# Alternatives to Nickel Coatings:
# Are they Needed and What Are They?

*E. W. Brooman, A. J. Kesslak, and M. A.B. Pavlik*
*Concurrent Technologies Corporation*
*100 CTC Drive, Johnstown, PA*

Like cadmium, chromium, and lead, nickel is on the US EPA list of 17 chemicals for voluntary reduction. Much work has been done on eliminating – or at least reducing – the use of the three former metals in coatings and electronics applications. However, attention is now being paid to the latter metal, nickel, especially when used in decorative and engineering coatings. Legislation to control nickel emissions is being considered in several countries, and some regulations already have been promulgated at the state/regional level in the United States. The background behind the need to evaluate possible, environmentally friendly alternatives to nickel-based coatings is described. Some property data for those alternatives that have been investigated, such as copper, gold, and palladium alloys, is reviewed.

## Introduction

Nickel is a metal that is extracted from mineral ores widely distributed in nature. It is a versatile metal and there are over 300,000 listed uses for it and its compounds. Major uses include:

- Engineering alloys (including stainless steels)
- Battery electrode and container materials
- Decorative, wear, and corrosion resistant coatings
- High temperature structural materials and coatings in the aerospace industries
- Catalysts for making synthetic fibers and petroleum-based products
- Coinage.

Its widespread use is based on its broad range of useful physical, mechanical and chemical properties, either as a metal or as a component in an alloy or coating. Some nickel-containing coatings also have found application as substitutes for cadmium and chromium coatings [1-2]. These two metals and their compounds are classified as hazardous materials and are heavily regulated.

## Regulations and Legislation

Unfortunately, the use of nickel also is governed worldwide by numerous regulations. In the United States, these regulations include:

- Clean Air Act
- Clean Water Act
- Compensation and Liability Act
- Comprehensive Environmental Response
- Emergency Planning and Community Right-to-Know Act
- Hazardous Materials Transportation Act
- Occupational Safety and Health Act
- Safe Drinking Water Act.

Many of the federal, state, and local regulations are inter-related and dependent on each other. Consequently, standards set in one regulation may trigger how another regulation is applied.  In the U.S., the states also are empowered to enact their own regulations, providing that they do not conflict with federal regulations, or are more restrictive.

Most of the environmental, health, and safety related regulations are driven by known or suspected adverse effects on health.  Where nickel is concerned, the health effects are not always clearly defined or understood, which leads to contention and frustration between the legislators/regulators and users.

Table 1 summarizes some of the regulations and their implications to the user and the metal finishing industry.

## Health Effects

As can be seen from the entries in Table 1, the carcinogenicity of nickel compounds is not clearly defined and is compound specific.  Regulations vary by country, and in the U.S., opinions about carcinogenicity vary at the federal, state, and local level. In addition, while some new legislation is promulgated, other legislation/regulations are rescinded.

Many studies of human exposures are flawed and yield conflicting results [3]. Similarly, studies of animal exposures contain flaws primarily related to the exposure pathway and extrapolation of carcinogenic effects for nickel forms that chemically differ from the compound being investigated.  In these studies, the most sensitive (allergen) threshold values are often used to draw conclusions and develop regulations.

The most common non-life-threatening health effect is the sensitivity of some of the population to contact with nickel (4 to 20%).  This results in a reddening of the skin or a rash, for example, and the condition is known as contact dermatitis or "nickel itch".  This is especially a problem when nickel is used on jewelry (such as earrings and posts, wristwatches) and fasteners for clothing.

In summary, because of worker exposure during manufacture, and exposure of the general population during use and disposal of nickel-containing products, there is a need to find alternatives to nickel for engineering applications.  And because of user exposure to consumer products, especially jewelry, there is a need for a nickel substitute for decorative applications.

## Nickel Alternatives

The following discussion is limited to alternatives for nickel used in decorative and engineering coatings.  Substitution of nickel in engineering alloys is beyond the scope of the present paper.

Decorative coatings require:

- Diffusion barrier
- Aesthetic appearance
- Tarnish resistance
- Hardness/durability (wear resistance)
- Solderability.

The diffusion barrier is to prevent copper in the substrate diffusing into the coating and changing its color/appearance (or from changing contact resistance in electrical contact applications).  Solderability is needed sometimes in jewelry applications, and also for electrical/electronic applications.

Engineering (functional) coatings require:

- Hardness
- Lubricity
- Abrasion and wear resistance
- Corrosion resistance
- Chemical resistance
- Solderability/brazeability
- Low contact resistance.

Approaches to developing alternatives to nickel fall into two categories. The first is to reduce exposure and lower emissions by lowering the nickel content in the coating, or by using other than wet deposition methods such as electroplating and electroless deposition. The second is to eliminate nickel and find a suitable substitute that provides satisfactory coating properties, or sometimes to change the substrate material so that a coating is not required. Both approaches are covered in this review of alternatives.

Table 2 summarizes the alternatives that are under development or have been commercialized, based on a survey of the unclassified, international, technical literature.

In the sections below, the properties of electroplated and electroless deposited nickel are used as a baseline for comparison, recognizing that the electroless nickel usually has some phosphorus incorporated. Although not an alloy, Ni-P coatings have significantly different properties than nickel coatings. Also, because there is a range of Ni-P deposits (e.g., low, medium, and high phosphorous) and nickel coatings (e.g., matte, satin, semi-bright, and bright finishes) each with different properties, a range is usually given in the tabulated data for a particular parameter.

**Conversion Coatings**

One pretreatment is listed under "copper-based alloys" in Table 2. A "nickel and nitrite free" phosphate-based pretreatment (conversion coating) is offered commercially for the automotive industry in which copper cations are substituted for the nickel cations (4). With this approach, it is possible to meet local wastewater discharge limits for nickel.

**Decorative Coatings**

Table 3 lists hardness and ductility data for some gold- and palladium-based decorative coatings (5-11). The hardness for these alloys tends to be below or at the low end of the range for electroplated nickel. Only the Pd-Zn alloy would be expected to have similar durability. Palladium on its own is used as a barrier coating to prevent copper diffusion into the decorative alloy finish.

Ductility for decorative coatings is usually not an issue because the finish is most often applied after part fabrication and assembly.

Table 4 provides data on tarnish and corrosion resistance, which is very import for jewelry, fasteners, personal items, appliances, and architectural hardware. A wide range of tests exist and data from some of the most common are presented in the table (5, 7, 9, 10-13). Pure palladium and the gold alloy exhibit good resistance to artificial perspiration. In general, performance in the salt fog test (ASTM B 117) is acceptable for decorative coatings. In addition, the gold and palladium alloys provide good tarnish resistance, particular in the presence of sulfur containing chemicals.

## Engineering Coatings

Table 5 includes property data [7-9, 14] for hardness, ductility, wear and abrasion resistance. The hardness of the copper- and tin-based alloys falls in the middle of the range for electroplated nickel with the exception of the Sn-Zn alloy and the composite coating containing a silicon carbide dispersion. The former is very soft, while the latter is very hard with a VHN over 1,000. The ductility of the alloy alternatives listed is acceptable, for the most part, with the Sn-Co alloy exhibiting the best percentage elongation value. The Sn-Zn alloy also is expected to be relatively more ductile. Although hardness values are comparable, the copper alloys listed have a lower abrasion resistance. Note that as a general rule, the "white" bronze coatings are harder and more wear resistant than the "yellow" bronze coatings, but neither are as abrasion resistant as a nickel coating.

Table 6 summarizes the little data found for corrosion resistance [7-11]. Results from the ASTM B 117 test show that the copper and tin alloys, for which there are data available, have at least as good corrosion resistance as electroless nickel coatings. As would be expected, a chromate conversion coating applied to an alloy deposit provides greater resistance to salt fog.

The Sn-Zn alloy tested appears to have better resistance to sulfur containing species when deposited on ferrous substrates.

Finally, Table 7 presents the electrical property data [6, 7, 11, 14] found in the literature. The copper- and tin-based alloy coatings are reported to exhibit good solderability compared to nickel coatings. In addition, the contact resistance of the alternative coatings is equal to, or better than that of nickel.

The alternatives listed are often used as barrier coatings on contacts to prevent diffusion [5, 6, 11]. The "white" and "yellow" bronze coatings can only be used at temperatures up to 80 $^{o}$C. Palladium as a barrier coating can be used at higher temperatures in service.

## Recent Developments

Table 2 includes some coatings that are more recent developments, and for which little data exist. One type of proprietary coating consists of a pseudo-amorphous micro-structure that provides good wear and corrosion resistance [15]. In another type of electroplated, amorphous nickel coating for industrial applications, some of the nickel content is replaced by iron[16], which would lower worker exposure and reduce emissions during the deposition process.

Similarly, some of the nickel and cobalt containing alloys and cermets applied by thermal spray methods have good wear, abrasion, and corrosion resistance. These types of coating are typically used in the aerospace industry. The limitation to this application method is that it is line-of-sight limited.

Thin, functional coatings such as titanium nitride applied by a physical vapor deposition technique, are extremely hard, wear resistant, and provide a good barrier to corrosion attack [12]. For some applications, where a hard, wear resistant surface is needed on a ferrous substrate, nitrocarburizing might be a suitable surface modification technique. However, this approach cannot be used on parts that are sensitive to elevated temperatures.

One reference was found for an organic decorative coating that contains metallic particles. This coating is said to simulate a nickel plus chromium finish, but the data show [17] that it is not a one-for-one replacement. Although it is said to have "good durability and chemical resistance" the coating system is still under development.

**Summary and Conclusions**

At this time, the need to find alternatives for nickel coatings is not as high a priority as for cadmium and chromium coatings because at present nickel is not currently as highly regulated. As a result, less information is available for alternatives to nickel than for the other two common coating metals.

As industry has to face more stringent requirements on the use of nickel in coatings, and measures have to be taken for facilities to be in compliance with all the regulations, several approaches to reducing or eliminating the use of nickel are possible. One is to reduce worker exposure and emissions by lowering the amount of nickel used in the coating system or by using alternative deposition techniques. Another is to use substitutes for nickel in the coating system. Both would lead to lowering the exposure of the general population when the coated articles are put into service or placed into commerce. The third approach, of course, is to change the substrate material so that a coating is not required and the use of nickel is eliminated.

This survey has shown that some copper, gold, and palladium containing coating systems are being investigated and some are being made available commercially, particularly for decorative applications. Less data appear to be available for functional, engineering coatings.

Finally, as with alternative coatings for cadmium or chromium, no single alternative will be feasible to replace nickel coatings because of the wide range of performance requirements relevant to decorative and engineering applications.

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**Table 1. Summary of Regulations and Legislation Affecting Nickel**

| Regulations or Legislation | Comments |
|---|---|
| Clean Air Act | • Federal: the USEPA is to develop emission standards for major sources by November, 2000. Ni is a targeted hazardous air pollutant (HAP) subject to this regulation<br>• States: California policy treats Ni as a carcinogen and the SCQMD has stringent limits for Ni emissions. Rule 1401 requires new source permitting and Rule 1402 requires a reduction of current cancer risk at the property line. California also considering technology based rules for small quantity generators. Other (proactive) states likely to follow California's example; however, all states will follow if soluble Ni is classified as a carcinogen. |
| Department of Health and Human Services | • Federal: In June, 2000 all Ni compounds not declared as carcinogens in air or water. |
| Food and Drug Administration | • Federal: In April, 2000 announces that Ni used under current industry practices is considered safe. |
| Occupational Safety and Health Administration | • Federal: Final Rule sets 8-hour TWA PELs for Ni compounds. One group called soluble Ni (not carcinogenic)= 0.1 $mg/m^3$, other is insoluble Ni (e.g., carcinogenic, such as Ni carbonyl) = 1 ppb. The IDLH lowered to 10 $mg/m^3$ for Ni and 2 ppm or Ni carbonyl. |
| Resource Conservation and Recovery Act | • USEPA: in March, 2000 changed the F006 waste storage rule for the surface finishing industry to allow storage on site for 180 days if it is to be recycled. |
| Safe Drinking Water Act | • Federal: USEPA in 1998 removed national standard for Ni in water of 100 µg/l (MCL as a non-carcinogen).<br>• States: California policy treats Ni as a carcinogen and has proposed a standard for Ni of 1 µg/l (1 ppb). |
| International Air Quality Guidelines | • World Health Organization: established a quantitative risk estimate for Ni air emissions of 380 deaths per 1 million of population exposed to a lifetime concentration of 1 $\mu g/m^3$ in air (higher risk than benzene). |
| World-wide Miscellaneous | • Many countries are proposing to restrict Ni use in jewelry. Europe developing guidelines for food contact and cooking.<br>• Germany recommending that Ni metal and alloys (with more than 50% Ni content) be classified as Category 2 carcinogens. International Agency for Research on Cancer classifies implants containing Ni as Group 2B carcinogens. |

**Table 2. Nickel Coating Alternatives Being Investigated and Available Commercially**

| Category | Alternative Coating Composition |
|---|---|
| Copper-Based Alloys | • Cu (pretreatment)<br>• Cu (electrodeposition)<br>• Cu+Cu-Sn (electrodeposition<br>• Cu-Sn (electrodeposition)<br>• Cu-Sn-Zn (electrodeposition) |
| Gold-Based Alloys | • Au-Cu-Pd (electrodeposition)<br>• Au-Cu-Ag (electrodeposition)<br>• Au-Fe (electrodeposition)<br>• Au-In (electrodeposition)<br>• Au-Pd (electrodeposition)<br>• Au-Ag (electrodeposition)<br>• Au-Sn (electrodeposition) |
| Palladium-Base Alloys | • Pd (electrodeposition)<br>• Pd (electroless deposition)<br>• Pd-Co (electrodeposition)<br>• Pd-Ni (electrodeposition)<br>• Pd-Zn (electrodeposition) |
| Miscellaneous Inorganic | • Ni (amorphous, electrodeposition)<br>• Ni-Fe (electrodeposition)<br>• TiN (physical vapor deposition) |
| Miscellaneous Organic | • Metallic Paint (powder coating) |

**Table 3. Hardness and Ductility of Some Alternative Decorative Coatings**

| Coating | Hardness, VHN | Ductility, % |
|---|---|---|
| Ni (electrodeposited) | 300-600* | (Fair→Acceptable)* |
| Ni-P (electroless) | 550** | (Fair→Acceptable) |
| Au-1.4-1.7%Fe | 220 | - - |
| Pd (electrodeposited) | 250-350 | (Fair→Acceptable) |
| Pd (electroless) | 250-290 | 4-5 |
| Pd-~20%Co | - - | 2-3 |
| Pd-0.2-1%Zn | 360-380 | - - |

* Matte Ni has a hardness of ~300 VHN and an acceptable ductility; bright Ni has a hardness of about ~600 VHN and a lower (fair) ductility.

** Hardness and ductility depend on the phosphorous content and heat treatment received.

**Table 4. Tarnish and Corrosion Resistance of Some Alternative Decorative Coatings**

| Coating | Salt Fog, hr | Kesternich ($SO_2$) | Acids | Artificial Perspiration |
|---|---|---|---|---|
| Ni (electrodeposited) | Good* | - - | - - | - - |
| Ni-P (electroless) | ≥50 | - - | - - | - - |
| Au-1.4-1.7%Fe | Good | - - | - - | Good |
| Pd (electrodeposited) | - - | Good** | Good | Good |
| Pd (electroless) | ≥70* | - - | - - | - - |
| Pd-~20%Ni | ≥24 | Good | | |
| Pd-~20%Co | Good | - - | - - | - - |
| Pd-0.2-1%Zn | ≥72 | Good | - - | - - |

* CASS Test. ** Sulfide resistance.

**Table 5. Hardness, Ductility, and Abrasion Resistance of Some Alternative Engineering Coatings**

| Coating | Hardness, VHN | Ductility, % | Abrasion Rate, mg*** | |
|---|---|---|---|---|
| | | | Erichsen Test | Taber Test |
| Ni (electrodeposited) | 300-600 | (Acceptable) | 1 | 15 |
| Ni-P (electroless) | 550 | (Acceptable) | - - | - - |
| Cu-45%Sn* | 550 | (Acceptable) | 7 | 50 |
| Cu-17.5%Sn-2.5%Zn** | 400 | (Acceptable) | 4 | 60 |
| Cu-30%Sn-15%Zn* | - - | (Acceptable) | 7 | 35 |
| Sn-30%Zn | 50 | - - | - - | - - |
| Sn-Ni+10-15%SiC | ≤1,000 | (Acceptable) | - - | - - |

* "White" bronze deposits. ** "Yellow" bronze deposits. *** Taber Test run for 1,000 cycles.

**Table 6. Corrosion Resistance of Some Alternative Engineering Coatings**

| Coating | Corrosion Resistance | |
|---|---|---|
| | Salt Fog, hr | Kesternich |
| Ni (electrodeposited) | - - | - - |
| Ni-P (electroless) | ≥50 | - - |
| Cu-45%Sn* | Better** | - - |
| Cu-17.5%Sn-2.5%Zn*** | - - | - - |
| Cu-30%Sn-15%Zn* | - - | - - |
| Sn-20-30%Zn | 800-1,200 | Better |
| Sn-20-30%Zn+chromate | 1,525-2,500 | - - |
| Sn-Ni+10-15%SiC | - - | - - |

* "White" bronze deposits. ** Better than Ni. *** "Yellow" bronze deposits.

**Table 7. Electrical Properties of Some Alternative Engineering Coatings**

| Coating | Electrical Properties | |
|---|---|---|
| | Contact Resistance, m• | Solderability |
| Ni (electrodeposited) | - - | Poor |
| Ni-P (electroless) | - - | Poor |
| Cu-45%Sn* | - - | Acceptable |
| Cu-17.5%Sn-2.5%Zn** | - - | - - |
| Cu-30%Sn-15%Zn* | - - | - - |
| Pd (electroless) | Equal or Better*** | Good |
| Pd-0.2-1%Zn | ~5 | - - |
| Sn-30%Zn | - - | - - |
| Sn-Ni+10-15%SiC | - - | - - |

* "White" bronze deposits. ** "Yellow" bronze deposits.
*** Equal to or better than Ni.