Shop Talk: Practical Information for Finishers

Selection & Application of Inorganic Finishes: Barrier Layer Protective Metal Deposits

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“Protective metal deposits often enable effective use of readily available and inexpensive structural metals. A number of metal deposits that are not sacrificially protective to a substrate play an important role in presenting an effective barrier between the substrate and the corrosion environment and are discussed herein.

“When a discontinuous metallic deposit is less active than the substrate, effective protection cannot be achieved in environments that are corrosive to the substrate. The electrochemical cell formed at the site of a discontinuity in the presence of electrolyte can lead to intensive substrate corrosion. A representation of a corrosion cell of this type is shown in Fig. 1.

“By contrast, with a sacrificially protective coating, the substrate metal at the base of a pore in a less-active deposit attempts to “sacrificially protect” the deposit; the high ratio of cathode-to-anode area tends to produce rapid failure. Underlying corrosion products will often cause the coating to be pushed upwards to form small volcano-like eruptions. Zinc or aluminum-alloy castings are considerably more active than the commonly used metallic deposits and may thus severely suffer from this corrosion phenomenon if coverage is incomplete and if subjected to aggressive environments. Likewise, steel coated with any but the sacrificially protective metals (*i.e.*, zinc, cadmium or aluminum) is subject to pitting-type corrosion at any discontinuity in the coating. In order for effective protection to be provided, the deposit must present a complete barrier between the substrate and the environment.

Nickel

“Nickel is the most important metal coating for providing barrier-layer protection of a substrate susceptible to corrosion. Electrodeposits of nickel are widely used for the primary purpose of protecting substrates of steel, zinc die-castings, aluminum and copper alloys against corrosive attack. Pore-free nickel deposits are widely used to protect steel equipment used in the automotive, chemical-processing and food industries. The thickness of nickel required for effective protection, *i.e.*, freedom from porosity, is dependent upon the roughness and condition of the substrate and upon the nature of the plating bath employed. Of course, it is not only necessary to provide sufficient thickness to ensure initial freedom from porosity, but additional thickness must be furnished to allow corrosion or physical damage to the

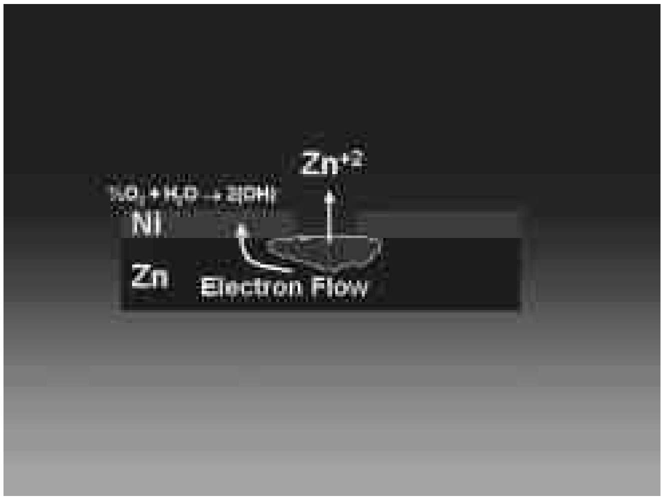

Fig. 1—A representation of a corrosion cell caused by poor deposit.

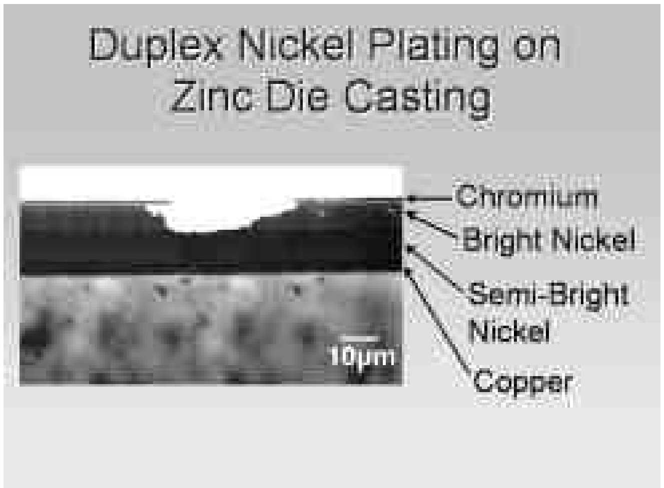

Fig. 2—Double-layer Nickel.

Table 1*

Application of Double-layer Nickel Deposits with Flash Chromium**

Service conditions	Basis metal	Minimum Ni thickness (µm)	(mm)	Typical applications
MILD - Normally warm, dry indoor atmospheres, subject to minimum wear or abrasion.	Steel	10	(0.4)	Toaster bodies, rotisseries, waffle bakers, oven doors and liners; interior auto hardware; trim for major appliances, hair dryers, fans; inexpensive utensils; coat & luggage racks; standing ashtrays; interior trash receptacles; inexpensive light fixtures.
	Zinc	10	(0.4)	
	Brass	5	(0.2)	
MODERATE - Indoor exposure where condensation of moisture may occur, such as in kitchens and bathrooms.	Steel	15	(0.6)	Stove tops; oven liners; home, office & school furniture; bar stools, golf club shafts.
	Zinc	15	(0.6)	Bathroom accessories, cabinet hardware.
	Brass	10	(0.4)	Plumbling fixtures; bathroom accessories; hinges; light fixtures, flashlights & spotlights.
SEVERE - Occasional or frequent wetting by rain or dew, or possibly strong cleaners and saline solution.	Steel	25	(1.0)	Patio, porch & lawn furniture; bicycles; scooters; wagons; hospital furniture; fixtures & cabinets.
	Zinc	25	(1.0)	
	Brass	20	(0.8)	Patio, porch & lawn furniture; light fixtures; bicycle parts; hospital & laboratory fixtures.
VERY SEVERE - Service includes likely damage from denting, scratching or abrasive wear, in addition to corrosive media.	Steel	30	(1.2)	Auto bumpers, (grilles, wheel covers) & lower body trim; light housings.
	Zinc	30	(1.2)	
	Brass	25	(1.0)	Boat fittings; auto trim; (wheel covers); lower body trim.

* Source: Metal Finishing Suppliers' Association, Inc.
**Microporous chromium - 0.25 µm (0.01 mm); microcracked chromium - 0.8 µm (0.03 mm).

NOTE: Somewhat greater nickel thickness recommended when conventional chromium flash applied; zinc or brass (.40 percent zinc) normally coated with about 7.5 µm (0.3 mm) copper prior to nickel plating.

deposit, depending upon the expected service conditions. Nickel is not normally plated directly upon zinc, aluminum or brass; a copper deposit [*i.e.*, a copper strike] is usually first applied to the substrate. In the case of aluminum, an immersion deposit (usually zinc from a zincate bath) is applied prior to the copper strike.

Double-Layer Nickel

"A double layer of nickel is much more effective than a single layer of the same total thickness in preventing substrate corrosion. The double-layer deposit usually consists of an initial deposit of leveling semi-bright nickel followed by a bright nickel deposit that comprises about 25 percent of the total nickel thickness. The improved corrosion resistance is the result of the fact that the bright nickel layer contains more than 0.04 percent sulfur (originating from the brightening agents) and is more active (anodic) than the semi-bright layer containing little or no sulfur (<0.005 percent). The bright layer thus provides sacrificial protection to the inner layer, thereby preserving its integrity as a barrier protective layer (Fig. 2).

"Some studies[1] showed that double-layer nickel deposits of 40 µm (1.6 mm) provided virtually complete protection to steel after 35 months of exposure at a severe tropical marine site or a near-marine open-field site, whereas steel with the same thickness of leveling semi-bright nickel was badly corroded. However, no benefit of the double-layer deposit was evident at tropical (high humidity) rain forest sites where (1) both single- and double-layer deposits of 40-µm thickness were protective but (2) neither was protective at a thickness of 20 µm.

"The double-layer deposits not only provide superior corrosion resistance, but the leveling and brightening action of the layers results in an attractive finish without the need for mechanical polishing. Such deposits are often used as-is for applications involving indoor or mild exposures, but the nickel will tarnish seriously at outdoor exposures.

"However, a flash deposit (approximately 0.5 µm; 0.02 mm) of chromium will maintain the surface in a bright tarnish-free condition for many years. The conventional chromium flash is quite thin and characteristically contains microscopic cracks; at severe environments, nickel corrosion will eventually occur at the crack sites and the appearance will be adversely effected. However, if the chromium flash is made microdiscontinuous, *i.e.*, many more crack sites present, visible effects of nickel corrosion are postponed for significantly longer times. It is generally accepted that the total amount of corrosion on a given surface is governed by the total exposed area. Therefore, when the microdiscontinuous chromium is applied, the total corrosion on the surface is unchanged but is distributed over the multitudinous sites of exposed nickel, and the visual appearance remains unchanged for a longer time. Attempts to deposit crack-free chromium have not been successful, as some cracks are likely to develop in service.

"Microcracked chromium (>300 cracks per linear cm) is provided by proper use of additives/catalysts in the bath; microporous chromium (>10,000 pores per cm^2) is usually formed by the interposition (between the bright nickel and the chromium) of a thin strike of nickel with codeposited fine particles (*e.g.*, aluminum oxide). Microporosity is thereby induced in the chromium flash without changing the decorative appearance. The combination of double-layer nickel and microporous chromium has considerably improved corrosion resistance and retention of decorative appeal. Some typical applications of decorative nickel plus chromium deposits are shown in Table 1.[2]

"A copper/white brass/bright nickel/chromium system has found use for auto exterior trim, providing substrate protection similar to the double-layer nickel described above.

"It has been suggested[3] that the following treatment applied to nickel/chromium-plated parts can significantly improve corrosion resistance: cathodic for 1.5 min at 0.3 A/dm^2 (3 A/ft^2) in 50 g/L $Na_2Cr_2O_7.2H_2O$ + 1 g/L $Cr_2(SO_4)_3$ at 93°C (200°F).

Satin Nickel

"A relatively nonreflective nickel deposit is sometimes required for decorative effects or to reduce glare on such items as instrument control dials, automobile panels and windshield-wiper arms. The desired finish can be obtained by scratch brushing or fine abrasive blasting the nickel deposit. An attractive nonglare nickel deposit can be obtained directly by codeposition of finely divided nonconducting particles dispersed in the plating bath.[4] Similar results are obtained by incorporating microscopic, emulsified organic droplets in the bath. The satin nickel deposits are normally overplated with a chromium deposit to prevent tarnishing.

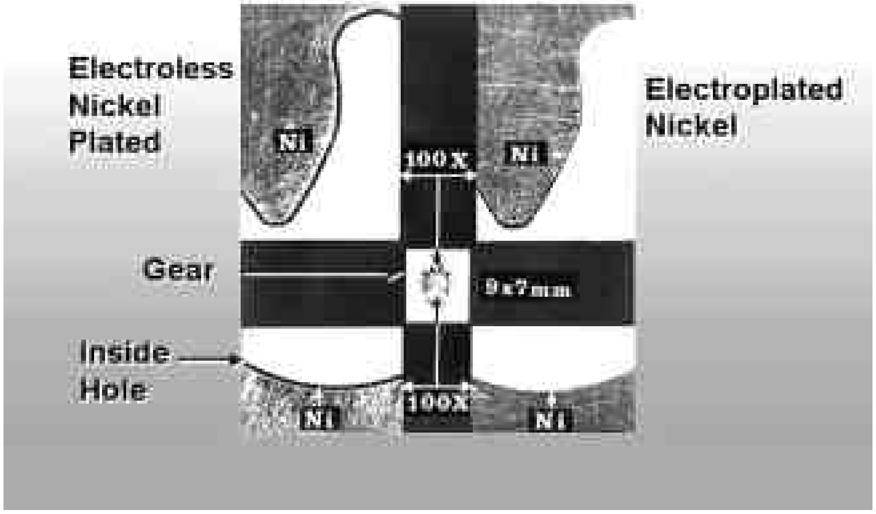

Fig. 3—Electroless nickel deposit.

Nickel - Iron

"A nickel-iron alloy containing 60 to 85 percent nickel [found increased interest] as a substitute for nickel plating. The principal advantage is reduced nickel consumption and consequent monetary savings. The process is claimed as simply and easily controlled as conventional bright nickel.[5]

Electroless Nickel

"Nickel deposited by the electroless (autocatalytic) process[6] has found numerous applications, and facilities for applying electroless nickel deposits are now commonplace in plating shops. Some of the advantages and disadvantages of electroless nickel are outlined in Table 2. The remarkable uniformity of deposition is an important factor in many applications and is illustrated in Fig. 3.

"Though the cost of applying electroless nickel is normally higher than that of electrodeposition, the need for expensive auxiliary-anode arrangements may be eliminated and parts with highly complex shapes can be effectively and economically plated to close tolerances. In addition, thinner electroless than electrolytic nickel deposits are generally capable of protecting smooth steel substrates exposed to a given environment because the electroless deposits tend to be less porous. It should be recognized that the electroless nickel deposit (from hypophosphite-based baths) contains significant quantities of phosphorus which account for its high hardness and relatively low ferromagnetic properties. Electroless nickel deposits are rarely chromium plated though it can be accomplished with difficulty, when required. Items as small as components for watch mechanisms and as large as interiors of tank cars (for handling various liquids) have been successfully and advantageously plated with electroless nickel to provide corrosion resistance. Zincated aluminum is readily electroless nickel plated and special solutions have been developed for application to magnesium; however, freedom from porosity is an absolute must if exposures to corrosive environments are expected.

"The following bath may be used for small-scale deposition to evaluate potential applicability of the process to a particular product: 25 g/L

Table 2

Advantages/Disadvantages of Electroless (vs. Electrolytic) Nickel

Advantages	**Disadvantages**
More uniform deposit	More expensive
Less porous deposit	Lower melting point deposit
Superior corrosion resistance	More brittle deposit
Harder deposit	Shorter bath life
Deposition on non-conductors	Higher bath temperature

$NiSO_4.6H2O$ + 9 g/L $Na_2C_2H_3O_2$ (acetate) + 0.001 g/L $Pb(C_2H_3O_2).3H_2O$ + 23 g/L $NaH_2PO_2.H_2O$ (hypophosphite) at pH 4.8 and 88°C (190°F); use until up to about 0.35 µm m^2 (0.15 mm ft^2) is deposited per liter of solution and discard. However, proprietary baths should be employed for maximum economy in production plating and samples of proprietary baths may be available for test purposes.

Chromium

"It is usually not considered economically feasible to apply chromium deposits primarily for barrier-layer protection. However, when applied for its numerous desirable characteristics (*e.g.*, wear resistance, low coefficient of friction, heat resistance), at thickness of more than about 25 µm (1.0 mm), effective barrier-layer protection of a corrodible substrate may be expected at numerous chemical and environmental exposures. A 25-µm chromium deposit has proven quite effective for protection of steel at industrial environments.

Copper

"Copper deposits are rarely used alone to prevent substrate corrosion. The galvanic effects on corrodible substrates are more pronounced with copper than with nickel, and copper does not retain a high polish even in mild environments, though chromate films or benzotriazole will inhibit tarnishing. However, copper deposits are indispensable as initial deposits on zinc die-castings and aluminum for achieving optimum adhesion, and the copper also contributes to the overall barrier-layer protection provided by the copper-plus-nickel system. During periods of nickel scarcity, copper undercoats for nickel are used more extensively and comprise a greater proportion of the total thickness than [was the case in 1980].

Tin

"Tin is electrodeposited or hot-dipped to provide a protective coating on steel or copper alloys during environmental exposure. Since tin is not sacrificially protective to steel at natural atmospheric environments, some corrosion is to be expected if the coating is discontinuous, *i.e.*, does not provide a complete barrier between the substrate and the environment. It should be noted, however, that in some atmospheres, initial corrosion sites may tend to plug with corrosion products and continued corrosion may be stifled. If corrosion is to be prevented, sufficient tin thickness (30 to 125 µm; 1.2 to 5 mm) should be applied to ensure freedom from porosity.

"Some common applications of tin deposits, where corrosion protection is a significant factor in its selection, are food vessels, kitchenware, TV chassis, washing-machine components and milk coolers. Copper wires are often tin plated to prevent discoloration from reaction with insulation substances.

"An application of special interest is tin plating of copper bars for chromium-plating tanks and rack hooks. The tin resists attack by chromic acid, prevents bath contamination with copper, and helps ensure good rack contact. Attractive, bright tin electrodeposits have been used to provide decorative appeal in addition to corrosion resistance for jewelry, holloware, wire goods, handbag frames, fish hooks, refrigerator shelves and locks.

"The barrier-layer coatings cited above are those most economically and generally used for this purpose, but virtually any deposited metal will provide barrier protection to the substrate if sufficient thickness is applied. Indeed, whenever a heavy deposit of any metal is applied for a functional application, barrier layer protection will also be obtained [as long as the article remains undamaged.]" ***P&SF***

References

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Editor's Note*: The preceding article is based on the original piece written by Fred Pearlstein for the AES Update series that ran in this journal in the late 1970s and early 1980s. The series, begun and coordinated by the late Dr. Donald Swalheim, and carried on by many others, brought practical information to the metal finisher. Much of the material remains relevant today and is presented here in the hope that those in today's industry might learn from past pioneers and practitioners. In some cases, words were altered [in brackets] for context. Certain sections were omitted that dealt with processes, such as cadmium and lead, which, for environmental and workplace safety reasons, are less prevalent today. Still, some material is left in for historical perspective, such as the occasional reference to nickel shortages and nickel-iron alloys.*