Nickel
Development
Institute

Nickel plating and electroforming

Essential industries for today and the future

by Ron Parkinson

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Nickel Plating and Electroforming

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Today nickel is recognized as an invaluable and indispensable metal, though when first identified by Axel Cronstedt in 1751, it was an unwanted material, often found in combination with copper ores. At the time, it did not have the properties that would warrant its being called a metal.[1] Specifically, it did not have the ductility required of a metal in those days, but this was due to the presence of impurities such as arsenic, copper and iron. Consequently, it was referred to as a semimetal.

When nickel was first produced in a pure form, a publication by Richter in 1804 described many of the properties for which it is well-known today, including corrosion-resistance, ductility, high strength, high melting point, good high-temperature oxidation-resistance and magnetic response similar to that of iron. It was then identified not only as a metal but as a noble metal. Even after identifying these very desirable properties, there were no major applications foreseen for nickel, no significant ore reserves located and, consequently, no great enthusiasm for its discovery. How things have changed. In the overall surface-to-core composition of the Earth, only four elements (iron, oxygen, silicon and magnesium (occur more abundantly than nickel.[2] Nickel now has innumerable important applications and is one of the most versatile metals known. It is designated a strategic metal in the U.S. and is widely used in all our major industries such as steel-making, aircraft/aerospace, defense, automotive, construction, computers and communications. In most current applications it is irreplaceable, and so it is important that we recognize our dependency on this invaluable metal.

Total use of primary nickel worldwide in 1999 was a huge 970,000 tonnes and forecasts call for increased demand over the next few years. By far the biggest market for nickel is in the production of stainless steels, which contain about 10% nickel on average. Other important sectors of nickel usage include high-temperature nickel alloys, cupronickel, batteries, catalysts and electroplating. This publication is dedicated to the nickel plating and electroforming industries, which typically account for 8 to 10% of total nickel use. It will describe a wide range of applications in various industries and will explain the benefits afforded by nickel plating and electroforming that cannot be achieved with any other metal. It will also address general environmental issues, mainly with reference to the North American market, in the hope that the excellent cooperation between the industry and environmental agencies and the resulting high level of compliance can be used as a model for other parts of the world.

Industry Review

In North America, organizations dedicated to the metal finishing industry present a balanced, informative view of the industry they serve. For instance, in their publications and at their technical conferences it is possible to learn not only of new developments and applications, and important research and development, but also of current environmental issues. For many years now, great emphasis has been placed on the latter and, to the credit of this industry, those who are part of it are kept well advised of environmental regulations and respond to them. A balanced view of the industry is not always presented to the public by the media, and so there appears to be a greater awareness of the problems facing the industry than there is of the benefits it provides to our economy and to our lifestyles. These benefits are indeed huge, but to the uninformed, the industry is still unfairly perceived as having a poor environmental reputation. In North America, the cooperation between the industry and environmental agencies is commendable and the extent of compliance impressive. In fact, at the most senior level, the U.S. Environmental Protection Agency (EPA) has described the commitment to environmental protection as a model for many other industries.[3]

Nickel plating and electroforming provide many advantages to our major industries, and the processes are used with respect for the environment and worker safety. Prior to describing some of the ways nickel plating and electroforming contribute to major industries, a brief review of these processes is offered below. An understanding of the materials used will also provide a basis for a review of environmental issues.

In the nickel plating and electroforming industry, nickel is used in metallic form and as soluble salts *(Figure 1)*.

Figure 1 Nickel units are provided by soluble salts and nickel metal in titanium baskets.

The most frequently used salts are chloride, sulphate and sulphamate in aqueous solutions. Nickel plating is done by electrolysis (electroplating) or by chemical reduction (electroless plating). Electroforming is an electrolytic process similar to electroplating but with a different objective. Electroplating and electroless plating are used mainly to enhance the properties of the substrate, that is, to improve appearance, corrosion-resistance, wear-resistance, solderability etc. and, consequently, maximum bonding to the substrate is preferred. This is not the case with electroforming, which is defined in ASTM B-832 as follows: “Electroforming is the production or reproduction of articles by electrodeposition upon a mandrel or mold that is subsequently separated from the deposit”. It is, therefore, a unique method of fabricating parts that are usually freestanding once separated from the mandrel or substrate. Nickel dominates this industry due to the versatility of the nickel electrodeposition process and the outstanding properties of the nickel products.

Electroplating and Electroforming

In any nickel electrodeposition process, there are four main components. The first is a container or tank containing a nickel salt solution, usually referred to as the electrolyte. The second is a source of direct current, usually a rectifier with voltage control, typically in the range 4 to 20V. The third and fourth are electrodes, which are immersed in the tank and are connected to the positive and negative poles of the rectifier to allow direct current to be passed through the electrolyte. The electrodes connected to the positive pole and the negative pole are the anode and the cathode, respectively. The cathode is the part on which nickel is to be deposited and the anode is normally a suitable form of nickel metal.

There are many variations in the composition of the electrolytes used but all contain nickel in solution, usually in the form of nickel sulphate, nickel chloride or nickel sulphamate or a combination of these salts. When dissolved in water, these salts produce positively charged, divalent nickel ions (Ni^{++}) which, under the influence of the direct current from the rectifier, are attracted to the negative electrode, that is, the cathode or the mandrel. At the cathode, the positively charged ions (cations) are discharged and are deposited on the surface as nickel atoms. Under controlled conditions therefore, a continuous layer of nickel can be

Table I Watts and Sulphamate Electrolytes

	Watts	Sulphamate
Nickel sulphate [$NiSO_4.6H_2O$]	240-300 g/l	–
Nickel chloride [$NiCl_2.6H_2O$]	30-90 g/l	0-30 g/l
Nickel sulphamate [$Ni(NH_2SO_3)2.4H_2O$]	–	300-450 g/l
Boric acid	30-45 g/l	30-40 g/l
pH	3.5-4.5	3.5-4.5
Temperature	40-60°C	40-60°C

deposited. Meanwhile at the positive electrode, which is the nickel anode, a reverse process is taking place. Nickel atoms on the anode surface are being converted to nickel ions in solution, replacing those being discharged at the cathode. Ideally, the system remains in balance, with the same amount of nickel being deposited on the cathode as is being dissolved at the anode.

Watts-type and sulphamate electrolytes are the most frequently used for nickel electrodeposition. Typical composition and operating conditions are shown in *Table I*.

Both types of electrolytes have extremely good stability when properly operated and maintained. Rarely are they discarded, and each can be regarded as having indefinite life.

Electroless Nickel Plating

Nickel use in electroless nickel plating accounts for only a small percentage of the total requirement for nickel plating. However, it is now an invaluable and irreplaceable process in many of our major industries. It is a process for depositing a nickel alloy from aqueous solutions without electric current. Nickel ions are reduced chemically, most frequently by sodium hypophosphite and occasionally by sodium borohydride or dimethylamine borane so that a nickel deposit containing phosphorus or boron will be deposited on a suitably prepared substrate. A suitably prepared surface will catalyze the reduction process and initiate the deposition of nickel. Once started, the nickel itself becomes the catalyst and the process is therefore described as being "autocatalytic".

A typical electroless nickel plating solution has the following constituents[4]: a source of nickel ions, a reducing agent, complexing agents, stabilizers and inhibitors. Nickel sulphate at a concentration of about 30 g/l is the preferred source of nickel ions, although nickel chloride is used in some bath formulations. Nickel concentrations are therefore only about one-tenth of that in solutions used for electrodeposition. Because the deposition process involves chemical reactions, by-products of the reactions build up in the solution and eventually affect deposition rates and deposit properties. When this occurs, the spent solutions are replaced and processed to recover the remaining nickel units.

Applications

Computers/Information Storage and Retrieval

With the phenomenal growth in the computer industry, the storage and retrieval of information has become a major requirement throughout the world. It is seen in all major industries, governments, military and technical organizations, educational institutions and almost everywhere we choose to look. In addition, advanced technology and miniaturization have resulted in a huge demand for personal computers and laptops. Electrodeposited and electroless nickel play a critical, indispensable role in the computer industry; without them, our ability to store and retrieve information would be greatly affected. Current technology is complex and highly sophisticated, but pales in comparison to what we can expect in the years ahead. One of the keys to this technology has been the development of optical storage and readout disks, that is, compact disks (CDs) on which information is digitally encoded as a series of microscopic pits with a width and depth generally less that a micron. Nickel is indispensable in the production of these disks and so has played a critical part in the development of the present technology. It will be equally important in future developments.

CDs are produced by injection-molding polycarbonate resin in nickel molds. These molds, incorporating the high precision surface detail that produces the pit pattern in the finished disks *(Figure 2)* are made by electroforming. This is a unique, versatile electro-deposition process which is capable of replicating the finest surface detail. Nickel is irreplaceable in this and many other applications for electroforming.

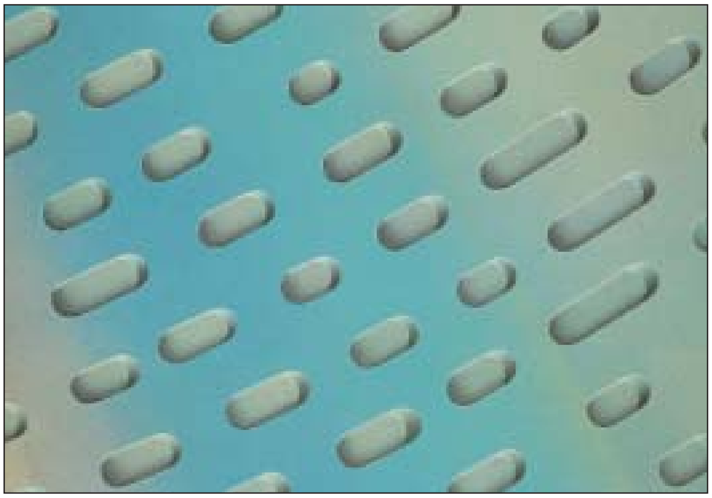

Figure 2 Spiral pattern of submicron pits on CD surface. Perfect replication depends on nickel electroforming.

The electroforming of molds for optical storage and readout disks is based on long established practices used to produce molds for the record industry, including 78-rpm disks, 45s, and LPs. In the industry the molds are referred to as "stampers". Electroforming was introduced into the record industry circa 1930 and obviously many improvements and refinements have been made since then; but none have been as great as those required to make nickel electroforming such a critical part of the CD industry.

Three electroforming stages[5] are required to produce stampers and each requires perfect surface replication. The original information, that is, the sound, is transcribed from tape by laser onto a photo resist film bonded to a polished, optically flat glass disk. Development of the film then produces the pit pattern. This part is referred to as the glass master and is the starting point for the electroforming stages. Before electroforming can begin, the surface of the glass master must be made electrically conductive. Once again, nickel is the metal of choice. Only an extremely thin layer is required, typically 1,000 to 1,500 angstroms, and this can be deposited by sputtering or electroless plating. The latter method is usually preferred. From this glass master is produced one electroformed nickel master which perfectly replicates the surface detail in reverse. This then becomes the cathode or mandrel for the second electroforming stage which produces "nickel mothers". Typically, four would be produced from the master and then these become mandrels for the third stage of electroforming. This stage produces the "stampers" and if, for example, ten are produced from each mother, then forty stampers are available for use in the injection molding machines to meet production requirements. One machine can produce a CD every four or five seconds.

In CD production the electroforming stages are fully programmed to control nickel properties such as stress and thickness. High deposition rates are obtained at current densities of up to 30 A/dm^2 so that stampers with a required thickness of 295 ± 5 microns are electroformed in less than forty-five minutes. Nickel is indispensable to this important industry for several reasons: the nickel electrolytes used are easy to control; they have an indefinite life and provide good current distribution; they can be operated at very high current densities, resulting in fast deposition rates; and the properties of nickel, such as stress and hardness, can be easily controlled. Nickel properties are such that one stamper is capable of producing 10,000 to 50,000 CDs and the stability of nickel to ambient conditions allows stampers to be stored and reused as required. The reliability of nickel electroforming in reproducing such great detail through three stages of replication is a key factor in the enormous advances made in the storage and retrieval of information. It provides us with high-quality audio and video equipment and computer software. It also allows industries such as automotive and aerospace to reproduce volumes of

Figure 3 CD electroforming station. Nickel stampers being rinsed over tank prevents solution loss.
(Coutesy of Sony Music Canada)

standards and specifications on compact disks. Similarly, encyclopedias are available on CD, and strategic military information can be stored for easy retrieval in the field.

There are few, if any, environmental concerns associated with nickel in this industry. The electroforming operations are necessarily clean and there is little or no electrolyte loss through “drag-out”. Rinsing can be done directly over the electroforming tanks (as seen in *Figure 3*) and so any loss of electrolyte is minimal, but, if necessary, it can be returned to the electroforming tanks or recovered by ion exchange. The nickel sulphamate electrolytes used are never discarded when properly maintained, and tank design incorporates sealed lids to ensure excellent air quality. Some metallic nickel scrap is generated by the trimming of the stampers to the required diameter; but as this is high purity, it is readily accepted by steel producers as charge material. Scrap stampers, mothers and masters are similarly recycled.

We have experienced phenomenal growth in the demand for rigid memory disks and disk drives due to the enormous increase in the use of personal computers and the Internet and the associated demand for increased computer memory.[6] For the past 20 years, electroless nickel, an essential part of this industry, has kept pace with the increased quality demands imposed by the rapidly advancing technology. In this time it has become universally accepted as the standard barrier coating for media manufacturers.

For this application one of the key properties of electroless nickel is magnetic response. Electroless nickel typically contains 2 to 14% phosphorus and this has a dramatic effect on magnetic properties, as shown in *Figure 4*. Deposits with over 11% phosphorus are described essentially as nonmagnetic. Typical storage disks, shown in

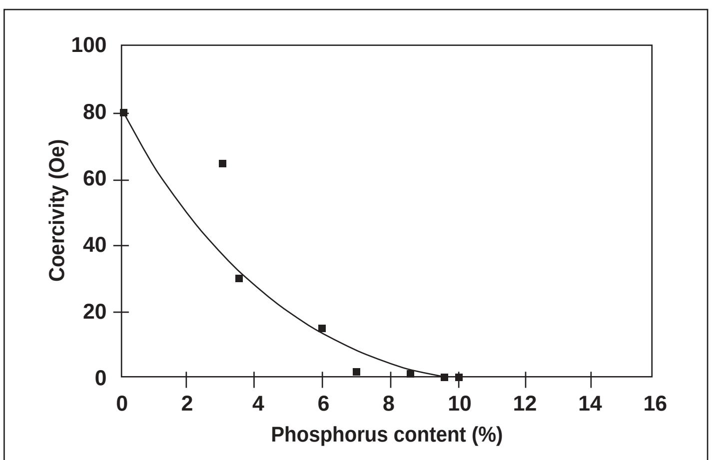

Figure 4 Effect of phosphorus content on magnetic properties of electroless nickel.

Figure 5 Computer memory discs - a huge and demanding market for electroless nickel.

Figure 5, consist of an aluminum substrate plated with nonmagnetic, hard, high-phosphorus electroless nickel to a thickness of 10 to 15 microns. This provides a protective barrier between the substrate and the magnetic data storage surface, which is nonmagnetic, very hard and easily polished. The magnetic coating, which is a sputtered cobalt alloy, is deposited on the polished electroless nickel and is subsequently covered with a protective wear-resistant carbon overcoat and a fluorocarbon lubricant to complete the disk manufacturing process.

The diameter and thickness of aluminum substrates for storage disk applications have consistently decreased in response to the size restrictions and torque requirements imposed by present-day portable computers and other electronic devices. The increased requirements for higher storage densities on progressively smaller sized disks have placed a huge demand on the quality of the aluminum substrate and the electroless nickel coating. The challenge has been met successfully.

The fact that modern computers are so compact and yet have such large storage capacity and high speed can be attributed to the complex thin film magnetic heads used and the processes that have been developed to produce them. These processes are heavily dependent on electroplating and electroforming of nickel/iron and cobalt/nickel/iron alloys and copper.

Since 1979, thin film magnetic heads have been used in computers in conjunction with magnetic storage devices using hard disks.[7] A typical inductive read/write head has 30 or more electrodeposited copper conductor turns and an electrodeposited horseshoe magnet. They are extremely small (as shown in *Figure 6*) and thousands are produced at a time by deposition on a ceramic substrate using plating

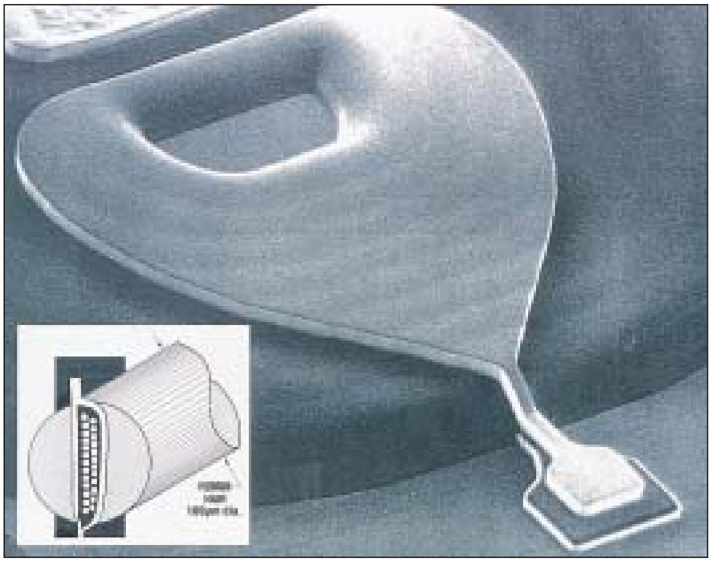

Figure 6 An electroformed thin film inductive head and a cross section comparing size with a human hair.
(Courtesy of IBM T.J. Watson Research Center)

through lithographic mask technology. Nickel is a critical component in this technology as the two legs of the horseshoe magnet on each head are electrodeposited magnetic alloy layers consisting of 81% nickel and 19% iron. Production involves sequential electro-forming of the first part of the nickel alloy horseshoe magnet, then the first copper coil, then the second copper coil and finally the second leg of the nickel alloy magnet. Each electrodeposit is separated by a hard-baked photosensitive dielectric, and plating through mask technology is used at each stage.

There is no other practical or cost-competitive method of producing these minute magnetic heads and the fact that nickel has such great versatility in its ability to codeposit in so many alloy forms has been of major importance to the computer industry. It was estimated in 1999 that the demand for thin film magnetic heads had reached about 4 billion per year. The nickel alloy is deposited from a sulphamate, or sulphate/chloride electrolyte, and methods of obtaining uniform current density on these small components have been developed using a paddle electrodeposition cell[8] which allows thickness and compositional uniformity of the nickel alloy to be obtained. It has been reported[9] that the introduction of thin film heads has permitted an increase in the storage density of magnetic recording by one order of magnitude every eight years since 1979. The Internet, on which modern society has become so dependent, has been a major beneficiary of high- density magnetic storage. The ability of servers to store and transmit huge amounts of data to our personal computers in fractions of a second is dependent on thin film magnetic head technology[7] and the nickel alloy electrodeposition process. This electrodeposition method of producing these absolutely essential components for the computer industry is now used around the world, and the economics cannot be matched by any other process.

Automotive

The automotive industry is a large user of electroplated, electroless and electroformed nickel. The largest and most visible application is in the production of bright finishes on parts such as bumpers, wheels and grilles. For exterior applications, these finishes would typically consist of 30 microns nickel and 0.3 microns chromium. Although the aesthetic appeal of the sheen is one of the major reasons for its popularity, there are other more compelling reasons for its use. For instance, the plating systems used provide excellent corrosion-resistance, wear-resistance and durability, as demanded by automakers.

In developing nickel plating processes for this application, the focus has been on optimizing corrosion-resistance. Present processes are now capable of protecting components for up to ten years, as required by industry warranties. In reaching this stage, nickel has been the subject of more research and development than any other electroplated metal, and for this application it is indispensable in terms of performance, practicality and economics. Nickel plating systems are quite complex and yet high-quality plated components for the automotive industry are produced in enormous quantities with great consistency and reliability.

A typical plating system for exterior use involves three layers of nickel, each of which has different properties that must be strictly controlled. The first and thickest is a semi-bright deposit which levels out minor imperfections in the substrate, has excellent corrosion-resistance and provides a very smooth base for the second layer, which is the fully bright nickel. To optimize corrosion-resistance, it is necessary to control the thickness, the sulphur content and the electrode potential of these two deposits. A key factor in obtaining the best possible corrosion-resistance is controlling the difference in the electrode potentials of the bright and semi-bright nickel. The difference controls the direction in which any corrosion will occur and greatly reduces the possibility of corrosion penetrating to the substrate. A third and extremely thin layer of nickel with specific properties which is then deposited over the bright nickel, has no significant effect on the brightness but a marked effect on the subsequent thin deposit of chromium. The properties of the final nickel deposit ensure that the 0.3 microns chromium will enhance the corrosion-resistance of the nickel system.

The automotive industry is the largest user of nickel for plating applications. The stable Watts-type electrolyte is the workhorse of the industry, regardless of the substrate being plated. Since the mid-1990s, the demand for automotive bright-work has been strong, particularly on small trucks, sport utility vehicles and prestige cars. Of the substrate materials being plated, steel, aluminum and ABS plastic are the most important, with the last two experiencing remarkable growth. Typical plated components are shown in *Figures 7, 8 and 9*.

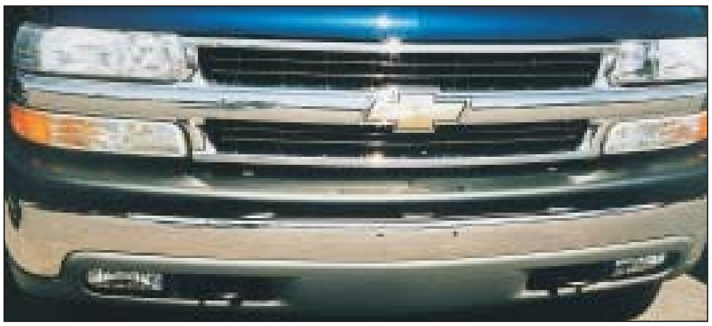

Figure 7 Demand for plated steel bumpers has been strong. Parts have visual appeal, excellent durability and good recyclability.

A major benefit of the nickel plating process is that it provides excellent durability to inexpensive substrate materials such as steel and to lightweight materials such as aluminum and plastic. The use of lightweight components improves fuel efficiency, and when their life cycle can be significantly extended by electroplating, they become even more environmentally attractive. The reduction in automotive scrap resulting from the excellent corrosion-resistance of nickel plating systems is huge. Plated components have an additional environmental benefit in that they are mostly recyclable. For example, plated steel is acceptable to stainless steel producers and plated aluminum to engine manufactures for the production of pistons. Copper is used in some plating systems for plastics but recent developments to eliminate it, combined with the recently introduced method of separating electrodeposits from plastic substrates by cryogenic methods, have greatly improved the recycling opportunities for plated plastic components. The plastic can be ground and reused, and the copper-free plate is acceptable to stainless steel producers. These are important factors when considering that a stated objective of the European auto industry is to produce vehicles that are completely recyclable.

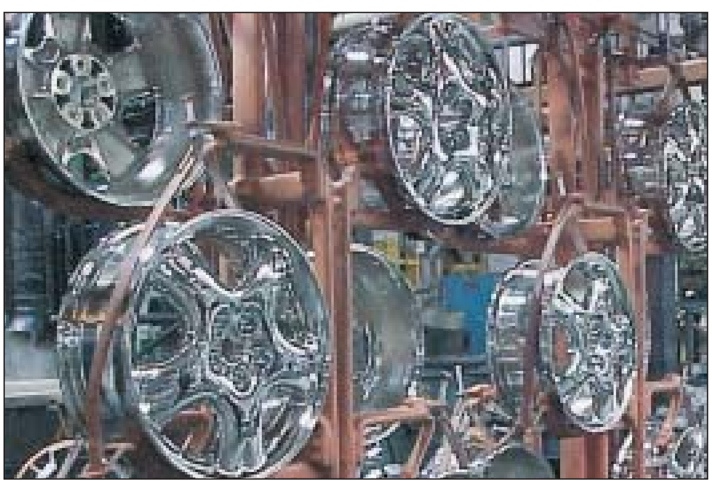

Figure 8 Popular plated aluminum wheels offer style, excellent corrosion resistance, lightweight and recyclability.
(Courtesy of Kuntz Electroplating Inc.)

Figure 9 Advantages of plated plastics include design flexibility, appearance, lightweight and good recyclability based on recent developments.
(Courtesy of Lacks Industries Inc.)

Suppliers of plated parts to the automotive industry include the largest nickel plating plants in the world. In North America, automakers demand not only very high quality parts but also complete environmental responsibility in the plants producing them. This has resulted in a level of compliance to environmental regulations within the plating industry that is commendable. Noncompliance has led to the closing of many small operations, and suppliers now mostly consist of large plants with the technical and financial resources required to meet the strict regulations imposed. It appears that these resources will be continually challenged, and it is important that industry and environmental representatives cooperatively establish future regulations that will be practical, achievable and protective of the environment and workers' health. This industry has shown remarkable strength in recent years and it has been predicted that the demand for bright work by consumers will remain strong until 2010.[10]

Automotive companies are focused on quality, performance and reliability. Consequently, electroless nickel properties such as corrosion-resistance, wear-resistance, lubricity and uniform deposit thickness have been used to great advantage in this industry. The performance of steel and aluminum components, for instance, has been enhanced by the use of electroless nickel, and typical applications are on heat sinks, pistons, engine bearings, hose couplings, gear assemblies, carburetor parts, fuel injectors, shock absorbers and exhaust system components. Recognizing the benefits of electroless nickel in these and other applications, automotive companies have their own specifications for its use.

When Brazil introduced ethanol[11] as an alternative fuel to gasoline for economic and environmental reasons, the use of electroless nickel on components in contact with the fuel (carburetors, injection systems etc.) became mandatory. Hydrated alcohol at high-temperatures produced conditions that severely corroded zinc diecast carburetors *(Figure 10)* and other components. The corrosion-resistance and thickness uniformity of electroless nickel deposits even on complex shapes resolved this problem and contributed to the success of this conversion program. Dramatic cost savings on imported oil and improved environmental performance resulted. In North America, alternative fuels have typically been gasoline/methanol mixtures (with a broad range of composition) which can also cause accelerated corrosion.[12] High-phosphorus electroless nickel provides excellent corrosion and wear-resistance in the most aggressive fuel mixtures.

The lubricity, wear-resistance and anti-galling properties of electroless nickel have been used to good advantage in this industry.[13] The coating is often a suitable alternative to chromium plating or nitriding, especially when wear is a factor. For instance, excessive wear can occur on differential pinion shafts *(Figure 11)* as a result of contact with the uncoated teeth on the two gears that ride along

Figure 10 Electroless nickel was required to resolve corrosion problems on carburetors using ethanol fuel.

Figure 11 Electroless nickel provides excellent wear and anti-galling properties to automotive pinion shafts.

them. Heat-treated, low to medium electroless nickel, typically 25 microns thick, has been used successfully to reduce wear and has an advantage over nitriding at the higher loads exerted on the differential in late-model cars. Concerns about embrittlement and possible fracture of nitrided shafts are eliminated when electroless nickel plating is used.

The anti-galling properties and thickness uniformity of electroless nickel have enabled automakers to overcome a noise problem, attributed to galling, in the U-joint of cast iron slip yokes used in vehicle power trains.[13] A medium-phosphorus electroless nickel deposit has prevented galling and improved the wear-resistance of mating surfaces without the need for a lubricant such as oil.

Although the wear-resistance and lubricity of electroless nickel are inherently good, these properties can be enhanced by the codeposition of particulate matter with the nickel to produce composite coatings. Important composites that have been used successfully in some applications are electroless nickel with polytetrafluoroethylene (PTFE) or fluorinated carbon (CF_x). Both provide an excellent nonstick, low-friction, dry lubricant surface, with the latter having the advantage of superior temperature-resistance. These composites have been used on carburetor and clutch parts, engine valves, bearings and gears. For one European producer, deposition on brass carburetor parts resulted in an increase in the life of pneumatic cylinders from 30,000 to more than 8,000,000 cycles and an associated increase in pump rotor life of 100%.[14] This dramatic improvement is an excellent example of the many benefits that electroless nickel has provided to the automotive industry.

Nickel electroforming is a versatile process capable of replicating shape and surface detail with great precision and cost-effectiveness. It is used extensively to produce molds for this industry. Starting with a model of the part required, a plastic casting is made to replicate in reverse the precise shape and surface texture. This would typically be made from fibre-reinforced plastic. From this, another similar plastic part is made which would be a perfect replica of the original model. This part, rather than the original model, will be the mandrel on which the electroformed nickel molds will be made.

In the automotive industry, electroformed nickel molds are used for producing structural and decorative components. For instance, they are used for producing fibre reinforced plastic (FRP) truck cabs, body panels and protective side-strip moldings. A large truck cab mold is shown in *Figure 12*. Interior applications have been mostly for nickel rotational molds used for producing vinyl skins for dashboards, door panels etc., but the trend now is to replace vinyl with more environmentally friendly, recyclable plastics. The perfect surface replication obtained by nickel electroforming enables any surface texture, such as leather, to be produced on the vinyl skins. A nickel mold for the new plastic door panels is shown in *Figure 13*.

Figure 12 Electroformed nickel mold for reinforced plastic automotive body component.
(Courtesy of EMF)

Molds are electroformed in nickel sulphamate electrolytes. The usual objectives are to obtain zero or low tensile stress in the deposit and to optimize current distribution and therefore thickness uniformity. Stress is normally maintained below 35 MN/m^2 and the ability to easily control the physical properties of nickel electroforms is a major advantage of the sulphamate electrolyte. The automotive industry has long recognized the excellent quality, precision and cost-effectiveness of electroformed nickel molds, and continued use can be expected.

Figure 13 Electroformed nickel mold for automotive door panel..
(Courtesy of Advanced Electroforming Inc.)

The Steel Industry

Steel production has been one of the worlds' most important industries for decades and there is no reason to believe this will change. In the production of stainless steel in 1999, 607,000 tonnes of nickel are estimated to have been used, accounting for about 61% of total nickel use.[15] Nickel is a key alloying element in many types of steel, but it also plays a very important role during steel production – nickel bearing or not. This role has been in the electroplating of molds used in the continuous casting of steel slab for the production of plate, sheet or strip. The advantages of nickel-plated molds have been demonstrated in steel plants around the world and the use of such molds is universally accepted. The nickel plating of copper molds has been responsible for increases in steel strip quality and production efficiency, and this major contribution to such a critically important industry as steelmaking is a measure of the importance of the nickel plating process.

To appreciate the requirements and the performance of nickel-plated molds, it is essential to understand the basics of continuous casting of steel and the demanding conditions that exist within the molds. A typical continuous casting machine is shown in *Figure 14*. Molten steel is transferred

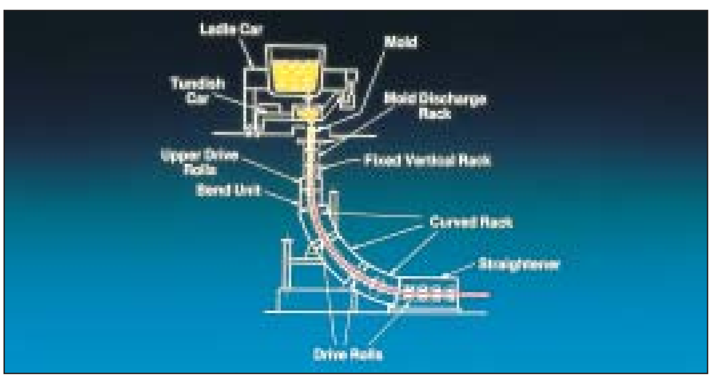

Figure 14 Continuous casting of semi-finished steel products.
(Courtesy of Association of Iron and Steel Engineers)

from a ladle into a tundish, which is basically a molten metal reservoir, and then into a water-cooled, oscillating, copper mold. While in the mold, sufficient heat is extracted from the steel to form a thin shell with adequate strength to contain the still-molten core of the cast slab. In this condition, the slab leaves the bottom of the mold and enters the secondary cooling zone where it passes through support rolls and more heat is removed by water spraying. Additional rolls then gradually bend the slab so that it leaves the casting unit in a straight, horizontal and completely solidified state. At this point, while still at about 600°C, the casting is cut by torch into slab lengths with typical cross sections of about 200 x 25 cm as shown in *Figure 15*. These slabs are then ready for immediate transfer to the hot rolling

Figure 15 Continuous steel casting being cut into slabs ready for hot rolling.
(Courtesy of Bethlehem Steel Corp.)

mill. Recently molds and processes have been developed for medium or thin slab continuous casting, to produce slabs as thin as 5 to 6 cm. By greatly reducing rolling costs, this development is creating much interest in the industry.[16] These molds will still be nickel-plated.

The greatly improved efficiency of this continuous operation over the old ingot casting process that dominated steelmaking until the 1960s has been further enhanced by nickel plating the molds. Improvements in steel quality can also be attributed to the nickel plate.

The mold is the heart of continuous casting, and the efficiency of steel production is dependent on its performance and life. In slab casting, the mold is an open-ended, water-cooled, copper shell consisting of two side

Figure 16 A typical copper mold for continuous casting of steel.
(Courtesy of Unimold)

plates and two end plates which form the desired shape and cross-sectional dimensions of the cast slab. A typical mold is shown in *Figure 16*. The inside surfaces of the side plates are usually machined with a slight taper and curvature, typically with a radius of about 11m, and the end plates are usually adjustable to accommodate different slab width requirements. In use, the mold is assembled in a rigid steel box through which tremendous volumes of cooling water pass over the outside surfaces of the mold.

The performance of the mold is obviously very critical and the operating conditions are extremely severe as can be seen in *Figure 17*. Heat must be withdrawn at a rate related

Figure 17 Aggressive conditions for nickel plate at the molten steel casting station.
(Courtesy of Bethlehem Steel Corp.)

to pouring temperatures and casting rates. Failure to maintain adequate heat transfer can have disastrous effects, resulting in a breakout of molten steel. When molten steel is poured into the copper mold, a complex series of heat transfer mechanisms begin. Influenced by air gaps, mold lubricants and mold taper, these mechanisms are beyond the scope of this publication. Air gaps caused by shrinkage of the steel during solidification, ferrostatic pressure and wear on the mold can affect heat transfer dramatically. Nickel plating of molds for continuous slab casting has greatly extended mold life by reducing wear and by improving heat transfer through limiting the width of the air gap. In addition, nickel plating overcomes the problem associated with the very poor wear-resistance of copper which results in copper pickup in the surface of the cast steel. Copper is known to cause star cracking or hot shortness in steel.

Initially, chromium plate was considered to be the answer to improving mold performance, but only small improvements were obtained. It provided some benefit in reducing copper pickup but very little improvement in mold life. The high internal stress of the chromium resulted in some spalling of the deposit, especially in the molten metal meniscus area, and wear-resistance at operating temperatures was not good. Not until nickel plate was used did dramatic improvements in steel quality, mold life and steelmaking efficiency occur.

Nickel offers many advantages over chromium. The thermal properties of nickel are better matched to those of copper, especially that of thermal expansion. Consequently, at operating temperatures, the stress on the deposit and on the bond is less. Mold producers generally believe that high hardness, good ductility and low tensile stress provide the best combination of properties, and these can all be well controlled in nickel. The “as deposited” hardness of chromium is normally greater than that of nickel but a nickel hardness of 200 to 250 VHN combined with low stress and good ductility provide excellent mold performance. In fact, control of the nickel plating process is such that the hardness of the deposit can be varied from the top to the bottom of the mold. Consequently, a hardness of 200 VHN at the top and 250 VHN at the bottom is a preferred, and attainable, combination.

In addition to these advantageous physical properties, the nickel plating process itself provides benefits not available in chromium plating. Nickel plating is a much more efficient process that provides fast deposition rates and excellent current distribution. These are very important factors when deposit thickness may be as great as 3mm. In addition, chromium plating is much less environmentally acceptable than nickel plating.

Nickel is normally deposited from sulphamate electrolytes. Typically, the thickness of the deposit would be

Figure 18 A pair of nickel plated side plates for a huge mold.

Table II Steel Production in Continuous Casters[17]

Mold	Mold Life (tonnes of steel cast)
Copper	20,000
Chromium-plated copper	30,000
Nickel-plated copper	200,000 to 575,000

1mm toward the top where maximum heat transfer is required and 3mm at the bottom where the major problem is wear. A pair of huge side plates after nickel plating is shown in *Figure 18*.

The improvements in mold performance resulting from nickel plating are dramatic. In addition to the improvement in steel quality due to the avoidance of copper pickup, enormous extension of mold life is obtained. This is best explained by comparing the tonnes of steel produced before a mold replacement is required. Direct comparison among different plants is difficult, as all steelmaking variables cannot be taken into consideration, but the tonnages shown in *Table II* are typical.

After use, molds are remachined to remove the remaining nickel and produce the required contour on the copper side plate prior to replating. The only scrap generated, therefore, is a mixture of high-conductivity copper and high-purity nickel. This mixture is readily accepted as charge material by melters producing copper/nickel alloys.

The obvious benefits provided to the steel industry by the use of nickel-plated molds have been accepted worldwide. The increase in the efficiency of steel-making is attributed to the great extension of mold life and to the concomitant savings resulting from the decrease in the number of mold replacements required. Nickel plating continues to play a significant role in maintaining the high quality and efficiency of this major industry.

Batteries

Our society has never been more dependent on battery power than it is today. Sixty years ago domestic uses for batteries were largely confined to flashlights, radio sets and starter batteries for cars and motorcycles. Today, modern households typically have 40 to 50 hidden away in all sorts of consumer products – from clocks and watches to portable CD players and mobile phones. Away from the home there are many other applications, particularly for large batteries. Examples include the standby batteries for emergency use in hospitals, hotels, department stores, telephone exchanges etc.; traction batteries for electric vehicles (tugs, tractors, forklift trucks, wheelchairs, golf carts); batteries for solar panels and wind generators; defense batteries in armaments, missiles, submarines, torpedoes.[18]

Nickel is an essential component in many widely used batteries. The best examples are the nickel/cadmium (Ni/Cd) and the nickel/metal hydride (Ni/MH) batteries. Electroplating and electroforming play a critical role in producing these batteries which not only power so many of the appliances on which we depend, but also have many important industrial applications. Both Ni/Cd and Ni/MH batteries are secondary, or rechargeable, and must therefore have a high electrical efficiency, be capable of many charge-discharge cycles, and be able to be recharged quickly. They are also sealed and maintenance-free. Typical applications are in audio devices, mobile phones, cordless phones, camcorders, portable computers, compact disc players etc. *(Figure 19)*. On an industrial level, they are used for engine starting, for example, by airlines and aircraft manufacturers;

Figure 19 Ni/Cd and Ni/MH batteries provide power for many small appliances.
(Courtesy of Sanyo Canada Inc.)

electric traction, including electric or hybrid vehicles; and by railroad and public utility operations.

Market acceptance of electric vehicles has been slow for several reasons, including limited range, recharging facilities and overall performance. Nevertheless, it appears inevitable that strong demand by environmental agencies for their increased use will continue. In fact, the California Air Resources Board voted unanimously in September, 2000 to keep its zero-emission vehicle program in place.[19] Ni/Cd and especially Ni/MH batteries will continue to be strong participants in electric vehicle programs. They have played an important part in the U.S. Department of Energy and the U.S. Advanced Battery Consortium program and, during this time, their use has expanded from small batteries for the consumer electronics market to large batteries capable of powering light-duty electric vehicles *(Figures 20 & 21)*. The number of applications continues to grow for heavy-duty use, e.g., in battery-powered electric buses and within electric utility systems for energy storage.[19]

Figure 20 Recharging an electric car powered by Ni/MH batteries.
(Courtesy of Electric Vehicle Association of Canada)

Figure 21 Typical Ni/MH battery pack for electric cars.
(Courtesy of Electric Vehicle Association of Canada)

The electroplating and electroforming industry is mostly involved in the production of the positive nickel electrode, of which there are two types. These are the long-established and still widely used sintered electrode and the more recently developed foam electrode. Both types are required to have an open, highly porous structure capable of holding the maximum amount of the electrochemically active component of the electrode, that is, nickel hydroxide. The sintered electrodes are produced from special filamentary, battery grade powders manufactured by the carbonyl process. The electrode is produced by slurrying the powder in a cellulose-based binder, applying it at a controlled thickness onto a nickel-plated, perforated steel substrate, drying it and then sintering it in a reducing atmosphere at about 800°C.[20] A porosity of at least 86% can be obtained, and the structure has very small pore size that provides excellent conductivity paths. The perforated steel substrate that provides mechanical strength and supports the sintered powder is nickel-plated, allowing sintering to occur between the powder and the substrate, thereby increasing the bond strength. This is extremely important as the sintered plaque is subjected to severe deformation in the assembling of some batteries. The electroplating stage is therefore an integral part of the process used for battery production. It is a continuous strip plating process in a Watts-type electrolyte. Deposit thickness can be precisely controlled by the rate of movement of the strip through

Figure 22 Continuous nickel plating of perforated steel strip for use as a substrate in the production of sintered nickel electrodes.
(Courtesy of Precious Plate Inc.)

the tank and by the current used. The continuous plating operation is shown in *Figure 22*.

Nickel foam electrodes have been introduced much more recently than the sintered electrodes and have gained a very prominent position in the market, especially Ni/MH batteries. Nickel foam can be produced by electroforming or by a chemical vapour deposition process using nickel carbonyl. The electroforming method has been used for many years in Japan and is now used in plants around the world. The product is another excellent example of the versatility of the electroforming process and how important it is in the production of numerous items on which modern society depends.

The foam electrode consists of self-supporting nickel foam with a typical porosity of 95% and a density of only 0.4 g/cm.[3] In theory, the electroforming production method is quite simple: the mandrel material is polyurethane foam with controlled porosity, onto which nickel is electroformed and the organic material is subsequently burned out. In practice, however, the process is more complex: practical and economic considerations require the foam to be produced on a continuous basis, which means that rolls of foam mandrel material are processed through the electroforming tank in a way similar to steel strip in a continuous strip plating line. Initially the foam must be uniformly coated with an electrically conductive layer, and both graphite and electroless nickel have been used, the former being applied by spray or immersion coating methods. The electroformed nickel is normally deposited from nickel sulphamate solutions to obtain low stressed deposits; and current density is initially maintained at low levels but may be increased to 10 A/dm^2 as the thickness of the deposit increases. In *Figure 23*, coils of foam coated with nickel are shown being rewound after passing through the electro-forming tanks. Following the electroforming stage, pyrolysis is used to remove the polyurethane foam. Obtaining maximum porosity while maintaining adequate strength and ductility in the nickel foam is a major requirement for this application. Electroformed nickel is capable of meeting these requirements. The skeletal structure and high porosity of the nickel foam is shown in *Figure 24*.

Figure 23 Nickel foam is coiled after continuous electroforming operation.
(Courtesy of RPM Ventures)

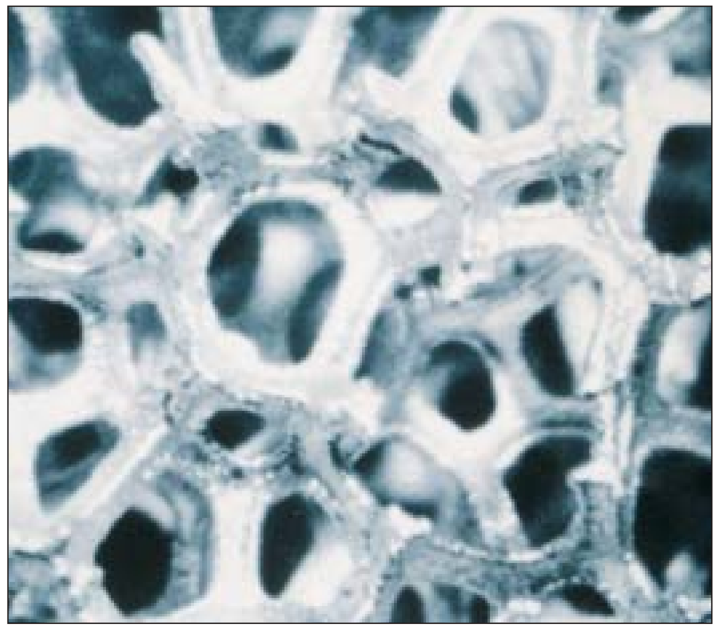

Figure 24 The high porosity skeletal structure of electroformed nickel foam.
(Courtesy of Sumitomo Electric Industries)

Nickel electrodeposition has another application in the production of Ni/Cd and Ni/MH batteries, and this also requires a continuous plating operation. Coils of thin gauge steel strip used to produce battery cases are plated with a very thin layer of nickel in continuous strip lines to provide corrosion protection. It has been estimated that about 20,000 tonnes of nickel were used in batteries in 1998 and an annual increase of up to 8% has been forecast until 2003, a move driven by the expanding use of mobile phones and laptop computers.[21] Electroplating and electroforming continue to play a major role in this important and still burgeoning industry.

The recycling of nickel-bearing batteries has progressed considerably in the last decade. For instance, technology is in place for the complete recycling and recovery of nickel and cadmium from Ni/Cd batteries. Undoubtedly, the major concern is the recovery of cadmium, but this can be efficiently achieved by reducing with carbon, vapourizing and condensing to produce cadmium metal.[22] This is then returned for reuse in the manufacture of new batteries. Nickel battery components can be processed pyrometallurgically to produce feedstock for stainless steel producers. Alternatively, a combination of mechanical and hydrometallurgical processes has been developed to recycle Ni/MH batteries to recover nickel, cobalt and rare earths.[23]

The collection of spent batteries has presented problems to battery producers – not so much in regard to large industrial batteries, but particularly the millions of small domestic batteries in use. Various approaches have been undertaken to improve collection services. For instance, in the U.S. the Rechargeable Battery Recycling Corporation (RBRC), funded by battery manufacturers, encourages the collection and recycling of consumer-type batteries in a legal, cost-effective and environmentally sound manner.

Figure 25 Only electroless nickel can provide the thickness uniformity and solderability required on complex heat sinks.

Electronics

Society depends heavily on the electronics industry to provide us with the means to enjoy the advantages offered by present technology. The metal finishing industry has benefitted from the high demands of electronic component manufacturers and has contributed greatly to the rapid technological advances and to miniaturization.Electroplated nickel, electroless nickel, electroformed nickel and several specially developed alloys are strongly associated with this industry, and in most cases there are no readily available substitutes. Important desirable properties include corrosion-resistance, wear-resistance, solderability, smoothness, uniformity and magnetic response. These advantages have all contributed to making the electronics industry the single largest user of electroless nickel coatings, and there are many different applications.[24]

Corrosion-resistance, solderability and the capability to deposit uniformly (even on parts of complex shapes) are some of the reasons why electroless nickel has become an essential part of many components used in the electronics industry. Heat sinks are devices used to cool semiconductor components during operation. Since they are required to possess good thermal conductivity, copper or aluminum is usually the material of choice. They are also required to dissipate heat efficiently, an ability achieved by maximizing surface area by the use of fins, as shown in *Figure 25*. The design entails deep recesses and they are often plated with electroless nickel to protect such parts from corrosion and to provide them with a hard, durable coating capable of being soldered or brazed.[4] Although electroplated nickel generally has superior soldering properties, it cannot be deposited uniformly on components with deep recesses such as heat sinks.

As a result of miniaturization and high-volume production, electroless nickel has replaced electroplated nickel in many areas. Nevertheless, nickel electroplating continues to be widely used and nickel sulphamate is usually the electrolyte of choice. It can provide fast deposition rates and very low stressed deposits with excellent soldering and brazing properties. The main disadvantage of electroplating for the electronics industry is that electrical contact must be made to every component, or area of a component, and miniaturization and circuit complexity often make this impractical. There is no such requirement for electroless nickel, and when millions of components are being produced, it is often the only practical and economical method of obtaining uniform, high-quality deposits. Other individual metals cannot provide the same range of properties required by the electronics industry.

A good example of the use of electroless nickel on small components manufactured on a large scale is the TO-3, a semiconductor component developed in the late 1950s as the original power transistor device.[25] It allows a small package to act as a voltage regulator for any electronic device from rectifiers to toasters. Millions are produced every year and, although they were initially electroplated with nickel, the greater productivity and reliability obtained with electroless nickel (as quantity requirements increased) contribute to its continuing huge demand. The use of nickel on this part has not been challenged since its introduction.

Most printed circuit boards are still solder mask over bare copper (SMOBC).[6] The hot air solder levelling process (HASL) is often used, whereby after application of the solder mask, the panel is fluxed and dipped into molten solder at about 230°C. Air knives using hot air are then used to smooth the solder surfaces. However, HASL has several disadvantages such as poor levelling of the solder, thermal shock to resins and solder mask, contamination caused by flux residues and design limitations in fine-pitch and ultrafine-pitch technologies. One alternative to HASL is an electroless nickel/immersion gold process that is rapidly becoming the process of choice for several reasons. It offers improved shelf life in hot, humid conditions and solderability remains excellent after long-term storage. It is compatible with all assembly solder pastes, fluxes and cleaning procedures and easily withstands multiple reflow cycles during assembly. In addition, it offers excellent planarity for ultrafine-pitch technologies, and the control of thickness ensures joint reliability by preventing embrittlement. A typical board is shown in *Figure 26*. For this

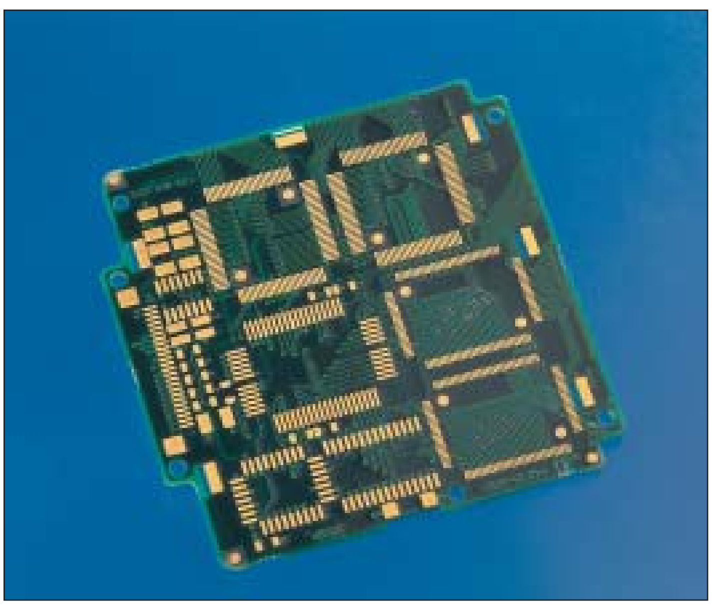

Figure 26 Electroless nickel/immersion gold deposits offer many advantages in printed circuit board production.

growing application, low or mid-phosphorus electroless nickel deposits are preferred as they enable better gold coverage and denser coatings to be obtained. Typical thickness for the nickel deposits is 5 microns. In some printed circuit board applications, electroless nickel has successfully replaced electroless copper. For instance, nickel has been shown to have technical and environmental advantages over copper for plated-through holes and additive circuits.[26] Technical advantages include improved metal coverage, especially in small holes, and greater hardness providing greater wear-resistance. Environmentally, the use of electroless nickel eliminates the use of formaldehyde, a recognized hazardous organic component in the electroless copper system.

When the application of solder paste is required for fine-pitch devices, nickel has also proven to be of great benefit. In this case, electroformed nickel stencils have been shown to be superior to the alternatives.[27] As the industry trend continues to be toward more complex devices, higher pin counts and smaller circuits, the degree to which miniaturization can occur is limited by the soldering process. For instance, when devices have over a hundred leads, with typical sizes of only 175 microns separated by as little as 325 microns, it is imperative that the amount of solder on each pad is the same. This allows planarity of the leads to be maintained and prevents shorting between the leads (caused by excessive amounts of solder). Electroformed nickel stencils for the critical, high-precision application of solder paste has provided technical and economic advantages over chemically etched and laser-cut stencils.

The high electrical conductivity of copper and the excellent high-temperature properties and corrosion-resistance of nickel make a combination of great benefit to the electronics industry. For instance, large quantities of copper wire are nickel electroplated at size to provide a barrier layer against diffusion of gold, silver and solder into copper when operating at elevated temperatures. There is no readily available, economical alternative to nickel as a barrier coating or as a corrosion-resistant coating at elevated temperatures. Nickel is used extensively throughout the industry for this purpose and a deposit only 1.3 microns thick is normally sufficient to act as a barrier layer between copper and gold or silver. Electroless nickel-phosphorus and nickel-boron coatings are reported to be slightly superior to electroplated nickel as barrier layers.[26]

The protection of copper wire by electroplating with nickel is an important requirement in many critical applications. The combination provides two main features: (1) the 100% International Annealed Copper Standard (IACS) conductivity of copper necessary for efficient electrical and thermal energy transfer and (2) the corrosion-resistance and thermal stability of nickel.[28] For military applications, the use of unplated copper conductors is usually limited to maximum temperatures of 105°C. Higher temperatures will cause severe oxidation, decreased ductility and lower conductivity. Nickel plating allows conductors to be used in continuous operations at temperatures as high as 450°C. For instance, with a nickel thickness equivalent to 10% by weight, continuous operation at 420°C is possible. Applications for nickel-plated copper include aerospace wiring in corrosive environments, aircraft engine and fire zone safety wiring, automotive engine and exhaust monitoring, high-temperature appliances, furnaces and downhole oil logging. Nickel-plated copper wire for these applications is normally produced by electroplating copper wire or rod at high speed on a continuous basis, followed by drawing down to wire of the required diameter. A uniform, coherent nickel layer is maintained through the drawing process. Continuous plating of heavy copper wire is shown in *Figure 27*.

Figure 27 Continuous nickel plating of heavy copper wire prior to being drawn down to fine, corrosion and heat resistant wire for critical applications
(Courtesy of Torpedo Specialty Wire Inc.)

Electroless nickel, with its excellent corrosion and wear-resistance properties, is widely used for the protection of connectors in the electronics industry. These are often aluminum or zinc alloy parts and, as the trend toward decreased size in this industry continues, electroless plating applications increase. Nickel also offers good lubricity, hardness, solderability, electrical conductivity and appearance for connector applications.

Nickel has a very important role in electromagnetic interference (EMI) shielding applications for electronic equipment. *(Figure 28)*. It is often used in conjunction with

Figure 28 Electroless nickel is widely used in EMI Shielding applications. The entire surface of these cell phone casings are plated with copper and nickel prior to the final paint finish.
(Courtesy of Siegfried Schaal Metallveredelung GmbH)

electroless copper on plastic housings, and this combination is reported to have better shielding characteristics than alternative coating systems.[26] The nickel also provides protection of the copper against corrosion and tarnishing. Shielding applications require very large areas to be covered and typically, nickel thickness varies from 0.25 to 0.50 microns.

Although there are a very large number of applications and requirements for nickel plating and electroforming in the electronics industry, the total amount of nickel used is less than in many other major industries. Miniaturization and generally thin deposits are major reasons for this. Nevertheless, electronic scrap material often contains nickel, although normally at low concentrations in association with copper. In many instances, precious metals or platinum group metals will also be present – so recycling of the scrap is both economically and environmentally preferred. Operations are established in North America to process copper and nickel-bearing scrap metallurgically to produce a concentrate suitable for recycling by primary metal producers.

Other Industries

Many industries other than the five already described have a very real need for nickel plating and electroforming. There are numerous applications: some in which nickel is indispensable and others where nickel properties have provided excellent performance, extended life, less scrap and cost benefits. Some applications in three other important industries – aircraft/aerospace, oil and gas and textiles – are briefly described next, further demonstrating the widespread need for, and use of, nickel plating and electroforming.

Aircraft/Aerospace

The aircraft/aerospace industry uses nickel coatings and electroforms for corrosion-resistance at elevated temperatures, to protect airfoil components from abrasion and erosion[29], to provide a surface coating that will allow high nickel/chromium alloy parts to be joined by brazing or welding, to produce nickel or nickel alloy components for space applications and to repair worn or damaged components, thereby enabling them to be returned to service rather than being scrapped. A heavily masked hub ready for repair by nickel plating is shown in *Figure 29*. Electroless nickel coatings have been used 4,[30] on bearing journals, servo valves, compressor blades, turbine blades, pistons, engine shafts, engine mounts, landing gear, hydraulic and manifold systems, gyroscope components and optics. In the space program, these same coating have been used effectively on the docking, cargo bay and rudder mechanisms of the NASA Space Shuttle.

Figure 29 Heavily masked CF-6 hub is nickel plated to repair a damaged or over-machined area..
(Courtesy of United Airlines)

Nickel electroforming has also made important contributions to the space program. For instance, it has been used to produce lightweight precision parts such as waveguides and antennae, bellows heat shields and regeneratively cooled thrust chambers for rocket engines.[31] Electroforming is a process ideally suited for the production of high-precision nickel bellows shown in *Figure 30* and is the most economical and, in some cases, the only practical method. These important parts are used for flexible electromagnetic interference shielding, metallic hermetic seals, volume compensators, temperature and pressure sensors and flexible couplings.

Figure 30 Multi-purpose electroformed nickel bellows are widely used in the aerospace industry.

Both the European and U.S. space programs have used nickel electroforming with great imagination and success. An impressive example of this is in the production of regeneratively cooled thrust chambers with internal cooling passages. These complex structures, with their demanding mechanical properties and weight specifications, have been produced by nickel electroforming for the third stage of the Ariane space launcher and the main engine of the NASA Space Shuttle *(Figure 31)*. Obtaining a wide range of excellent mechanical properties in electrodeposited nickel by controlling deposition conditions or by alloying with other metals such as cobalt or manganese is an important ability of the electroforming process.

The Hubble Space Telescope (HST) is providing scientists and astronomers with exceptional images from space that will improve our understanding of the universe. It is a remarkable achievement and nickel electroforming has had an important role in the manufacture of parts for the HST because of the ability of the process to meet extremely stringent dimensional specifications. The slit wheel segments for the Space Telescope Imaging

Figure 31 An electroformed nickel combustion chamber for the Ariane rocket.
(Courtesy of Messerschmidt - Bölkow Blohm)

Spectrograph (STIS) were produced by nickel electroforming[32] and then vacuum-laminated to stainless steel wheel segments. The precision required for the slit wheel demanded the production of multilayer electroforms with tolerances of ±1 micron. This was achieved and this application of nickel electroforming has made a significant contribution to the success of the HTS exploration program. The STIS and the slit wheel segments are shown in *Figures 32 and 33*, respectively. In this application, the extremely high precision obtained by nickel electroforming has made it possible to produce enhanced coronographic HST images such as the bright, optically visible, isolated Herbig star AB Aur, as seen through an electroformed slit wheel segment *(Figure 34)*.

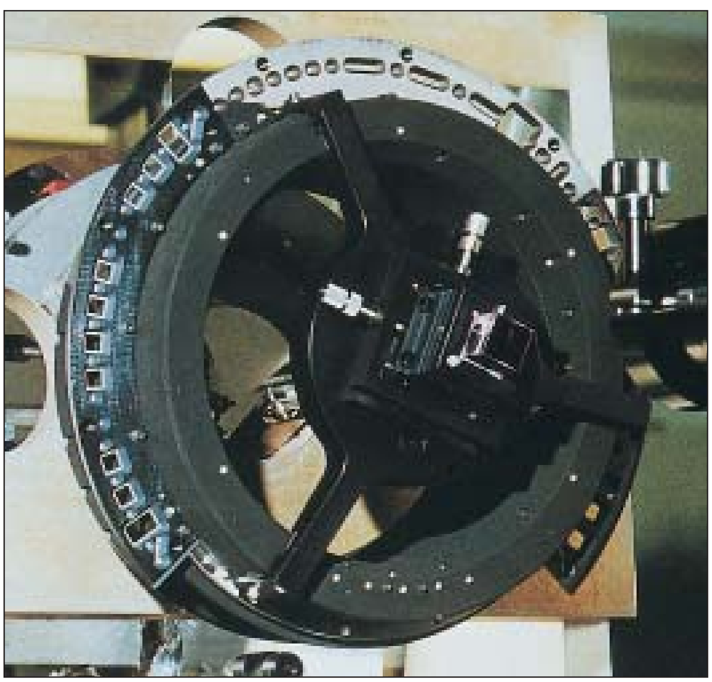

Figure 32 Critical components on the Space Telescope Imaging Spectrograph (STIS) used on the Hubble Space Telescope (HST) are made by electroforming.
(Courtesy of Max Levy Autograph, Inc.)

Figure 33 One of four high precision, electroformed nickel slit wheel segments essential to the success of the STIS and the HST.
(Courtesy of Max Levy Autograph, Inc.)

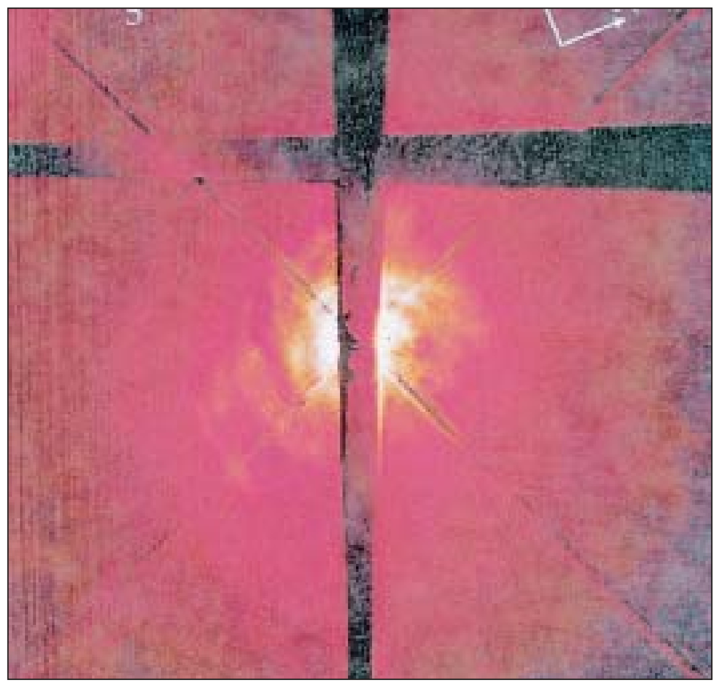

Figure 34 Electroforming contributed to the production of this enhanced coronographic image of the Herbig star, AB Aur, a valuable tool in studying the universe.
(Courtesy of Max Levy Autograph, Inc.)

Oil and Gas

Electroless nickel has been particularly useful in the oil and gas industry. Advantage has been taken of the thickness uniformity of the deposits and the wide range of properties attainable by control of their chemical composition.[11]

Phosphorus content is the major consideration and an extremely useful variation in properties can be obtained within the range of 3 to 14% phosphorus. The performance and service life of many of the base materials traditionally used in the industry have been greatly enhanced by applications of electroless nickel. Properties such as corrosion-resistance (especially of the high-phosphorus coatings) and abrasion/erosion-resistance have been of great value.

Electroless nickel is used successfully in all three major areas of the industry: surface operations, subsurface or downhole operations and offshore operations. The number of components whose performance has been enhanced by nickel plating is impressive, and the resulting reduction in scrap remains substantial. Typical components include[33] blowout preventers, chokes, compressors, pumps, pump housings, manifolds, valves, plungers, packers, safety valves, tubing, heat exchangers and riser connectors. For instance, the failure rate of mud pumps as shown in *Figure 35* has been greatly decreased by electroless nickel plating.

Figure 35 Electroless nickel plated mud pump bodies.

Of special interest is the widespread use of nickel plate in valves and flow control devices. This situation has resulted not only from the smoothness, corrosion-resistance and wear-resistance of electroless nickel but also from the unique property of thickness uniformity which allows strict dimensional tolerances on these parts to be maintained. Electroless nickel has largely replaced chromium and now dominates this market. A thickness of 75 microns on a mild steel ball valve is typical in this industry, and large plated ball valve plugs and bodies are shown in *Figure 36*.

The oil and gas industry has an enormous demand for tubular components.[4,33,34] For instance, 30,000 metres of

Figure 36 Electroless nickel plated ball valve plug, 105 cm diameter. Thickness uniformity and corrosion resistance are major requirements of the deposit.

tubing coated with 50 microns of electroless nickel were installed downhole in the Permian Basin area of Texas over a four-year period.[34] Mild steel is the preferred material for tubing, but it is not always cost-effective, owing to poor corrosion and abrasion-resistance. Limited life, frequent replacement and plant downtime are serious cost factors but, when coated with 50 to 100 microns of high-phosphorous electroless nickel, the cost/performance factor can be very positive. There is an obviously strong need for electroless nickel in this industry which it has been estimated, accounts for approximately 15% of all electroless nickel plating in North America.[33]

Textiles

We live in a society that is very fashion-conscious. The fashion industry is huge and fashions rarely stay constant over long periods of time. Trends in the textile industry are of great importance to many electroformers and platers. In fact, one of the largest applications for nickel electroforming is in the production of high-precision screens for printing fabrics *(Figure 37)*.

For many years, the industry has used electroformed rotary screens for printing textiles.[31] The printing process requires one screen for each colour in a pattern; so the more colours and the more complex the pattern, the more screens are required for printing. The screens are installed on the printing machine and rotate in precise synchronization with

Figure 37 Fashionable textiles are printed with rotary nickel screens.

each other as the textile to be printed passes beneath and in contact with them. Each colour, therefore, requires its own pattern on the screen, which consists of an open mesh area through which dye can flow and a sealed area which prevents flow. Dye is forced through the open area of a screen from the inside as it rotates and contacts the textile. Typical patterned, electroformed screens and a close-up of the open and sealed areas are shown in *Figure 38*, and a set of screens in use on a textile printing machine is shown in *Figure 39* with the printed fabric seen at the far end of the machine. The requirement for high-precision screens with accurate alignment on the machine is obvious. Imagining the astronomical number of patterns that are printed on textiles around the world each year, gives an indication of the importance of nickel electroforming to the textile industry.

Typical rotary printing screens for textiles are 3 to 6 metres long with a diameter of approximately 20cm and a thickness of 100 microns. Mesh size is usually in the range 40 to 200 mesh. With a typical hole size of 125 microns and

Figure 38 Typical electroformed rotary screens with patterns applied by photoresist techniques. Close-up shows sealed areas and open areas through which dye can flow.

Figure 39 Textile printing machine using electroformed nickel screens.

60 holes/linear cm, each screen contains millions of holes, all of which are produced with remarkable precision by electroforming. The mechanical properties and especially the ability to control the internal stress of nickel electroforms are major reasons why nickel is a definite requirement for this important application.

Electroless nickel also has many applications in the production of textiles and has contributed significantly to cost reductions and improved quality.[35] The requirements are mainly for good corrosion-resistance and wear-resistance. Wear on textile machinery, one of the most serious industry problems, results from the movement of fibres at extremely high speeds. Consider the fact that a single machine can produce over ten million metres of yarn per week on a continuous basis. Traditionally, hard chromium plate has been used to provide wear and corrosion-resistance, but only with limited success. Electroless nickel is now the coating of choice to provide the smooth, abrasion and corrosion-resistant finishes on most components in contact with textile fibres. These include thread guides, fibre feeds, bobbins, shuttles, rapiers, ratchets, needles and picks.[36] There are also some applications in this industry for the use of electroless nickel composites, that is, nickel with codeposited diamond particles, silicon carbide and polytetrafluorethylene. These are usually special requirements, such as in the production of cotton/polyester blends and the “texturing” of polyester yarns.

The textile industry also requires corrosion-resistant coatings. In the weaving process, for instance, various chemicals are applied to the fabric to assist its progress through the loom. Some of these chemicals are corrosive to some of the steel components of the loom (for example, the drop wires and needles). Corrosion not only reduces the life of these components but can cause unacceptable staining of the fabric. High-phosphorus electroless nickel provides the necessary protection.

Of great benefit to the textile industry, electroless nickel provides a method of greatly extending the life of many critical components on complex machinery and consequently has a marked positive effect on product quality and the economics of fashion.

Environmental Issues

The applications for nickel plating and electroforming described in this publication explain the importance of these processes to some of our major industries and to technological progress in general. Certainly nickel is currently indispensable in many of these applications, and it is important to be aware that the processes operate under strict environmental regulations. Some of the environmental issues facing the industry will be mentioned now, accompanied by brief descriptions of certain methods for controlling nickel-containing materials in the metal finishing industry.

For many years, environmental agencies have imposed strict regulations on the metal finishing industry, and the level of compliance in North America is high. As a result, the overall standards within the industry, and its image, have improved considerably. Cadmium, chromium and cyanide compounds have experienced some of the strictest legislation because of their proven toxicity, but their use is far from over. Cadmium, for instance, is a known carcinogen but it is still used for many applications where there is no suitable alternative – in some military and aircraft applications, for example. Since there are health risks associated with the inhalation of chemicals and fumes found in the plating and electroforming industry, including nickel metal and nickel salts, very strict regulations on their use and disposal are in place. There can be no argument about the paramount importance of health and safety in the industry, but it is also necessary that the regulatory goals be proportionate to the potential risk, realistically attainable and based soundly on the results of rigorous science. Most of our major industries have some dependency on nickel plating and electroforming, and inappropriate regulations could have serious repercussions on their efficiency. Compliance with present regulations constitutes a large part of the total cost of plating operations, and further increases caused by more stringent regulations could result in more plant closures. Industry representatives, the Nickel Development Institute (NiDI), the Nickel Producers Environmental Research Association (NiPERA) and government agencies such as EPA must continue working toward establishing regulatory standards that reflect the proven status of nickel products used in the plating and electroforming industry. Any tightening of environmental regulations must result from cooperative studies agreed upon by these organizations.

Nickel platers have long recognized that environmental control is crucial to their survival as an industry. Two of their major objectives have been to minimize the amount of nickel-bearing waste generated and to implement recycling or reclamation programs wherever possible, rather than disposing of metal units. Today’s plants have addressed and met these objectives. The industry has strongly advocated reduction of waste at the source, followed by recycling, recovery or reuse as preferred options to disposal. There are many ways in which nickel can be lost from plating lines and enter waste streams. This nickel is usually in solution as sulphate, chloride or sulphamate. These compounds are generally not recognized as carcinogenic in animals or humans via oral ingestion. Loss can occur as solution drag-out with plated parts, during anode maintenance or solution transfer, and through poorly maintained pumping and filtering equipment.

At present, in the United States, platers are required to reduce the nickel content in effluent leaving their plants – the daily maximum being 3.98 parts per million, and a monthly average of less than 2.38 ppm. However, much stricter regulations have been proposed. Several methods are used to meet present standards but initially it is extremely important, both practically and economically, to ensure that the volumes of solution to be treated are minimized. This has been done most efficiently by introducing counter-flow rinsing after nickel plating, which requires two or three rinse tanks to be used instead of one. Deionized water is added to the final rinse tank and the overflow transferred to the previous tank and so on. The water is "counter-flow" or running opposite to the direction of the movement of the plated parts. The major advantages of counter-flow rinsing are:

- very clean final rinses are possible
- most nickel salts concentrate in the first rinse and are ready for recycling/reclamation
- rinse water requirements can be reduced by over 90%

Several methods are in common use for the recycling/reclamation of nickel from in-plant solutions. Some are complicated by the type of nickel deposition processes being used and it is not the intention of this publication to present details of solution treatment methods as these are well-documented in literature dealing specifically with environmental issues. The intention here is to identify the range of processes now being used by the nickel plating and electroforming industry, in its dedication to complying with demanding environmental regulations.

In-plant process methods include evaporation, reverse osmosis, ion exchange, electrowinning and sludge precipitation. Atmospheric and vacuum evaporation is used to concentrate rinse waters. These solutions can then be returned to the plating tanks to compensate for evaporation losses or used for other metal recovery processes. If returned to the plating tanks, it is important to recognize that impurities in the solutions are also concentrated during evaporation and should not be allowed to reach critical levels. Organic impurities and metallic impurities can be removed by carbon treatment and low-current density electrolysis, respectively.

Reverse osmosis is an alternate method of concentrating nickel-bearing solutions but because it requires the use of membrane technology, it is not widely used. If two solutions with different concentrations of dissolved solids are separated by a semipermeable membrane, water will flow from the more dilute solution through the membrane and into the more concentrated solution until an equilibrium is reached. The pressure required for this to occur is the osmotic pressure. In reverse osmosis, water is driven in the opposite direction by applying pressure to the more concentrated solution. The pressure is applied by a pump and, at the membrane surface, ionic species such as Ni^{++} are repelled, while pure water passes through. Water can, therefore, be recovered and nickel solutions are concentrated for either return to the plating line or for further treatment. Nickel concentrations are typically 10 to 20 g/l.[37]

Successfully used for nickel recovery in many plants, ion exchange has the advantage of eliminating organics so that the recovered nickel can be transferred back to either bright or semi-bright tanks without the risk of cross-contamination of additives. Recovery requires the nickel-bearing solutions to be passed through a bed of cation exchange resin. Nickel replaces hydrogen in the resin and it is possible to reduce nickel concentrations in solution from several grams per litre to a few milligrams per litre. When the resin has accepted all the nickel it can, the resin is regenerated by passing sulphuric acid or hydrochloric acid through the bed, and nickel is removed as nickel sulphate or nickel chloride solution, typically at concentrations up to 30 g/lNi^{++}. Since these solutions are too acidic to return to the plating tank the pH level can be increased to about 3 to 5 by passing them through another ion exchange bed which will absorb the excess acid. The recovered acid can then be reused in the previous regeneration step, while the recovered nickel solutions can be returned to the plating line or retained for further processing.

Nickel can be recovered as metal by electrowinning, which is similar to electroplating except that insoluble anodes are used. Nickel is plated out on cathodes but, rather than nickel being dissolved at the anodes, only gaseous products are produced. For instance, if a sulphate electrolyte is used, from ion exchange recovery, only oxygen will be released at the anodes. Several types of electrowinning cells have been developed for metal recovery and these can be operated with continuous recirculation of solution between the first rinse tank and the electrowinning cell. Because nickel concentrations are low, solution movement must be very fast and the pH must be adjusted to maintain good nickel deposition rates. Special porous cathodes are used to allow solution to flow through them and to provide very large surface areas, which help to improve cathode efficiency. The nickel metal deposited at the cathodes is usually sold as scrap and is typically recycled by stainless steel producers.

The removal of metal units by precipitation as hydroxide sludges is a method frequently used by the metal finishing industry to meet regulations for plant effluent. Many nickel platers generate such sludges, but the problems of storage, transportation and disposal as landfill have become increasingly difficult. There are several good reasons for this:

- very high cost
- valuable metal units are permanently lost
- the number of landfill sites has decreased dramatically
- liability remains primarily with the producer of the waste

Consequently there has been a very strong trend in North America toward recycling as an alternative to disposal at landfill sites. Many recycling companies are now accepting plating waste sludges, and some are also willing to accept liquid waste. Sludges for recycling are normally required to meet compositional requirements which are determined by the recycling process used and the resulting end product. Sludges are thoroughly examined and analyzed before acceptance, and any single recycler is unlikely to accept all types of sludge. The use of recycling services eliminates landfill liability and returns nickel and other metal units back to industry.[38] Typical nickel-bearing products from recycling plants include cast nickel/chromium/ iron ingots for return to the stainless steel industry and nickel/copper concentrates needed by major primary metal producers.

The determination shown by the U.S. metal finishing industry to address environmental issues is evident in many ways. As one of six sectors targeted by the EPA, in 1993, the industry introduced its Common Sense Initiative (CSI) aimed at developing cost-effective, flexible and environmentally protective practices for specific industries.39 Out of this came the Strategic Goals Program (SGP) which called for cleaner, cheaper and smarter environmental practices in metal finishing companies. The SGP is a cooperative effort involving the EPA, the American Electroplaters and Surface Finishers Society (AESF), the National Association of Metal Finishers (NAMF) and the Metal Finishers Suppliers Association (MFSA). To represent the industry in this program, AESF, NAMF and MFSA created the Surface Finishing Industry Council (SFIC), and EPA representatives have commended the industry for its cooperation in addressing important environmental issues. Through the SGP, participating companies have been encouraged and assisted in meeting the required levels of compliance. More specific to nickel issues, a Nickel Strategy Group has been formed and organizations supported by nickel producers, such as NiPERA and NiDI, are now more heavily involved in metal finishing industry activities than ever before.

Evidence of the importance of environmental control is also clearly seen at industry conferences and exhibitions. An industry has grown within an industry. A large segment of the metal finishing industry now consists of companies providing environmental control services. Their importance is unmistakable, and the amount of available technical information provided is truly impressive.

In spite of industry cooperation with regulatory agencies and the high level of compliance of nickel platers and electroformers, the threat of stricter legislation for nickel still exists. Current knowledge of the toxicity of soluble nickel compounds does not warrant more stringent regulations. Any revisions to present acceptable levels of nickel would need to be carefully evaluated to avoid unnecessarily increased costs to nickel platers and electroformers. Moreover, the environmental benefits realized from plating, e.g., durability, conservation of resources, fuel efficiency and recyclability, would be lost and the resulting environmental costs would be considerable.

Summary

The enormous value of nickel plating and electroforming to major industries and to our present society is rarely recognized, even by many members of the plating community. The range of properties that can be obtained in nickel deposits is unmatched by any other plated metal. Electroplating and electroless plating provide resistance to corrosion, abrasion/wear and high-temperature oxidation for many substrates in many industries. Consequently, these processes contribute significantly to reduced generation of scrap and to conservation of a variety of materials. Nickel electroplating, for instance, produces attractively bright corrosion-resistant finishes that allow automakers to offer extended warranties – a true indication of the value of these finishes in extending the life of substrate materials such as steel, aluminum and plastic. Electroplating has also been used to great advantage by the steel industry to improve productivity and enhance quality. Electroless nickel provides unique magnetic properties and thickness uniformity for industries as diverse as electronics and oil and gas. The nature of the electroless process has benefitted the electronics industry in its ongoing trend to miniaturization and, at the same time, provides protection for huge ball valves and great quantities of tubulars in the oil/gas industry.

The value of nickel electroforming is equally impressive. Our current capacity for rapid information storage and retrieval by computer relies on electroformed thin film magnetic heads, and the production of compact disks is entirely dependent on nickel electroforming at this time. The fashion industry and the closely associated textile industry are both dependent on electroformed nickel screens for printing patterns on textiles. The increasingly important battery industry uses nickel foam electrodes produced by electroforming; and the aircraft/aerospace industry, recognizing the value of the mechanical properties and great dimensional accuracy that nickel electroforming can provide, is using the process to manufacture critical components for the space program. All these examples (and others described in this publication) clearly demonstrate the immense value of electroplated nickel, electroless nickel and electroformed nickel to the world's major industries.

As in all sectors of the metal finishing industry, nickel platers and electroformers have been under strong pressure to meet demanding environmental requirements. In North America, the metal finishing industry has responded extremely well in addressing environmental issues and has been commended for its cooperation with the EPA.[3] Increasingly, the emphasis is on minimizing the amount of in-plant waste and implementing programs for the recycling or reclamation of metal units.

Three industry organizations, NAMF, MFSA and AESF, created the Surface Finishing Industry Council (SFIC) to represent the industry in negotiations with environmental agencies and, more recently, a Nickel Strategy Group has been formed to address issues relating specifically to nickel. Nickel producers are also represented in this group by NiPERA and NiDI. The formation of the Nickel Strategy Group was considered to be appropriate in view of the possibility of stricter legislation being introduced for nickel plating operations.

Strict environmental regulations on the use of nickel and its salts are already in place, and the cost of compliance to platers and electroformers has been high. The industry agrees that there can be no argument about the health and safety aspects of the industry, but it feels strongly that regulatory goals should be proportionate to the potential risk, be realistically attainable and be based soundly on the results of rigorous science. The Nickel Strategy Group will represent the industry in negotiations with environmental agencies. It is anticipated that the information contained in this publication will be beneficial in demonstrating how serious the repercussions could be in our major industries, and to our society as a whole, if nickel platers and electroformers are faced with additional costs and possible plant closures resulting from inappropriate regulations.

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The Nickel Development Institute is an international nonprofit organization serving the needs of people interested in the application of nickel and nickel-containing materials.

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