



# The William Blum Lectures

#47 – Eric Brooman – 2008



**The 47<sup>th</sup> William Blum Lecture  
Presented at NASF SUR/FIN 2009  
in Louisville, Kentucky  
June 15, 2009**

## **Nickel and Surface Finishing: A Glorious Past - an Uncertain Future**

by  
**Dr. Eric W. Brooman**  
Recipient of the 2008 William Blum  
NASF Scientific Achievement Award





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### Introduction

Let me start by saying that it was a great privilege to present this year's William Blum Lecture as part of the recognition that accompanies the honor of receiving the 2008 Scientific Achievement Award.

Normally, this Lecture provides the opportunity for the awardee to present some highlights of their research and development accomplishments over the years that led to their nomination and selection. However, in light of the important Plenary Session on "The Global Outlook on Nickel", I was asked to tailor my presentation towards: (1) the significant contributions nickel has made to the manufacturing base in the past and present; (2) the contributions made by the metal and surface finishing industries, research at academic institutions, and research, development and technology transfer at government and military laboratories and related facilities; (3) the concern about the impact of present and proposed regulations and legislation pertaining to nickel; and finally (4) describing the opportunities for surface finishing relating to nickel to contribute in the future.

This more formal version of my presentation follows the original outline:

- What is nickel and why is it important in the present context?
- The role of surface finishing in the use of nickel, and a brief history of significant developments
- Some examples of applications and developments in a range of industries, including:
  - General commercial and industrial products
  - Ground transportation
  - Aerospace and astronomy
  - Medical devices and treatments
  - Micro-electro-mechanical devices
- A brief reference to some environmental drivers that relate to:
  - Nickel
  - Chromium alternatives
  - Nickel alternatives
- A discussion of some options for responding to these environmental drivers
- Where do we go from here?

It concludes with some final thoughts to summarize the lecture and the implications that have been made with respect to how changing nickel regulations can affect the surface finishing industry.

### What is nickel and why is it important?

Nickel is a finite resource and is the fifth most common element on earth after iron, oxygen, silicon and magnesium.<sup>1</sup> Once extracted, however, nickel can be recovered, recycled and re-used. Fortunately, only relatively small amounts are lost during

use and re-use, so the availability of nickel at this time is not a major issue. The losses result primarily from nickel containing emissions to air, water and soil during processing, which are not economically viable to recover.

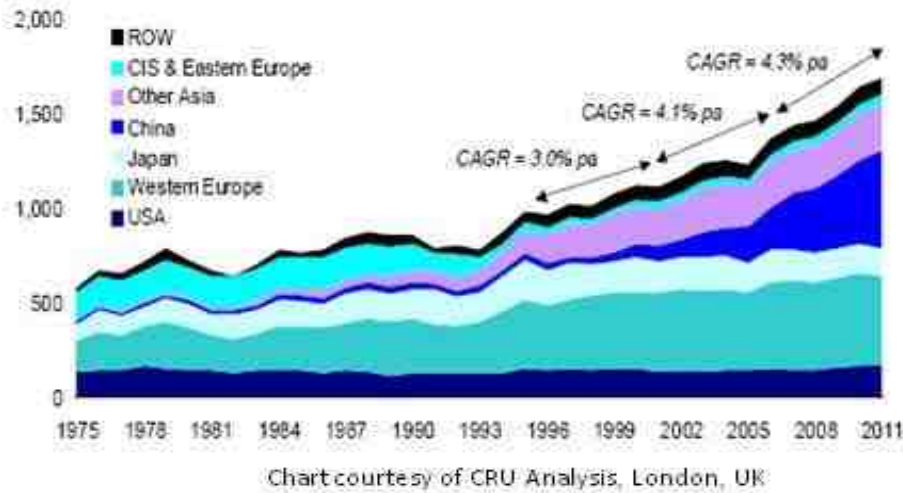


Figure 1 - World consumption of primary nickel (in thousand tonnes) (Chart courtesy of CRU Analysis, London, UK).

Although the current supply of primary nickel can meet demand, the major source (*i.e.*, sulfide ore deposits) is diminishing, and it has been stated that mining and refining of laterite ores must increase after 2010. As a consequence, new extraction methods will have to be developed, which in turn will result in increasing prices. Figure 1 shows the actual world-wide use of primary nickel and a projection through 2011.<sup>2</sup> Demand was relatively flat until about 1993, after which time the demand increased

at a compounded average rate of about 4%. As might be expected, the increase in consumption has been largely the result of the rise in manufacturing capacity in China, as it becomes more industrialized. In the industrialized countries, the smaller increases may be a function of the number of new technologies that have been developed in recent years, offset by the relatively small amounts of nickel used in each of these applications (See Figure 4 and the corresponding text).

Nickel is important because it has a wide range of desirable properties and is very versatile. It is an important alloying constituent in many industrial materials, such as stainless steels and proprietary aerospace, heat-resistant alloys. It is used also in a number of surface finishing applications to provide improved properties and aesthetic appeal. To illustrate this point, Fig. 2 shows the world-wide consumption of nickel by sector, while Fig. 3 shows it by product form.<sup>3</sup>

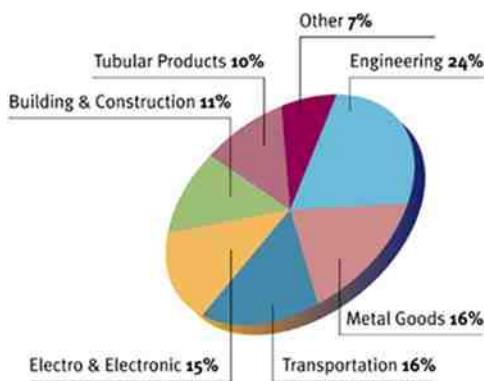


Figure 2 - World consumption of primary nickel by sector (2008) (Chart courtesy of the Nickel Institute).

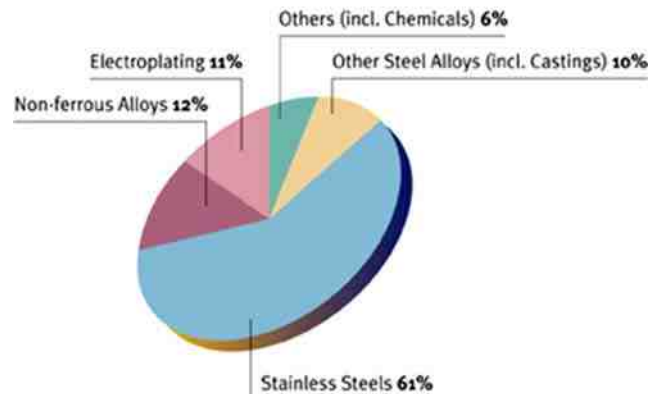


Figure 3 - World consumption of primary nickel by end use (2008) (Chart courtesy of the Nickel Institute).

Nickel and its alloys are used in so many products that affect our daily life that is hard to catalog them all. A few of the applications are listed in Table 1, and the nickel surface finishing technologies associated with some of these are described briefly in later sections of this paper.

Table 1 - Examples of typical applications relying on nickel and its alloys.

Building materials, architectural hardware	Ground, rail, sea, aerospace vehicles
Catalysts, chemical processing	Batteries, fuel cells, solar panels
Transportation infrastructure	Tools, dies, moulds
Fasteners, general hardware	Household appliances, lighting fixtures
Electrical, electronic devices	Office equipment, furniture
Medical products, instruments, devices	Photogravure plates, printing screens
Consumer products, jewelry	Farm, dairy equipment, structures

### The role of surface finishing

Surface finishing refers to processes that modify a surface or provide a new surface, such as anodizing or applying a coating. Methods to accomplish this are varied and incorporate sanding, grinding, blasting, cleaning, passivation, chemical conversion coating, anodizing, sealing, painting, and the application of coatings by chemical, physical, electrical or electrochemical means, with and without the use of a vacuum. Other methods may include electrochemical machining (to remove metal from the surface in a controlled manner) and electroforming to produce structures with desired shapes and features, as well as free standing, near net shape components. In the context of this paper, the discussions are limited to electroplating and electroforming to meet component or product requirements, with the focus on nickel and its mixtures, composites or alloys.

As seen above, nickel alloys used in cast, wrought and machined form are a significant portion of the world-wide consumption. However, for many applications nickel surface finishing is necessary to provide desirable properties, improve performance, and in some cases to allow product differentiation. Figure 3 shows that 11% of world consumption by end use is associated with surface finishing (“electroplating”), which according to Fig. 1 amounts to about 165,000 tonnes in 2009.

The value-added features and properties resulting from surface finishing include:

- Coatings with a desired composition and structure
- A desired smoothness or texture
- Different color and luster options
- Hardness and wear resistance
- Lubricity
- Corrosion control and heat resistance
- Providing a diffusion barrier
- Controlled magnetic permeability.

Examples of many of these benefits are discussed under “some nickel finishing applications” for a range of manufacturing categories.

### A brief history of developments

Surface finishing involving nickel has been documented for over 150 years, but most of the developments have occurred in the last 100 years. Figure 4 tries to capture some important milestones, based on a brief historical survey by the author, and it is not meant to be comprehensive or overly selective. Its purpose is to provide an overview of how we arrived at where we are today, and the inset chart depicts a trend in these developments over time.

Although the electroplating of nickel from a chloride solution was first described in 1837,<sup>4</sup> it was not until 1840 when an English patent was issued for a commercial nitrate bath.<sup>5</sup> A few years later, in 1843, an acid ammonium sulfate bath was described in Germany, which became the principle process used in commerce for the next 70 years.<sup>6</sup> During those years a neutral ammonium sulfate (“double nickel salts”) bath also was available.<sup>7</sup> This was commercialized in the USA in 1866.<sup>8</sup> In 1916, the formula for the ubiquitous Watts Bath was made available, and also around this time, bright nickel plating baths were developed. Around 1945 a leveling, semi-bright nickel bath was in use.<sup>6</sup> A “duplex nickel”, consisting of a sulfur-free, leveling layer followed

by a sulfur-containing, bright nickel layer, was patented in the early 1950s<sup>9</sup> to provide improved corrosion resistance, especially under plated, decorative chromium. In more recent times, other developments have been described in the open literature.

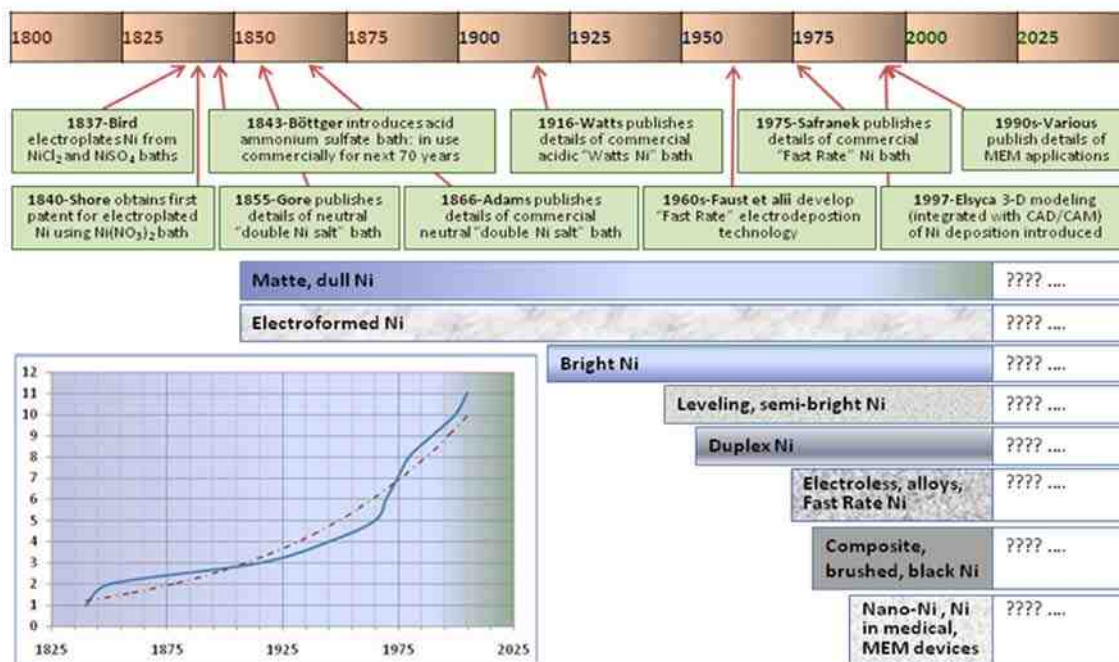


Figure 4 - Highlights of nickel surface finishing developments.

These later, somewhat arbitrary "milestones" that have been important to nickel surface finishing, in the context mentioned earlier, also have been used to develop the chart inset in Fig. 4. They may be summarized as follows:

- ~1840 Early work on nickel electroplating
- ~1850 A few commercial electroplating and electroforming baths now available
- ~1915 Watts Bath introduced and consistent bright deposits possible
- ~1945 Leveling and duplex nickel baths available
- ~1965 Fast-rate electroplating using conforming anodes and solution flow gaining interest
- ~1970 Commercial electroless nickel baths more popular
- ~1975 Brushed, satin and black nickel baths available and used in the electrical and plumbing fixture sectors
- ~1980 Amorphous ("glassy") nano-structured nickel alloy coatings with unique properties introduced
- ~1990 Nano-composite coatings and nickel-containing MEM\* devices being developed and documented
- ~2000 A variety of corrosion resistant and biocompatible materials and coatings being used in medical devices, as well as "memory" alloys similar to nickel-containing Nitinol®
- ~2005 Nickel electroforming for MEM devices more widely used, devices becoming smaller.

While not duplicating the rapid rise in developments in the semiconductor/electronics industry (*i.e.*, "Moore's Law" or exponential growth) the number of innovations relating to nickel surface finishing is impressive. The opportunity for additional developments in the future is shown by the question marks in Fig. 4, and may involve the application and/or the manipulation of nano-scale materials, monolayers and even individual atoms with new tools,\*\* for applications yet to be identified. Similarly to their application for plating other metals and alloys, the increased use of fluid dynamics, electrochemical theory and three-dimensional modeling of processes will be used to optimize efficiency, reduce pollution and conserve resources for nickel surface finishing

\* MEM = micro-electro-mechanical.

\*\* Perhaps atmospheric plasmas, lasers, photons and even sound energy, in contrast to the electrical fields used today.



activities (such as anodizing, passivation, deposition, electropolishing, electrochemical machining, electroforming, as well as designing fixturing and masking).

### Some nickel finishing applications

Both electroplating and electroforming of nickel and nickel-based materials are widely used to provide or improve the tooling to make components and products, to enhance or finish components or products that have been made by other fabrication or manufacturing techniques, and to fabricate free standing components and devices. To support the claim that nickel as a natural resource, and nickel surface finishing technologies are both important to the world economy, this section provides some examples.

#### *General commercial and industrial*

The variety of applications in this category is impossible to describe in this relatively short lecture, but ranges from very large molds for making simulated wood paneling and tiled floor coverings; to coatings on rolls to make paper; to molds for making chocolate and ice cream novelties; to rotogravure rolls for making paper currency and other financial instruments, as well as postage stamps; to molds for making plastic bottles; to screens for printing textiles, wall papers and foils for electric shavers; to fabricating ball-point pens; for functional and decorative purposes; to electrical contacts and connectors; to costume jewelry.

Nickel plated copper and steel wire are used in a wide range of applications, especially when woven to make meshes, sieves and decorative components, such as loud speaker covers in audiovisual products for the home, in vehicles and office accessories. The nickel coating provides corrosion resistance and a decorative finish in its own right, but may often be painted (black is a common color for speakers).



Figure 5 - Printing with electroformed nickel screen cylinders  
(Photo courtesy of Nickelmesh AG, Rudolfstetten, Switzerland).

Figure 5 shows electroformed nickel screen cylinders being used (some decades ago) in a factory in Switzerland for printing designs on fabric. The photograph provides some idea of the size of the screens and scale of the continuous process.



Figure 6 - Examples of nickel plated razors and electroformed razor foils (Photos courtesy of Spectrum Brands/Remington Razors and Proctor & Gamble/Gillette Razors).

Figure 6 depicts two types of shaving devices. One is an electric razor that incorporates two electroformed nickel foils with a pattern of small holes that are positioned above the reciprocating cutter blades. The other is a conventional razor with a decorative, bright nickel-plated assembly that holds razor blades. Nickel is used for the former to provide flexibility, strength, wear and corrosion resistance for the foil, and electroforming is used because of the precision, size, shape and location of the holes that allow the hairs to be captured and cut.

Nickel is used in contacts on printed circuit boards and other similar components to provide a diffusion barrier between the copper substrate and the precious metal (e.g., gold alloy) and to provide wear and corrosion resistance, while maintaining a low contact resistance. Without the nickel barrier, there is the possibility that diffusion could occur, forming a brittle phase or compound that could lead to degradation in performance, or even failure. Recently, a high-speed, low ammonia Pd-Ni plating process has been introduced, in conjunction with a bright or semi-bright underlayer and a gold flash finish coating.<sup>10</sup> In an industrial trial, its suitability as a replacement for a hard gold coating was shown.



Figure 7 - Nickel and nickel alloy plated electrical connectors.

Nickel is used on electrical connectors instead of cadmium, primarily to provide corrosion resistance while maintaining good electromagnetic and radio frequency interference blocking capability. Many non-military connectors use electroless nickel coatings over aluminum bodies where corrosion is not a concern. However, in a corrosive (*e.g.*, marine) environment, this surface finishing system will fail

catastrophically due to galvanic corrosion. The MIL-DTL-38999 specification has added non-cadmium coatings, including nickel-Teflon® composites and zinc-nickel (“black nickel”) alloys as acceptable alternatives. Figure 7 shows some connector used in the audiovisual, marine and mass transport industries.<sup>11</sup>

Nickel composite coatings containing Teflon [poly(tetrafluoroethylene) = PTFE] particles (Fig. 8c) not only provide corrosion resistance, but also provide some lubricity. Other ways to achieve the same properties are shown in Figs. 8a and b. Here, suspended inert particles (*e.g.*, carbon) are co-deposited with nickel from a Watts or sulfamate plating bath to provide irregular deposits containing crevices, open pores and/or surface features that can hold and retain a solid (or liquid) lubricant. Such coatings were developed in the last century for the U.S. Army for rifles used in desert warfare to prevent the loading and firing mechanisms from seizing in repeated use.

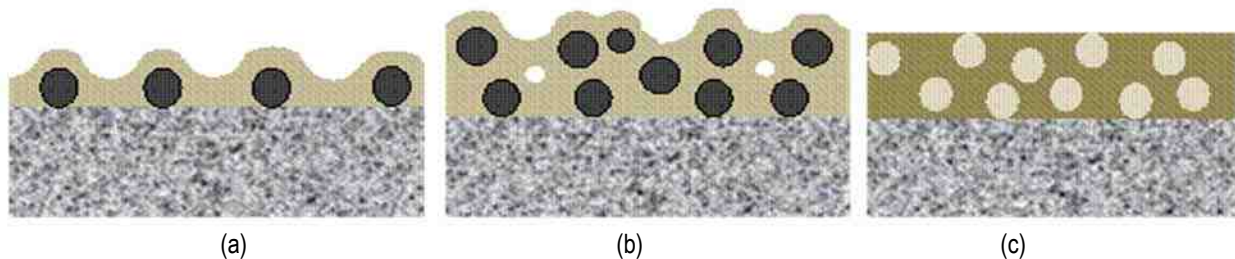


Figure 8 - Nickel-based self-lubricating, wear-resistant coatings: (a) occlusion plating with inert particles; (b) additional layers to hold lubricants; (c) plating with lubricant particles.

Nickel is often used as the material of choice for electroforming mandrels, molds, mold liners and mold coatings because of its ease of use, heat and corrosion resistance, and its ability to reproduce surface details accurately. Applications can be found in many industries that use blow or injection molding techniques to produce items to their near net or final shape. These items can range in size from a few square inches (compact memory discs and digital video discs) to many square feet (wall panels) or larger for laying up polymer and glass composite structures, as described later.<sup>1,12</sup> Recently, pulse, periodic reverse plating is being offered by a few companies<sup>13</sup> because of its better control over thickness distribution and structure of the deposited metal from both types of nickel plating baths.

Figure 9 depicts how one such injection mold liner and mold is made from a prototype, with integral cooling or heating channels added for a high volume application.<sup>14</sup> Products such as wood, ceramics and leather can be used to produce - by nickel electroplating - wood grain, tile and leather textures on surfaces, from which molds (or mold liners) can be electroformed, again using nickel. Other electroformed mold applications are described later.

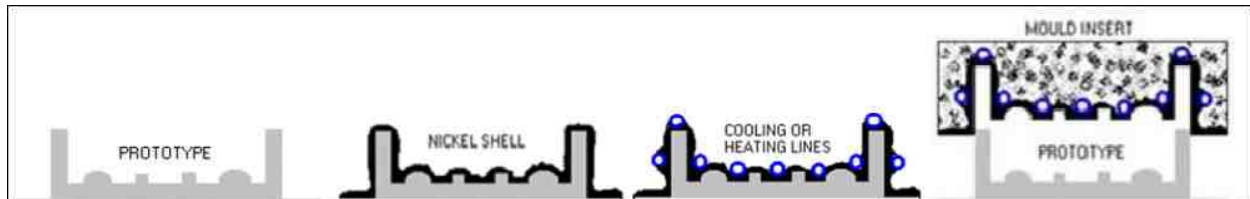


Figure 9 - Example of an electroformed nickel injection mold liner production (Diagram courtesy of Metalon Technology, Ltd.).

### Ground transportation

In the previous section, the use of nickel-plated wire woven into screens and subsequently painted for covers on audio components was described. These also can be used in automobiles and other ground vehicles. The use of nickel and zinc-nickel coatings on connectors also has been mentioned, and these find uses as well in automobiles and commercial vehicles, as well as components in wiring harnesses.

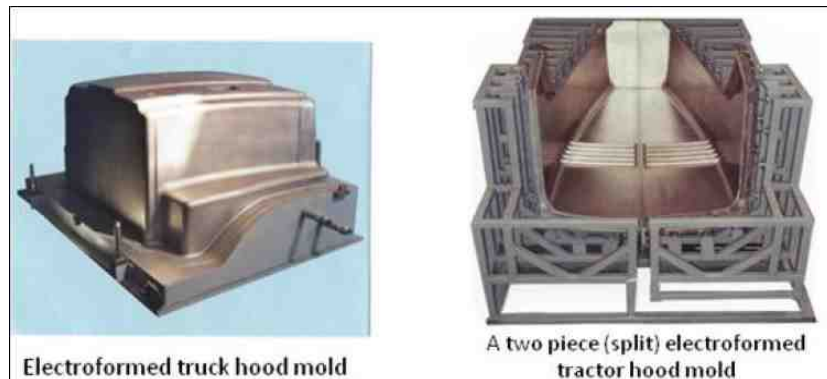


Figure 10 - Electroformed injection molds for truck and tractor hoods (Photos courtesy of EMF Corporation).

Nickel electroforming has been used to fabricate molds for making door pulls found in some automobiles.<sup>13</sup> Electroforming also has been employed to make the molds/forms for laying up composites that are used as lightweight, corrosion-resistant hoods on trucks and farm vehicles (Fig. 10).

Another widespread application of nickel electroforming is the fabrication of molds to provide a textured surface (*e.g.*, to simulate stitched leather) for interior finishes in vehicles, such as arm rests, console/storage compartment lids, door panels, fascias and instrument panels. The latest trends include using a foam core to the molded product to give it a “soft touch,” and the increasing use of long glass fibers in a polypropylene (LGFP) composite to provide strength with lightweight.<sup>15</sup>

Different types and combinations of nickel coatings, are often used as an underlayer to decorative coatings on components, including bumpers, grilles, lamp and instrument panel bezels and handles. These nickel coatings, about 0.001 inch thick, provide a number of functions, such as promoting adhesion of the final decorative finish to the steel, aluminum or ABS plastic substrates,<sup>1</sup> and corrosion protection by acting as a physical barrier to the operating environment.

Electroless nickel coatings are well suited to applying continuous, uniform coverage on complex shapes and internal diameters of tubular structures, open and blind holes, and complicated designs. Examples of its use in ground transportation are in carburetors to provide corrosion protection against fuels containing ethanol, and (after heat treatment) wear-resistant surfaces on automotive differential pinion shafts.<sup>1</sup> The latter application eliminates the need for nitriding the appropriate surfaces or applying an electroplated, hard chromium coating.

### Aerospace and astronomy

Electroless nickel coatings, primarily nickel-phosphorus compositions, are used for many applications in the aerospace industry, and many are described in Reference (1). These include bearing journals, pistons, engine mounts, gyroscope components, turbine blades on aircraft, and docking bay and other mechanisms on space shuttles.



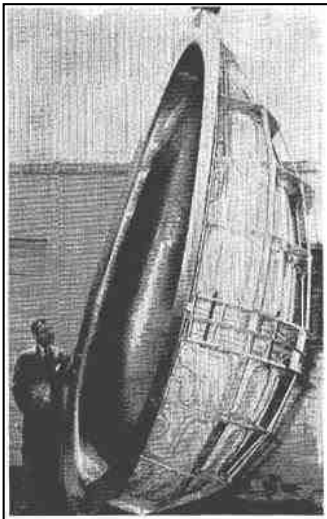


Figure 11 - Stationary and pivoting lay-up tools for composite aircraft radomes (Left photo courtesy of Bone Engineering Corp., Glendale, CA; right photo courtesy of Nickel Institute).

Electroformed nickel alloys are being used to fabricate structures for spacecraft that would be extremely difficult, if not impossible to do by conventional manufacturing methods.<sup>1</sup> One example is the electroforming of internally cooled thrust chambers for rockets, including the Ariane space launcher and the NASA space shuttle. Electroformed, seamless, flexible nickel bellows are widely used in the aircraft industry for seals, couplings, sensors and compensators, and to provide electromagnetic shielding.<sup>1</sup>

Nickel electroformed molds and forms also play an important role in this category.<sup>12,16</sup> One application is the use of forms to lay up composite materials for radomes on aircraft, as shown in Fig. 11. These forms come in

a wide range of sizes, depending on the end use application. Wing fairings are produced by the same technology, as shown in Fig. 12, for different types and sizes of aircraft (the form shown on the left, for example, is for an Airbus 320). These forms/molds can range from a few feet in length to tens of feet.<sup>17,18</sup> A company in Colorado has one of the world's largest nickel sulfamate electroforming tanks (6,750 cubic feet/45,000 gallons) to handle large parts, such as a form for molding graphite-epoxy composite aircraft wing skins measuring 32 feet long and 12 feet wide.

Electroplated, nickel-based coatings are used to provide corrosion, wear and heat resistance in a number of aerospace applications. They are used also for the build-up and repair of worn or corroded parts, which are then ground to final dimensions and finished.<sup>1</sup>

Examples are the use of electroplated nickel to repair landing gear components, and electroplated nickel with occluded silicon carbide particles for hard, wear-resistant coatings on pistons and in small engine cylinders, particularly for general aviation. Recently similar coatings are being investigated - for environmental reasons - for use in commercial and military aircraft engines,<sup>\*\*\*</sup> and on landing gear to replace electroplated hard chromium coatings.<sup>19</sup>



Figure 12 - Electroformed lay-up tools for aircraft wing fairings (Left photo courtesy of Galvanoform GmbH, Lahr, Germany; Right photo courtesy of Airbus/Nickel Institute).

A nickel-silicon-aluminum containing, chemical vapor-deposited coating has been used to provide a heat and corrosion resistant surface on the internal cooling channels in gas turbine blades<sup>20</sup> used in aircraft engines (Fig. 13). Before commercial use, however, the coating and process must be optimized then qualified.

\*\*\* "NiPlate 700®," Surface Technologies, Inc., web site: [www.surface-technology.com](http://www.surface-technology.com).

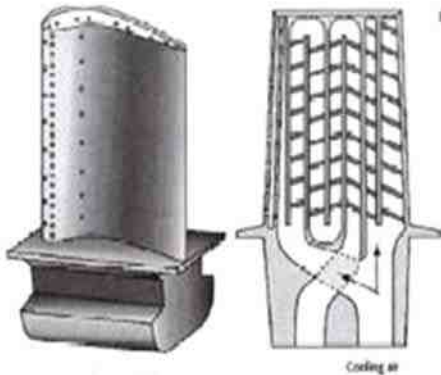


Figure 13 - Turbine blade showing internal channels to be plated with a Ni-Si-Al diffused coating (*Diagram courtesy of Kohlscheen & Stock (2009)*).

Electroforming - using nickel and its alloys - is extremely important in space astronomy. Examples include components used on the Hubble Telescope,<sup>1</sup> and the HERO X-ray mirror/camera.<sup>21</sup> The latter works on the principle that x-ray photons can glance off surfaces at low angles and be directed towards a collection (“focal”) point to obtain an image. To achieve this, nests of concentric, tapered cylindrical tubes of gradually decreasing diameters (shown on the left hand side of Fig. 14) are assembled about a common axis in a protective container. Two such containers are shown assembled in a prototype camera fixture shown on the right in Fig. 14.

used to take images of the Crab Nebula. In the future, lighter weight, larger mirrors will be electroformed from a “glassy” or amorphous nickel-cobalt-phosphorus alloy. Figure 15 shows a large test cylinder - with a diameter of a few feet as opposed to a few inches - made at the University of Alabama at Huntsville from this material,<sup>22</sup> after being separated from the mandrel.

The camera that was flown recently on a balloon to the edge of the Earth’s atmosphere (120,000 feet) consisted of 96 electroformed, nickel-phosphorus concentric cylinders. It was

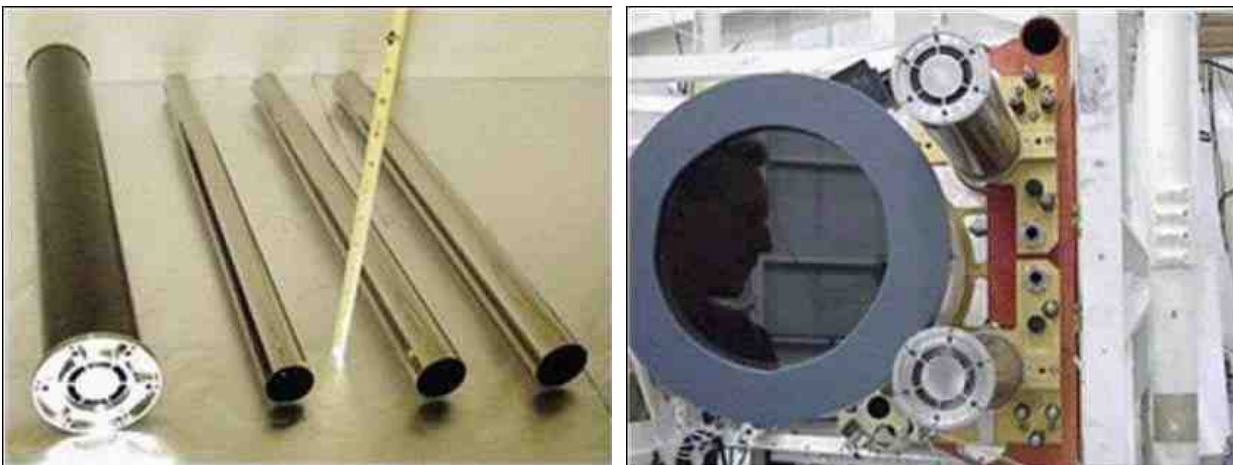


Figure 14 - Electroformed nickel x-ray mirror nesting cylinders (left) and prototype camera (right).

### Medical devices

Nickel coatings have been used for some time on implantable devices, such as drug delivery systems (pumps) and pacemakers, such as those shown in Fig. 16, to provide corrosion resistance and biocompatibility.

Drug or radioisotope delivery from thin film coatings is being explored as an alternative localized delivery system. The drugs or isotopes are occlusion plated using an electroless nickel bath.<sup>23</sup> Nickel-based alloys play another important role in modern medicine, especially the super-elastic, “memory” nickel-titanium alloys containing 50 to 60% nickel. These can be used to form structures, such as tubular or wire stents (Fig. 17, top photograph), compressed to a much smaller volume, inserted into an artery, for example, and using body heat to restore the device to its original size.<sup>24</sup> This approach provides an alternative approach to balloon angioplasty, and the alloy exhibits good biocompatibility and physiological compatibility. Stents and other similar devices may receive other surface treatments, such as electropolishing to remove burrs formed by some fabrication techniques, or porous and/or ceramic coatings to assist in biocompatibility, and metallic or plastic coatings to prevent blood clotting, or provide lubricity.<sup>25</sup>



Figure 15 - Ni-Co-P alloy large x-ray mirror test cylinder (Photo courtesy of University of Alabama, Huntsville, AL).



Figure 16 - Examples of coated medical devices (Photos courtesy of Medtronic).

The other example shown is an atrial septal-defect occlusion device (shown at bottom). Two closed, umbrella-shaped Nitinol® wire loop and microporous polyurethane webbing components are inserted along a guide wire on either side of the hole in the heart, expanded, and then screwed together to form a seal.<sup>26</sup> No other material combination could allow this procedure to be done.

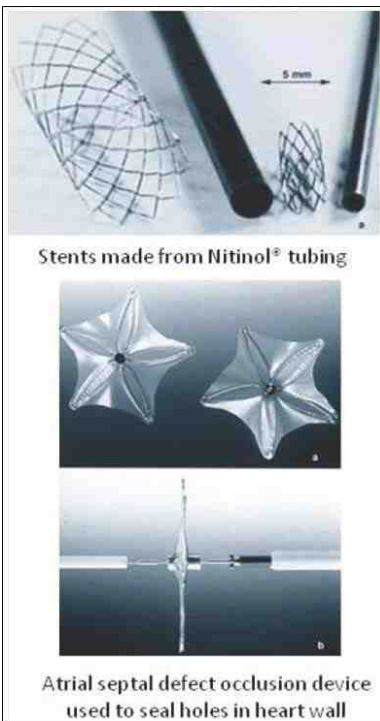


Figure 17 - Examples of electroformed nickel alloy medical devices (Photos courtesy of Nitinol Devices and Components).

### Micro-Electro-Mechanical devices

The development of MEM structures, components and devices was facilitated by the application of established fabrication methods to form 3-D structures on silicon wafer substrates as part of integrated circuits, and later by the use of “plating through masks” technology, such as “LIGA.” The acronym LIGA (in German) refers to lithography (to prepare a mask); electroplating (to define the structure/component) and removal (of the photoresist/mask). This type of technology is developing rapidly, and devices are becoming more complex, and performing a wider range of actions.

MEM device fabrication now is said to embrace a philosophy or approach rather than a single process. It is characterized by the following attributes:<sup>27</sup>

- Sizes ranging from nanometers to millimeters
- Wide range of fabrication processes and materials available (with LIGA electroforming being a key process)
- Many types of parts and components, including gears, beams/cantilevers, springs, hinges
- Components operate alone or in arrays, such as micro-mirrors
- Few to millions of components in a system/application
- Newer applications now connected to computers to allow response to signals from sensors (i.e., passive → active control; closed loop feedback).

Some examples of MEM structures and components are shown in the photocollage<sup>28</sup> in Fig. 18. Others are shown in Figs. 19 - 22. Applications include inkjet

printer cartridges, accelerometers, pumps, miniature robots, micro-engines, locks, pressure and flow sensors, inertial sensors, optical scanners, micro-batteries and fluid pumps.

The role of nickel surface finishing varies according to the end use application, and includes:

- Electroless Ni-P, Ni-B as metallization layer for “multi-chip-module” (MCM) fabrication
- Nickel-based electroformed parts and molds, such as those for micro-lenses
- Nickel-based coatings as diffusion barriers
- Nickel alloys as magnetic components.

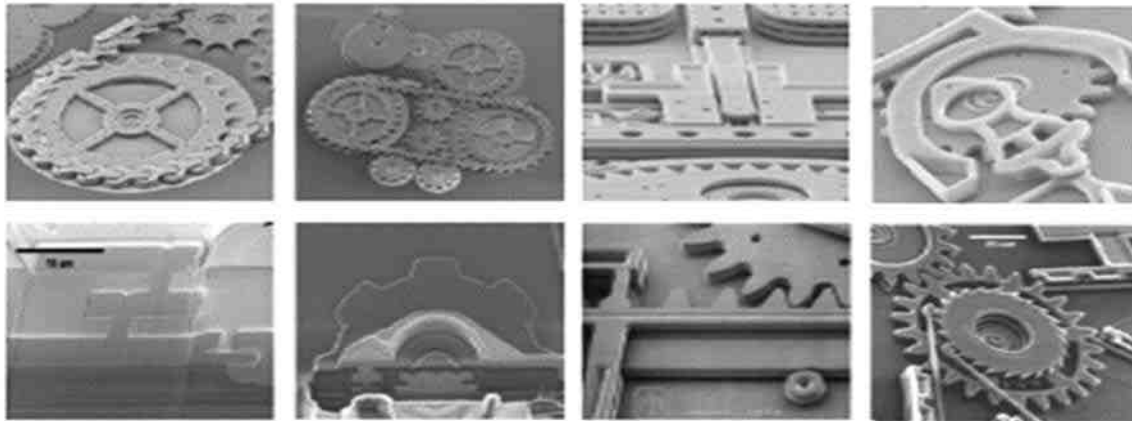


Figure 18 - A montage of some examples of electroformed MEM devices.

The previous sections have shown why nickel surface finishing is important. Some of the reasons are:

- There is a proven history of using nickel-based materials to meet challenges as new applications and products present themselves.
- There are so many processes and parameters that can be controlled to provide a wide range of properties to meet the requirements of many industrial and commercial applications.
- New processes, materials and finishes are constantly being developed to meet identified needs and requirements, or to enable companies to diversify.

Driving change to provide new opportunities are the following:

- Industry, the defense industrial base, other federal departments, facilities and NASA continue to need new materials and processes to meet specifications for new weapon systems, research tools, space structures, instruments and so on
- Industry and academe have a vested interest in developing new materials and surface finishes to build markets and/or reputation for providing the basis for new technologies and facilitating technology insertion, respectively.
- Industry and government facilities provide grants and funds to develop new technologies, including materials and processes, many of which have dual uses - for example, military or nuclear research and development can be adapted and optimized for the commercial and industrial sectors, and vice versa.

Some environmental drivers

Barriers to change with respect to nickel surface finishing often relate to environmental, safety and health issues.<sup>33</sup> These are discussed briefly in the following paragraphs. The impact of environmental regulations relating to chromium and cobalt are also discussed because these have relevance to the use and new applications for nickel surface finishing, or nickel's ultimate replacement.



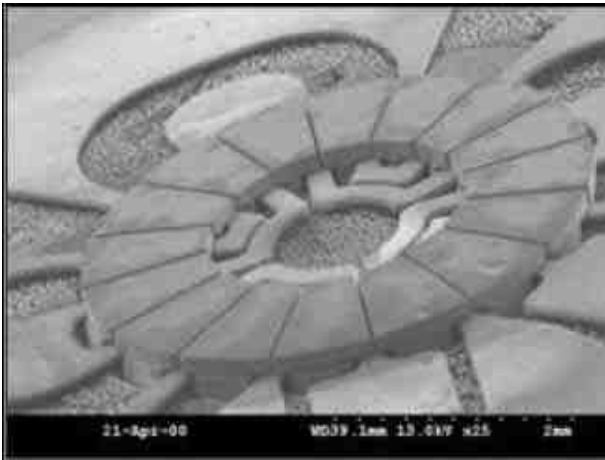


Figure 19 - Electroformed Co-Ni array of precision hard magnets.

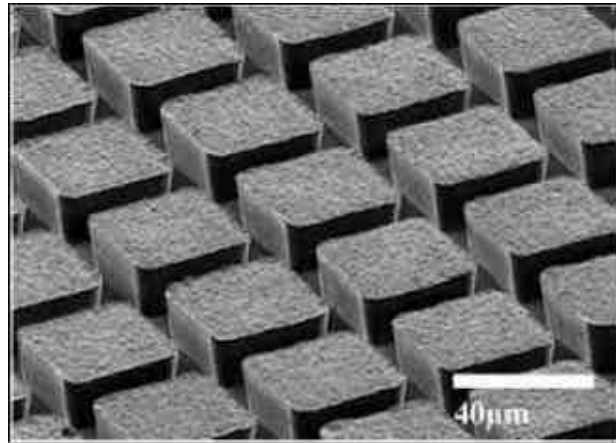


Figure 20 - Electroplated Ni-Fe alloy core and copper windings in a planar induction motor.

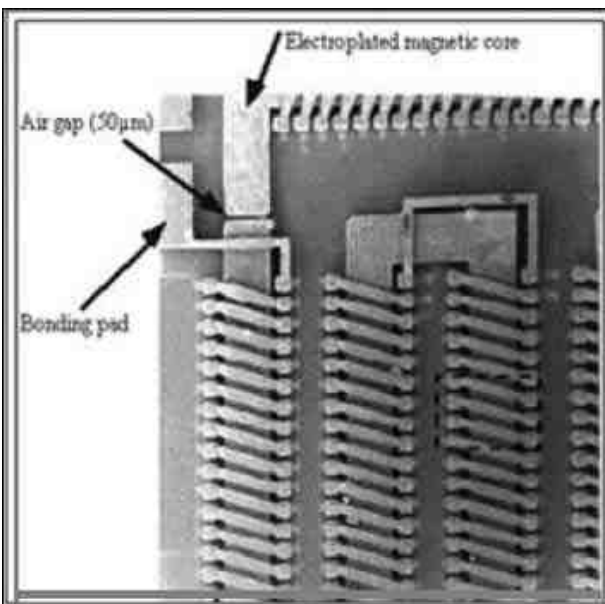


Figure 21 - Electroplated Ni alloy magnetic core for an electric motor.



Figure 22 - Electroformed nickel micro-turbine made by the LIGA process.

### *Chromium reduction and elimination*

The environmental, health and safety issues associated with electroplated hard chromium have been a concern for many years. The American Conference for Government Industrial Hygienists (ACGIH) has classified it as a confirmed human carcinogen, and the U.S. Environmental Protection Agency (EPA) has stated that it is carcinogenic to humans. As a result of the concerns with chromium, the Occupational Safety and Health Administration (OSHA) recently (2006) further reduced the Permissible Exposure Limit (PEL) for hexavalent chromium (Cr VI) to 0.005 milligram per cubic meter (mg/m<sup>3</sup>),<sup>34</sup> as shown in Table 2. In addition, lower discharge limits at public owned treatment works have escalated the burdens associated with using this material. These worldwide directives, mandates, government policy and legislation have focused more attention on reducing and eliminating the use of chromium.



Table 2 - Environmental safety and health restrictions on the use of chromium, nickel and cobalt.

Constituents* (CAS #)	OSHA	NIOSH		ACGIH	Carcinogenicity			
	PELS	IDLH	RELS	TLVs	IARC	ACGIH	NTP	EPA
<b>Chromium Baseline</b>								
<b>Chromium (VI)</b> 7440-47-3	0.005 mg/m <sup>3</sup> (2038a)	250 mg/m <sup>3</sup>	0.5 mg/m <sup>3</sup> <sup>a</sup>	0.01 mg/m <sup>3</sup> (insoluble compounds)	Group 1 (AEDR, 2000)	Group A1	Group 1	Group A (IRIS, 200E)
<b>Chromium Interim Alternative?</b>								
<b>Nickel (soluble salts)</b> 7440-02-0	1 mg/m <sup>3</sup> (2036b)	10 mg/m <sup>3</sup>	0.015 mg/m <sup>3</sup>	0.1 mg/m <sup>3</sup>	Group 1 (AEDR, 2005)	Group A4	Group 1	NA <sup>c</sup>
<b>Nickel Interim Alternative?</b>								
<b>Cobalt (dust, and fumes)</b> 7440-48-4	0.1 mg/m <sup>3</sup> (2088c)	20 mg/m <sup>3</sup>	0.05 mg/m <sup>3</sup>	0.02 mg/m <sup>3</sup>	Group 2B (AEDR, 2004)	Group A3	Group 2 <sup>b</sup>	NA

**Notes:** NA = Not available; \* PEL = permissible exposure limit; IDHL = immediately dangerous to health or life; REL = reference exposure level; TLV = threshold limit value.

<sup>a</sup> This value is based on chromium metal; <sup>b</sup> this value is based on data for cobalt sulfate; <sup>c</sup> the U.S. EPA has not evaluated nickel soluble salts as a class of compounds for potential human carcinogenicity; however, evaluations were conducted on nickel refinery dust as Group A, nickel carbonyl as Group B2 (probable human carcinogen), and nickel subsulfide as Group A.

human carcinogen by the International Agency for Research on Cancer (IARC); and (3) considered a known carcinogen (no specificity to humans) by the National Toxicology Program (NTP). Currently, OSHA has placed a PEL of 1 mg/m<sup>3</sup> on exposure to nickel (as metal, insoluble compounds and soluble compounds). With further study and more extended use, as hazardous materials are replaced by nickel-containing substances, there is the likelihood that nickel may eventually be as regulated as chromium. As a result, there is a need to identify, evaluate and qualify interim to long-term chromium alternatives that do not contain nickel. Until that time, nickel reduction and elimination strategies are appropriate.

Currently, the best long-term candidates contain cobalt, often as a direct substitute for nickel. A number of electroless, electroplated and composite coatings are being evaluated as long term replacements for chromium and nickel should it be more stringently regulated.<sup>19</sup> Inspection of Table 2 shows that the environmental safety and health risk associated with cobalt is less than that of nickel, which in turn is less than that for chromium. This conclusion has been substantiated by a formal guidance document issued by the Ministry of Defense in the United Kingdom.<sup>35</sup>

Where do we go from here?

Consideration of the options available for nickel and nickel surface finishing technology immediately suggests that two scenarios are possible:

- For the continuing use of nickel and nickel-based materials and finishes
  - Existing nickel regulations, mandates and Executive Orders driving need to be changed.
  - Improved processes and engineering controls to reduce emissions are necessary.
  - More recovery, recycling and reuse of nickel and nickel-based materials is encouraged and allowed.
  - Chromium (VI) reduction and elimination proceeds with some exemptions for critical uses.
  
- For reduced use or elimination of nickel and nickel-based materials and finishes
  - More and better scientific data become available, which justify more restrictive regulations.
  - Restrictive regulations, mandates and Executive Orders drive change to replacements.

- More emphasis on environmental safety and health and other risk assessments in business decisions is necessary to support need for change.
- Decisions will be made to eliminate use of nickel in anticipation of more restrictive regulations with a few exemptions for critical uses.
- Acceptable alternatives to nickel - meeting performance and environmental requirements - are developed and made available.

If these two scenarios are accepted as reasonable, then there are perhaps four ways in which to respond to the scenarios as part of a business strategy over time. These are listed below, and discussed later:

- Do nothing and maintain existing level of nickel emissions.
- Continue to improve and expand surface finishing technology for unique applications in the near- term while being in compliance.
- Reduce the amount of nickel emissions in the near- to mid-term and, as a corollary, modify the use of surface finishing technology.
  - Change to processes that generate lower emissions (e.g., physical and chemical vapor deposition methods, thermal spray) or require less rework, post-treatment finishing or frequent repair.
- Eliminate nickel emissions from the surface finishing technology that produces them.
  - Replace nickel with one or more metals or alloys that are more environmentally acceptable; e.g., gold, palladium alloys for decorative or barrier coatings, tin alloys for corrosion resistance, titanium nitride for hardness and wear resistance.
  - Change the substrate material so that surface finishing is limited to grinding, polishing, buffing, etc. rather than coatings.

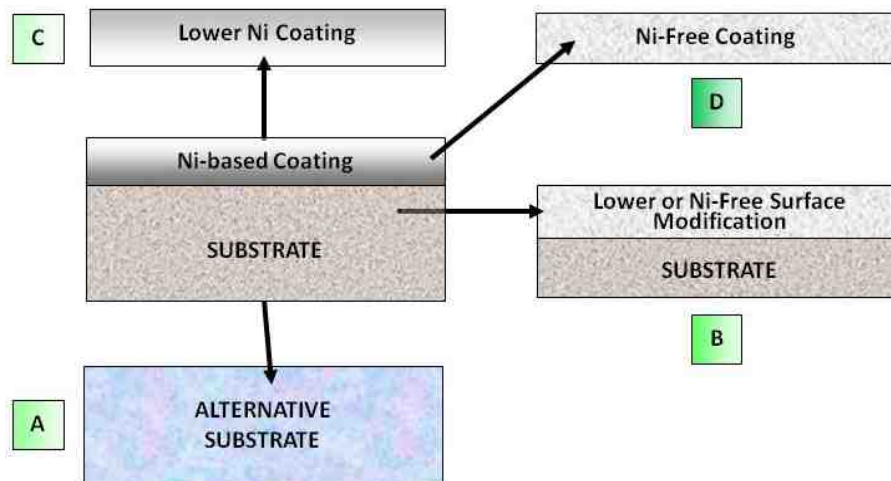


Figure 23 - Alternative approaches to replacing nickel coatings.

By analogy with chromium,<sup>36</sup> the “reduce” or “eliminate” scenario for nickel surface finishing can be indicated graphically (Fig. 23). The technologies currently available to satisfy the four approaches (A - D) are listed in Table 3. The choices are numerous and must be considered on a case-by-case basis.

The four ways presented above to respond to the two scenarios all have associated consequences - some positive and others negative - that vary with the decision that is made. The consequences for the first response - Do nothing - are summarized in Table 4, and are self-explanatory, as they are for the other three responses.

Table 3 - Technologies/processes appropriate for the alternative approaches.

A – Alternative Substrates	B – Surface Modification	C – Lower-Ni Coatings	D – Ni-Free Coatings
<ul style="list-style-type: none"> <li>• Change in design</li> <li>• Cladding</li> <li>• Change to corrosion resistant alloys</li> <li>• Change to wear resistant alloys</li> </ul>	<ul style="list-style-type: none"> <li>• Thermal diffusion</li> <li>• Laser diffusion</li> <li>• Plasma discharge</li> <li>• Electrolytic diffusion</li> </ul>	<ul style="list-style-type: none"> <li>• Electrodeposition</li> <li>• Electroless deposition</li> <li>• Micro-welding</li> <li>• Thermal spraying</li> <li>• Physical vapor deposition</li> <li>• Ion implantation</li> </ul>	<ul style="list-style-type: none"> <li>• Electrodeposition</li> <li>• Electroless deposition</li> <li>• Micro-welding</li> <li>• Thermal spraying</li> <li>• Laser cladding</li> <li>• Chemical vapor deposition</li> <li>• Physical vapor deposition</li> <li>• Explosive bonding</li> </ul>

Table 4 - Advantages and disadvantages of Response 1 - Do nothing.

ADVANTAGES	DISADVANTAGES
<ul style="list-style-type: none"> <li>• Easiest path to take</li> </ul>	<ul style="list-style-type: none"> <li>• Assumes naively that regulations will not become more stringent</li> <li>• Customer technical and stewardship requirements remain the same</li> </ul>
<ul style="list-style-type: none"> <li>• Current regulations understood and may not change</li> </ul>	<ul style="list-style-type: none"> <li>• Regulations may change</li> <li>• Time to respond and become in compliance could be lengthy</li> </ul>
<ul style="list-style-type: none"> <li>• No new investments needed in capital, intellectual property, licensing, training</li> </ul>	<ul style="list-style-type: none"> <li>• May fall behind on the learning curve, resulting in additional costs to catch up</li> </ul>
<ul style="list-style-type: none"> <li>• Environmental, safety, and health risks understood and managed</li> </ul>	<ul style="list-style-type: none"> <li>• Improvements would not be achieved in worker safety and health, as well as environmental impact</li> </ul>

The consequences for the second response - Continue to improve technology - are summarized in Table 5. Taking the continuous improvement approach may provide some temporary advantages for a facility, not necessarily relating to environmental safety and health issues, but relating to near term financial growth through offering performance improvements and/or product differentiation compared to the competitor's offerings. Table 6 provides a listing of some of the current developments in nickel coatings for a variety of end user applications, or uses yet to be identified.

The list in Table 6 is extensive, and the majority of the alloys and composite materials are being evaluated as alternatives to electroplated hard chromium for providing hardness, wear and corrosion resistance, as well as good fatigue properties without causing hydrogen embrittlement.<sup>37</sup> Other candidates reported since the list was prepared also may be of interest. Nickel + nano alumina coatings deposited by a conventional method and "sediment co-deposition" from a Watt's bath have been studied.<sup>38</sup> The nano-size particles (100 nm) provide a coating with improved corrosion resistance and high temperature oxidation resistance. The sediment co-deposition method is claimed to provide better properties. Nickel-tungsten coatings are receiving more attention recently - also as a hard chromium replacement - especially as a result of some development work done at the Massachusetts Institute of Technology funded by the Army, and subsequently by a commercial licensee.<sup>39</sup> Field trials are underway on truck bumpers, and the U.S. Air Force Research Laboratory is conducting a preliminary evaluation of these coatings for providing impact, wear and corrosion resistance on landing gear components.

The consequences associated with the third response - Reduce nickel emissions - are summarized in Table 7. While there is an environmental benefit from reducing, but not eliminating nickel emissions, some facilities might consider that this does not offset the expenses incurred, and the competition may focus on maintaining or improving other performance characteristics to provide a competitive edge.

Table 5 - Advantages and disadvantages of Response 2 - Continuous improvement.

ADVANTAGES	DISADVANTAGES
<ul style="list-style-type: none"> <li>• Maintain the status quo if regulations do not change</li> </ul>	<ul style="list-style-type: none"> <li>• May have to change ESOH practices to stay in compliance – increased costs</li> </ul>
<ul style="list-style-type: none"> <li>• Provide competitive edge (performance, product features) or pick up sales from others deciding not to continue offering nickel surface finishing services</li> </ul>	<ul style="list-style-type: none"> <li>• Improving technology or developing new technology incurs costs</li> <li>• Lack of skills or facilities: will incur new costs in licensing improved or new technology and buying new equipment</li> </ul>
<ul style="list-style-type: none"> <li>• Discover new markets and applications</li> </ul>	<ul style="list-style-type: none"> <li>• Costs incurred in identifying new markets and making sales</li> </ul>
<ul style="list-style-type: none"> <li>• Positive change in company culture and business/strategic planning</li> </ul>	<ul style="list-style-type: none"> <li>• May be some initial resistance to change by management and employees</li> </ul>

Table 6 - Examples of nickel-based coatings found in the literature.

NICKEL-BASED COATINGS	
• Ni-Al-Si alloy	• Ni-P-Fe alloy
• Ni + Al <sub>2</sub> O <sub>3</sub> particles	• Ni-P-W alloy
• Ni-B-Mo alloy	• Ni + SiO <sub>2</sub> particles
• Ni + B <sub>4</sub> C particles	• Ni + TiC particles
• Ni + Cr <sub>2</sub> C <sub>3</sub> particles	• Ni-P + TiO <sub>2</sub> particles
• Ni + CrAlY particles	• Ni + WC particles
• Ni + diamond particles	• Ni-W alloy
• Ni-Co + CrAlY particles	• Ni-W + SiC particles
• Ni-Co + Cr <sub>2</sub> C <sub>3</sub> particles	• Ni-W-B alloy
• Ni-Co + diamond particles	• Ni-W-B + CeO <sub>2</sub> + SiC particles
• Ni-Co-P alloy	• Ni-W-B + SiO <sub>2</sub> particles
• Nano-Ni-Fe alloy	• Ni-W-B + TiO <sub>2</sub> particles
• Ni-Fe-W-S alloy	• Ni-W-B + ZrO <sub>2</sub> particles
• Ni-Mo alloy	• Ni-W-Co + SiC particles
• Ni-P + diamond particles	• Ni-W-P alloy
• Ni-P + SiC particles	• Ni-W-P + SiC particles
• Ni-P+ SiC + PTFE particles	• Ni-W-P+ CeO <sub>2</sub> +PTFE +SiC particles



The consequences of implementing the fourth response - Eliminate nickel emissions - are summarized in Table 8. At this time very few alternatives to nickel-based materials are available, and most contain cobalt, as Table 9 indicates. Many of these candidates are in the early stages of development, and performance data are limited. Only electroplated nano-cobalt-phosphorus coatings have moved forward to the demonstration/validation stage with private sector and government funding.

Table 7 - Advantages and disadvantages of Response 3 - Reduce nickel emissions.

ADVANTAGES	DISADVANTAGES
<ul style="list-style-type: none"> <li>• Still be compliant with changed regulations</li> </ul>	<ul style="list-style-type: none"> <li>• Need to keep abreast of planned and actual changes to regulations</li> <li>• May have to change ESOH practices to stay in compliance - increased costs</li> </ul>
<ul style="list-style-type: none"> <li>• Set a standard that rest of surface finishing industry may have to follow</li> </ul>	<ul style="list-style-type: none"> <li>• Competition may decide to focus on technical and performance issues, not ESOH issues</li> </ul>
<ul style="list-style-type: none"> <li>• Use environmental stewardship as a marketing tool</li> <li>• Create positive image in community</li> </ul>	<ul style="list-style-type: none"> <li>• Impact on environment is relatively small and others may not care</li> </ul>
<ul style="list-style-type: none"> <li>• Retain jobs or add new employees</li> </ul>	<ul style="list-style-type: none"> <li>• Dependent on the global market and economy</li> </ul>

Table 8 - Advantages and disadvantages of Response 4 - Eliminate nickel.

ADVANTAGES	DISADVANTAGES
<ul style="list-style-type: none"> <li>• Be in compliance with Ni regulations: avoid ESOH costs</li> <li>• Improved worker safety and health</li> </ul>	<ul style="list-style-type: none"> <li>• Reduction in sales: may only be able to fill “niche” applications</li> <li>• Possible reduction in employees if sales in new markets do not offset those lost</li> </ul>
<ul style="list-style-type: none"> <li>• Able to offer nickel-free solutions to meet customer appearance and performance requirements</li> </ul>	<ul style="list-style-type: none"> <li>• Developing necessary data to document claims or meet specifications incurs costs</li> </ul>
<ul style="list-style-type: none"> <li>• Opportunity to diversify and find new markets: brand recognition</li> </ul>	<ul style="list-style-type: none"> <li>• Costs incurred in identifying new markets and making sales</li> </ul>
<ul style="list-style-type: none"> <li>• Be regarded as an industry leader</li> </ul>	<ul style="list-style-type: none"> <li>• May not translate to a positive impact on bottom line</li> </ul>

Environmental safety and health issues have been raised with the use of cobalt, but as described earlier, the risks associated with using a cobalt-based alternative have been shown to be less than for nickel, which in turn offers less risk than chromium. From a business perspective, the environmental benefits have to be weighed against the disadvantages, and these may vary by application and product category, as well as import and export restrictions. In addition, there is also the possibility that, like nickel, cobalt use may become more regulated because of environmental issues.



Table 9 - Examples of cobalt-based coatings found in the literature.

COBALT-BASED COATINGS	
• Co + Al <sub>2</sub> O <sub>3</sub> particles	• Co-P + B <sub>4</sub> N particles
• Co-B alloy	• Co-P + diamond particles
• Co-B + diamond particles	• Co + PTFE particles
• Co-Fe alloy	• Co + SiC particles
• Co-Fe-P	• Co-Sn alloy
• Co-P alloy	• Co-W alloy
• Co-P + B <sub>4</sub> C particles	• Co + WC particles

### Some final remarks

Finally - as a disclaimer - this is my personal interpretation of the current situation with respect to how changing nickel regulations can affect the surface finishing industry. The information presented is provided solely to stimulate discussion and highlight some of the factors that have to be addressed when making decisions about materials choices.

### In summary:

- Nickel-based materials and coatings offer a wide range of useful properties and are widely used.
- Surface finishing activities comprise a significant fraction of nickel use world-wide.
- Nickel is likely to be more regulated in the near- to mid-term, presenting challenges to designers, manufacturers and users.
- New materials, processes and applications will continue to be developed in the near future.
- Demand for Ni-based materials and surface finishing should remain high, at least in the near future.
- Medical instruments/devices, MEM devices and the aerospace industry are likely to be growing markets.
- Options exist for dealing with more restrictive legislation and regulations world-wide.
- There are advantages and disadvantages associated with the option/approach chosen. The choice has to be made on a case by case basis, often guided by business concerns in conjunction with environmental, safety and health concerns. Remember that the two are not mutually exclusive. Sound environmental decisions can provide positive financial returns, but that is another story.

Note that nickel regulation is a global issue and regulations promulgated by one country can have an effect on others as far as export/import activities are concerned. This impact can be felt in commerce, industry, and the military and defense industrial base.

### Acknowledgements

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#### Woodhead Publishing

For access to historical data relating to the development of nickel plating in *Nickel and Chromium Plating*, by J.K. Dennis & T.E. Such, published 1993.

#### The Nickel Development Institute/Nickel Institute, and INCO

For background information on the metal and its uses, safe use of nickel in the workplace, and the educational cartoons used in the presented lecture.



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Numerous presentations and publications at AESF/EPA Week, SUR/FIN and other meetings dealing with environmentally preferred materials.

Scientific and Technical Journals, Magazines, Brochures and the World Wide Web/Internet

The numerous authors and companies not mentioned by name in this lecture that have published information, results of research and development, new product information and applications.

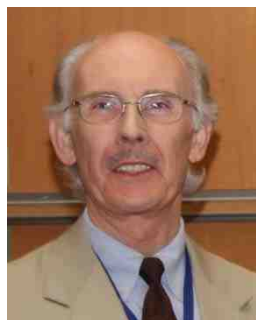
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### About the author

*This piece was largely written at the time Dr. Brooman was announced as the recipient of the 2008 Scientific Achievement Award.*



The NASF Scientific Achievement Award is the Association's most prestigious award. Its purpose is to recognize those whose outstanding scientific contributions have advanced the theory and practice of electroplating, metal finishing and allied arts; have raised the quality of products and processes; or have advanced the dignity and status of the profession.

Dr. Eric Brooman, President and Chief Technical Officer, Materials & Processes Professional Services, Dublin, Ohio, was selected as the 2008 recipient of the award. The announcement was made at SUR/FIN 2008 in Indianapolis, Indiana. Dr Brooman joined a list of esteemed technologists in the field of surface finishing, and at SUR/FIN 2009 in Louisville, Kentucky, he delivered the 47<sup>th</sup> William Blum Memorial Lecture at the Plenary Session on June 15, 2009.

A scientist with recognized leadership, program management and business development experience, Dr. Brooman is a creative technologist with a background in materials and process development and improvement, clean manufacturing, energy conservation and storage, surface finishing, pollution prevention and waste treatment applied to the defense industrial base and a wide range of industries worldwide. He has provided contract research and consulting services to the aerospace, automotive, coil coating, electronics, energy supply/distribution, glass, hardware, optical, semiconductor, surface finishing industries, as well as the DoD and DOE. He has been involved in developing new materials and processes, such as in-mold plating of plastics and circuit boards, electrodeposited stainless steel coatings, and controllable transmission electro-chromic coatings. For the Air Force Research Laboratory, he has been responsible for the evaluation of emerging technologies, such as ionic liquids for cleaning and electrodeposition, self-assembling layered coatings for pretreatments, self-cleaning coatings and nano-structured and nano-composite coatings with unique and improved properties.

Dr. Brooman has served the AESF Foundation and NASF for many years. For the AESF, he has been Chairman of the Nanomaterials Committee, the Emerging Technologies Committee and the Research Board. He has been a member of the



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Publications and Research Boards, as well as the Alloy Deposition, Pulse Plating, Recognition, Scientific Achievement, and Advance Planning, and other *ad hoc* committees. He is currently a Trustee of the AESF Foundation, a member of the NASF Technology Committee, and Chairman, of the Nanotechnology Subcommittee.

Dr. Brooman's scientific and technical accomplishments are also recognized as a Peer Reviewer for *Plating and Surface Finishing*, the *Journal of Applied Surface Finishing*, the *Journal of the Electrochemical Society*, *Surface & Coatings Technology* and *Applied Surface Science* journals. He served on the Editorial Advisory Board for the *Journal of Applied Surface Finishing*.

He has published over 100 scientific papers and technical articles; co-authored one handbook on surface finishing and the MIL HDBK on corrosion and prevention; written chapters in several books; given many presentations and keynote talks; organized and co-chaired several international symposia relating to environmental issues, sensors, corrosion and metal finishing, and edited several symposia volumes. He is also the author of a Column on *Emerging Technologies* in *Plating & Surface Finishing*