Nickel Plating

Dr. George A. DiBari

Applications
The nickel plating process is used extensively throughout the world for decorative, engineering and electroforming purposes. Decorative electroplated nickel coatings are lustrous, smooth and mirror-bright. Used with top layers of electrodeposited chromium, modern-day decorative nickel coatings have remarkable resistance to corrosion. The combination brightness and durability—accounts for the utility, value and sales appeal of bright nickel-plated consumer goods and other manufactured products.

Engineering nickel coatings are smooth, matte deposits that are most often applied to improve corrosion performance of industrial equipment. But these pure nickel deposits are used to control wear, erosion, surface hardness and lubricity, for magnetic and electromagnetic characteristics; and for optical properties such as reflectivity, emissivity and absorptivity. Engineering nickel coatings applied by various means are used to solve electromagnetic interference problems. In electronics applications, nickel coatings are widely used as under-layers beneath precious metal deposits where nickel acts as a barrier to prevent interdiffusion of substrate and coating, and additionally, improves the reliability of electronic components. Engineering nickel coatings thus enhance the value and usefulness of industrial equipment and components.

Electroforming involves the manufacture of tools and products by electroplating nickel onto a mandrel, which is subsequently separated from the nickel deposit. Electroformed tools and products are often impossible to make economically by other fabrication methods. Examples of electroformed products are: Textile printing screens; seamless belts; record stampers; components of rocket thrust chambers; molds and dies for making plastic composite automotive and aerospace parts; mesh products for batteries and porous electrodes; molds for optical end-uses; bellows and radar wave guides. These diverse applications exist because the properties, including the appearance, of electrodeposited nickel can be controlled and varied over broad ranges.

Processes
Nickel coatings are most widely applied by electrodeposition from aqueous solutions. They are also applied by electroless (autocatalytic) techniques; by chemical and physical vapor deposition techniques; and by thermal spray methods. Nickel-rich organic paint coatings are applied by traditional methods (spraying and roller coating), and by newer techniques such as powder spraying and electrophoretic deposition.

ASTM Standard B-456 and ISO Draft International Standard 1456 provide important information on how to control the quality of decorative electrodeposited nickel coatings. The composition and operating conditions of some typical nickel plating solutions are given in the table. The solutions for decorative nickel plating differ from those for engineering and electroforming applications in that they contain organic addition agents, which control the nucleation and growth of the deposits, as well as their composition. Fully bright deposits, for example, contain significant amounts of co-deposited sulfur. Processes exist that yield satin-like, semi-bright and mirror-bright deposits directly from solution without the need for polishing after electroplating. These processes are proprietary and are operated within the limits recommended by suppliers, but the constituents and operating conditions of most decorative nickel plating solutions are similar to those given in the table for the Watts solution. The electrolytes given in the table are used in engineering applications, but the all-chloride solution is not as popular. As far as it is known, the all-chloride solution is never used for electroforming, because the deposits from that solution are hard and highly stressed. The Watts solution is suitable for electroforming, but most electroforming operations involve deposition of nickel from sulfamate solutions.

Post-Nickel Plating
Decorative nickel coatings are commonly plated with chromium immediately after deposition of the nickel layers. Thin layers of regular chromium have always (since 1923) been used to prevent the tarnishing of nickel, but the more recently developed micro-discontinuous types of chromium contribute greatly to improved corrosion resistance.

Decorative nickel coatings are also post-plated with gold, silver, brass, palladium, tin-nickel and other metallic coatings to achieve a variety of decorative surface finishing effects. In engineering and electroforming applications, the nickel is often left unprotected, but there are end-uses where the nickel is over-plated with heavy chromium and with other metals.
Corrosion Resistance—Engineering
The progress made in decorative plating technology has led to great improvement in the corrosion performance of nickel plus chromium coatings. Although single-layer bright nickel coatings are lustrous and attractive, they are not highly protective and are therefore only specified for mild service.

Multilayer nickel coatings (double- or triple-layer) are much more corrosion resistant and are specified for severe and very severe service. Double-layer nickel coatings consist of an initial layer of highly leveled semi-bright nickel followed by a layer of fully bright nickel. On steel, the initial layer is at least 60 percent of the total thickness of the coating. Because the initial layer is sulfur-free and more noble than the top layer, corrosion of the top, bright nickel layer occurs preferentially i.e., a pit begins at a pore in regular chromium, then proceeds through the bright nickel, the pit becoming flat-bottomed at the interface. Penetration to the underlying substrate is thus delayed.

Triple-layer nickel coatings require the deposition of a thin, highly reactive nickel layer between the semi-bright and bright nickel layers. When corrosion reaches the highly reactive layer, corrosion proceeds laterally beneath the bright nickel, again delaying penetration to the substrate. Double-layer coatings are more than adequate for most applications and are easier to apply, and as a result, are more widely used than triple-layer coatings.

When corrosion is initiated, it begins at a few sites on the surface of regular chromium. Electroplaters have learned to control the initiation of corrosion by using micro-discontinuous chromium deposits, which are either highly porous or highly cracked on a microscopic scale. Corrosion is initiated at countless sites on the surface. The result is to spread the corrosion over a large surface area rather than having it concentrate at one or two isolated pores. Corrosion proceeds more or less uniformly over the surface and the rate of pit penetration is slowed down dramatically. The use of micro-discontinuous chromium coatings in combination with double-layer nickel has improved corrosion performance by an order of magnitude.

Corrosion Resistance—Decorative
Corrosion resistance in engineering applications, when nickel is used alone, is controlled by optimizing nickel thickness. The more corrosive the service conditions, the greater the thickness of nickel required. See ASTM Standard B-689.

Quality Control
Nickel plating quality control is a critical concern whether the process is used for decorative, engineering or electroforming purposes. Nickel plating quality control involves maintaining the purity of plating solutions, preparing surfaces prior to plating to obtain adherent deposits, and using techniques to improve the uniformity of the thickness of the coatings. Testing and controlling the properties of nickel deposits, and eliminating rejects are important aspects of quality control. The design of a product or component affects its plateability, and hence its quality. Quality nickel plating requires attention to these and other details.

Health & Environmental
Nickel and nickel-containing substances can and are being used safely. Some hazards associated with nickel are:

• Explosion—Like other metals, metallic nickel can react with acids to liberate hydrogen, which may create an explosion hazard.
• Hazardous Gas—in certain circumstances, finely divided metallic nickel, in the presence of activators such as sulfur or sulfate, can react with carbon monoxide in reducing atmospheres to form nickel carbonyl, a very toxic chemical. It is liquid at ordinary temperatures and pressures, and readily vaporizes.
• Contact Dermatitis—Physical contact with nickel or certain nickel compounds may cause allergic dermatitis. However, with modern-day personal hygiene and the use of appropriate protective gloves and clothing, this is not a common occupational problem.
• Irritation—Soluble nickel salts can be irritating to skin and eyes. Rare reports link asthma to soluble nickel compounds. “Animal tests at high exposure levels cause irritated tissues of the lung and mucous membrane.”

There is no evidence to indicate that inorganic nickel is carcinogenic when ingested. Elevated levels of respiratory cancer have been associated with now-discontinued refining operations where nickel subsulfide was sintered or calcined. Mortality studies of the nickel-using industry suggest no elevated cancer risk when airborne levels are below the current OSHA permissible limit of one milligram of nickel per cubic meter.

At least two studies have concluded that “certain nickel compounds may be reasonably anticipated to be carcinogens” without identifying the specific compounds involved. As a result, “OSHA has mandated that everyone who makes or imports these substances or alloys containing these substances must warn of a cancer hazard on MSDSs and on shipping labels.”

EPA has established limits on the amount of nickel present in wastewater discharged as a result of nickel plating operations and nickel-bearing sludges generated must be disposed of according to law.

Trends
The consumption of nickel for electroplating in the Western world increased by about 25 million pounds between 1970 and 1985. There have been significant shifts in the patterns of consumption during that period; consumption, for example, increased significantly in the Far East, Latin America and India/Africa, but decreased in North America, Western Europe and Japan. Decorative applications continue to dominate the end-uses of nickel plating, but engineering and electroforming applications continue to grow in importance and sophistication.

*Parts of this section are excerpted from the pamphlet Nickel and OSHA, available from Inco.