-based process always contains boric acid and may also contain small concentrations of nickel chloride. A typical make-up of this type of solution is shown below.

Nickel sulphamate	$\text{Ni}(\text{SO}_3 \cdot \text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$	400 g L ⁻¹
Nickel chloride	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0–15 g L ⁻¹
Boric acid	H_3BO_3	40 g L ⁻¹

Sulphamate-based solutions produce nickel deposits with a much lower internal stress than those deposited from the Watts bath. It is therefore widely used in nickel electroforming operations where deposit stress is of critical importance. Also, since the electrical conductivity of the sulphamate bath is inherently higher than sulphate-based solutions it is quite frequently used in nickel barrel plating operations.

The main reason why these processes are not more widely used is that nickel sulphamate is more expensive than nickel sulphate.

Electroless deposition

Electroless nickel plating is also, occasionally, called autocatalytic plating. It is a process for depositing nickel metal from solutions containing nickel salts without the use of impressed direct electrical current. Ni²⁺ ions in solution are reduced from the di-valent ionic state to the zero-valent metallic state by the action of a chemical reducing agent rather than by an electric current.

The most commonly used reducing agent is sodium hypophosphite. As a consequence the deposit produced by the electroless reduction is not pure nickel, as it frequently is with electrolytic processes, but a nickel–phosphorus

alloy. Boron hydrides are also used as reducing agents in electroless nickel processes; these produce nickel–boron alloy deposits.

The solutions frequently also contain complexing agents such as a salt of an organic acid, such as citric acid, which also acts as a pH buffer. Nickel acetate is also used in electroless nickel formulations since the acetate anions can also act as a complexing agent for Ni²⁺ ions.

There are two types of electroless nickel solution – acidic baths operating between pH 4 and 7 and alkaline baths between pH 8 and 11. In both types of solution, the source of nickel ions is either nickel sulphate or nickel chloride and the mechanism of metal deposition always involves the reduction of Ni²⁺ ions to the appropriate nickel alloy deposit.

What freedom is there for substitution of these nickel salts?

All of the aqueous solutions commonly used for the deposition of nickel – both electrolytic and electroless – contain high concentrations of Ni²⁺ ions (almost certainly hydrated). This consideration applies to the three most widely used salts listed above and to the four salts that have found less use. In solutions of all of these seven salts, it is accepted that nickel deposition involves the reduction of Ni²⁺ ions to nickel metal.

At the conclusion of the Nickel Risk Assessment programme in 2007 nickel sulphate was classified as a Category 1 Carcinogen, Category 3 Reprotoxicant, Category 2 Mutagen. Nickel chloride and nitrate were similarly classified. (*Nickel sulphamate, however, was outside the remit of the Risk Assessment and therefore not formally classified at that time.*)

A common objective of EU legislation dealing with health, safety and environmental matters – such as the Nickel Risk Assessment programme and subsequently REACH – is that materials considered hazardous should wherever possible be substituted by less hazardous substances. This must obviously apply to materials classified as CMRs (Carcinogenic, Mutagenic, Reprotoxic) including the nickel salts so classified.

The classification of nickel sulphate as a carcinogen was based primarily on a study of the incidence of respiratory organ cancer in employees working in an atmosphere in which there was a considerable concentration of this salt.

Since there is no evidence to suggest that the sulphate anion is carcinogenic the conclusion reached is that the Ni²⁺ ion is responsible for the carcinogenic effects observed in the study.

In 2009, through a series of controversial steps, the European Union extrapolated the hazard properties of nickel sulphate and the other salts included in the Risk Assessment programme to a very wide range of other nickel organic and organo-metallic compounds. The assumption made was that the nickel ion is the cause of the carcinogenic behaviour and therefore any salt or compound containing nickel was *de-facto* to be considered not only as hazardous but also carcinogenic. Little or no validation testing was done to confirm the degree of hazardousness of any of the individual compounds or their groups. Solely on the basis of this principle, known as ‘*Read Across*,’ approximately 118 nickel compounds, including all of the commonly available soluble salts and a host of obscure substances, were classified as having hazardous properties identical to those of nickel sulphate. The full list appears in 1st APT of the EU CLP legislation.

As a result, irrespective of any technical considerations, none of these compounds can possibly be considered as substitutes for the commonly used sulphate, chloride or sulphamate salts. This effectively means that there is no available substitute for the currently used nickel salts in either electrolytic or electroless nickel deposition processes.

Substitution of nickel by depositable metals

Relatively few of the metallic elements in the periodic table can be electrodeposited from aqueous solutions and even fewer can be deposited by electroless processes. There are only five metals that are commonly electrodeposited

<i>Chromium</i>	<i>Nickel</i>	<i>Copper</i>
<i>Zinc</i>	<i>Tin</i>	

commercially in large quantities.

(*Of these only nickel and copper can be deposited by electroless processes.*)

There are only about nine other metals that have been deposited on a

<i>Cadmium</i>	<i>Cobalt</i>	<i>Iron</i>
<i>Lead</i>	<i>Manganese</i>	<i>Indium</i>
<i>Gold</i>	<i>Silver</i>	<i>Platinum</i>

commercial scale, albeit in much smaller quantities.

Many metals in common commercial use cannot be deposited from

*Aluminium Molybdenum Titanium
Tungsten Vanadium Zirconium*

electrolytic or electroless processes including:

There are some specialised techniques available for the deposition of aluminium. However, these invariably involve very complex materials, processes and equipment which means that under no circumstances could they be used for general commercial metal deposition.

Depositable single metals

An examination of the properties of those metals that can be readily deposited on an industrial scale reveals that none of them exhibit the combination of chemical and mechanical properties shown by nickel.

Chromium

Electrodeposited chromium is primarily employed in 'decorative' applications in combination with nickel (and sometimes copper) as part of a coating system normally known as 'chrome plating'. The principal function of the chromium is to prevent the nickel layer from tarnishing. However, development work carried out in the 1960s and 1970s demonstrated that the structure of chromium deposits can be modified to provide significant increases in corrosion resistance of the overall nickel/chromium coating system. Although the chromium top-coat is extremely hard (~900 HV) and therefore wear resistant the thickness that can be used is limited since it is also extremely brittle.

It is possible to electroplate thicker layers of pure chromium to produce what is known as 'hard chromium' deposits which are used in wear resistant applications. Again these are extremely hard but also very brittle and dull in appearance. Owing to this brittleness chromium deposits can suffer from a tendency to cracking which could be detrimental to the corrosion protection offered by the deposit, particularly if a nickel undercoat is not used.

Furthermore, hard thick chromium deposits can only, at present, be produced from hexavalent chromium solutions which are the subject of extremely severe use restrictions in all

recent health and safety and environmental legislation.

In terms of both deposit properties and process suitability considerations chromium cannot therefore be considered as a substitute in applications where nickel is currently used.

Copper

There are a number of processes commonly used to electrodeposit copper metal including strongly acid solutions, cyanide-based solutions and pyrophosphate. Regardless of the type of plating system used, however, the copper deposits are inevitably much softer than nickel deposits because of the inherent properties of the two metals. Copper also exhibits very poor corrosion resistance in comparison with nickel. For this reason components plated with either electrolytic or electroless copper must then be coated with a protective top-coat (either metallic or organic) to provide a finish that exhibits adequate corrosion and wear resistance for use even in relatively mild environments.

There are no additives that can be used in copper plating processes to produce deposits with equivalent corrosion resistant or mechanical properties to those of nickel. Furthermore, a deposit of chromium applied directly on top of copper, in the absence of a nickel interlayer, will not prevent corrosion of the copper in the way that it enhances the corrosion resistance of nickel deposits.

Similar considerations apply to electroless copper deposits.

Zinc

Zinc electrodeposits are also much softer than nickel and do not provide the same level or type of corrosion protection. Zinc acts as a sacrificial coating on steel substrates, corroding in preference to the steel and thereby protecting the underlying substrate from attack. Consequently the visual properties of the zinc deposit deteriorate, in order to protect the underlying substrate, in a manner that nickel deposits do not. This effectively prevents zinc coatings from providing the long term durability obtained with nickel coatings.

Tin

Tin is electrodeposited in extremely large quantities to produce 'tin-plate' used in the manufacture of food cans. It is also used in the electronics industry. As with zinc, however, the

properties of tin deposits do not match those of nickel either in terms of mechanical properties, long-term corrosion resistance or durability.

There is also a strong commercial argument that supports the proposition that tin coatings do not constitute a substitute for nickel. During the period from July 2006 to July 2007 when the price of nickel reached \$55 000/tonne and tin cost approximately \$9000 to 14 000/tonne there was no move to substitute nickel plating with tin in any of its applications.

Cadmium

Cadmium metal and its salts are extremely toxic and as a result there have been strenuous efforts in recent years to ban their use on human health grounds. Currently the use of cadmium plating is restricted to a few selected applications in the aerospace industry where its particular properties are deemed essential for safety reasons.

Thus, there is obviously no way in which cadmium could be accepted as a substitute for nickel.

Cobalt

Cobalt is generally regarded from a health, safety and environmental point of view as being at least as problematical, if not more so, than nickel.

In electrodeposition terms cobalt cannot be regarded as a nickel substitute since pure cobalt electrodeposits are so highly stressed and brittle that they are, in practical terms, useless.

During occasions when nickel has been in very short supply due to strikes or other commercial circumstances then plating with nickel-cobalt alloys has been tried to a limited extent in decorative nickel-chromium plating. However, as soon as nickel became freely available once more the alloy system – which was much more difficult to control – was dropped and plating with pure nickel resumed.

Iron

Iron can be electrodeposited from strongly acidic chloride-based solutions. However, the processes are inherently unstable due to the readiness of the ferrous ion to oxidise to ferric in working solutions. Also, of course, iron electrodeposits are of no practical value since they rust so readily.

Lead

As well as the deposit properties being totally unsuitable, lead plating would obviously be considered totally

unacceptable on health & safety as well as environmental grounds.

Manganese

Manganese can be deposited but coatings of this metal have never found commercial applications since they do not show useful properties.

Indium, gold, silver, platinum group metals

These are obviously ruled out as nickel substitutes on economic grounds.

Alloy deposits

Considering the success of wrought and cast alloy development technology during the last 100 years or so it might reasonably be assumed that alloy electrodeposits or alloy electroless deposits might be available, or possibly be especially developed, as substitutes for nickel.

However, most of the commercially successful alloy plating processes are nickel-based, including nickel-tin, nickel-cobalt, nickel-iron and nickel-zinc, which all employ the same nickel salts as those used in pure nickel deposition thus immediately ruling them out as potential substitutes.

Commercially successful non-nickel alloy plating processes

Lowenheim¹ points out that although possibly hundreds of alloy electrodeposits have been investigated

Gold alloys	Brass	Bronze
Tin-lead alloys	Tin-zinc	

at the laboratory scale only a very few have any practical significance. These he lists as:

Gold alloys are obviously ruled out as nickel substitutes on cost grounds. Neither the mechanical properties of electrodeposited brass or bronze nor their corrosion resistance compare to those of nickel. The same is true for both tin-lead and tin-zinc alloys.

Furthermore, many of the solutions from which these alloys have been successfully deposited are cyanide-based and so cannot be considered on the grounds of toxicity.

One of the major reasons why electrolytic alloy plating processes in general have not found greater commercial success is that the deposit composition is difficult to control since basically it depends on deposition current density. Maintaining uniform deposit composition over complex three-dimensional surfaces therefore becomes a major and possibly insurmountable problem.

Summary

This review has deliberately been confined to considering the question of substituting existing nickel electrodeposition or electroless deposition processes with less hazardous alternatives – but using similar deposition technology – or of substituting nickel itself by another plated metal or alloy.

In examining the range of nickel compounds that might, in theory, be substituted for those currently in use the fundamental considerations of possible modification the three basic types of chemicals – organic, inorganic and elemental – are of critical importance. As a result, this review demonstrates clearly that there is no possibility of a straightforward exchange of nickel compound 'A' by nickel compound 'B' in order to reduce either hazard or risk. The possibility of substitution is governed by the basic laws of science and these appear to put an insurmountable barrier in the way of an easy solution to the problem.

Similarly an examination of the properties of metals that can be deposited either by an electrolytic or an electroless process demonstrates that nickel is quite unique in terms of its critical properties. These properties,

such as hardness, ductility, toughness, electrical conductivity, magnetic permeability and corrosion resistance, even if considered individually would result in nickel being considered an immensely useful material. Taken together they provide a formidable combination of benefits that cannot be found in any other of the 91 naturally formed elements in the periodic table. The most basic laws of chemistry and physics prevent modification of the structure and properties of elements including metals. There is therefore no possibility that the properties of another element could be changed to be comparable with those of nickel let alone of combining this with freedom from any environmental or human health downside.

One other factor, of vital significance is that nickel plating is by no means the cheapest method of coating surfaces. Market forces, therefore, dictate that those applications where nickel is used are only ones where the inherent properties of this particular metal are vital to the creation of a product that will give high quality service in the specific, and frequently very demanding, circumstances of its application. As a result of the continuing demand for nickel plated products the industry has risen to the challenge of ensuring that those risks which are inherent in any of the processes involved in nickel plating are minimised and well managed.

As a consequence of looking at the detailed situation related to the substitution of different salts in nickel plating processes and the substitution of nickel metal by another metal or alloy by plating it can be concluded that in neither case is substitution possible.

Reference

1. F. A. Lowenheim: 'Electroplating'; 1978, New York, McGraw-Hill, Inc.