3

ELECTRODEPOSITION OF NICKEL

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Nickel electroplating is a commercially important and versatile surface-finishing process. Its commercial importance may be judged from the amount of nickel in the form of metal and salts consumed annually for electroplating, now roughly 100,000 metric tons worldwide, as well as its versatility from its many current applications [1]. The applications of nickel electroplating fall into three main categories: decorative, functional, and electroforming.

In decorative applications, electroplated nickel is most often applied in combination with electrodeposited chromium. The thin layer of chromium was first specified to prevent the nickel from tarnishing. It was originally deposited on top of a relatively thick, single layer of nickel that had been polished and buffed to a mirror-bright finish. Today decorative nickel coatings are mirror bright *as deposited* and do not require polishing prior to chromium plating. Multilayered nickel coatings outperform single-layer ones of equal thickness and are widely specified to protect materials exposed to severely corrosive conditions. The corrosion performance of decorative, electroplated nickel plus chromium coatings has been further improved by the development of processes by which the porosity of chromium can be varied and controlled on a microscopic scale (microdiscontinuous chromium). Modern multilayered nickel coatings in combination with microdiscontinuous chromium are capable of protecting steel, zinc, copper, aluminum, and many other materials from corrosion for extended periods of time. The complexity of modern-day nickel plus chromium coatings is more than offset by the greatly improved corrosion resistance that has been achieved without significantly increasing coating thickness and costs.

There are many functional applications where decoration is not the issue. Instead, nickel and nickel alloys with matte or dull finishes are deposited on surfaces to improve corrosion

and wear resistance or modify magnetic and other properties. The properties of nickel electrodeposits produced under different conditions of operation are of particular interest in this connection.

Electroforming is electroplating applied to the fabrication of products of various kinds. Nickel is deposited onto a mandrel and then removed from it to create a part made entirely of nickel. A variation of this is electrofabrication where the deposit is not separated from the substrate and where fabrication may involve electrodeposition through masks rather than the use of traditional mandrels.

The many current applications of nickel electroplating are the result of developments and improvements that have been made almost since the day the process was discovered. This is evident in the following retrospective on the development of nickel electroplating solutions as well as in subsequent sections that deal with basics, decorative electroplating, functional applications and deposit properties, nickel electroforming, nickel anode materials, quality control, and pollution prevention.

3.1 RETROSPECTIVE ON NICKEL ELECTROPLATING SOLUTIONS

Bottger developed the first practical formulation for nickel plating, an aqueous solution of nickel and ammonium sulfates in 1843, but earlier references to nickel plating can be found. Bird apparently deposited nickel on a platinum electrode in 1837 from a solution of nickel chloride or sulfate, and Shore patented a nickel nitrate solution in 1840 [2, 3]. The solution developed by Bottger remained in commercial use for 70 years, however, and he is acknowledged to be the originator of nickel plating [4].

Dr. Isaac Adams, Jr., a medical doctor educated at Harvard University and at the École de Médicine in Paris, was one of the first to commercialize nickel plating in the United States, and his patented process gave his company a virtual monopoly in commercial nickel plating from 1869 to 1886. His patent covered the use of pure nickel ammonium sulfate. Although Adams's solution was similar to Bottger's, his emphasis on operating the bath at neutral pH was undoubtedly vital for controlling the quality of the nickel deposited, since excessive amounts of ammonia would tend to lower cathode efficiency and embrittle the deposit. Largely as a result of the publicity generated by Adams, nickel plating became known worldwide, and by 1886, the annual consumption of nickel for plating had grown to about 135 metric tons [5, 6].

Remington, an American residing in Boston, attempted to market a nickel ammonium chloride electroplating solution in 1868, but perhaps of greater significance, in view of subsequent developments, were his attempts to use small pieces of electrolytic nickel as an anode material in a platinum anode basket [7]. Weston introduced the use of boric acid and Bancroft was one of the first to realize that chlorides were essential to ensure efficient dissolution of nickel anode materials [8, 9].

Professor Oliver P. Watts at the University of Wisconsin, aware of most of these developments, formulated an electrolyte in 1916 that combined nickel sulfate, nickel chloride, and boric acid and optimized the composition of the nickel electroplating solution [10]. The advantages of his hot, high-speed formula became recognized and eventually led to the elimination of nickel ammonium sulfate and other proprietary solutions. Today the Watts solution is widely applied, and its impact on the development of modern nickel electroplating technology cannot be overstated.

Decorative nickel plating solutions are variations of the original Watts formulation, the main difference being the presence in solution of organic and certain metallic compounds to brighten and level the nickel deposit. Because of his use of organic additives like benzene and naphthalene di- and trisulfonic acids, Schlotter's decision to market a bright nickel plating solution in 1934 is a milestone in the commercial development of decorative nickel plating [11].

The introduction of coumarin-containing, semibright nickel plating solutions by DuRose in 1945 was a major contribution because it subsequently led to the development of double- and triple-layer nickel coatings with greatly improved corrosion resistance [12]. His introduction of semibright nickel processes came at a critical time in the history of decorative nickel electroplating, when confidence in the ability of single-layer, bright nickel coatings to prevent corrosion of automotive components was at a relatively low point.

The dominant position of Watts solutions has been challenged from time to time, but the only ones that have been adopted on a substantial scale are nickel sulfamate solutions [13]. The Watts solution is the basis for most decorative nickel plating solutions, although considerable variation in the chloride content of different proprietary decorative processes may be specified by the suppliers of those processes. Sulfamate solutions are rarely, if ever, used for decorative plating. Watts and nickel sulfamate solutions are used for functional plating and for electroforming, but sulfamate is more popular for the latter.

3.2 BASICS

Nickel electroplating is similar to other electrodeposition processes that employ soluble metal anodes; that is, direct current is made to flow between two electrodes immersed in a conductive, aqueous solution of nickel salts. The flow of direct current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with nickel. The nickel in solution is present in the form of divalent, positively charged ions (Ni^{2+}). When current flows, the positive ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni^0) at the cathode surface. The reverse occurs at the anode where metallic nickel is dissolved to form divalent, positively charged ions which enter the solution. The nickel ions discharged at the cathode are thus replenished by those formed at the anode.

3.2.1 Application of Faraday's Laws to Nickel

The amount of nickel deposited at the cathode and the amount dissolved at the anode are directly proportional to the product of the current and time and may be calculated from the expression

$$m = 1.095 \times aIt \tag{3.1}$$

where m is the amount of nickel deposited at the cathode (or dissolved at the anode) in grams, I is the current that flows through the plating tank in amperes, t is the time that the current flows in hours, and a is the current efficiency ratio (see Chapter 1 for the definition of current efficiency). The proportionality constant (1.095) in grams per ampere hour equals M/nF, where M is the atomic weight of nickel (58.69), n is the number of electrons in the electrochemical reaction (2), and F is Faraday's constant, equal to 26.799 A-h (more commonly given as 96,500 C).

The proportionality constant must be multiplied by the actual electrode efficiency ratio if precise values are required. The anode efficiency for nickel dissolution is almost always 100% under practical electroplating conditions; that is, $a = 1$ when estimating anode weight loss. If the pH of the solution is too high and/or the chloride ion concentration too low, hydroxyl ions may be discharged in preference to the

dissolution of nickel, and oxygen will be evolved. Under those unusual conditions the nickel anode becomes passive, and the efficiency of anode dissolution is close to zero.

The cathode efficiency of different nickel plating solutions may vary from 90 to 97% and, accordingly, *a* will vary from 0.90 to 0.97. A small percentage of the current is consumed in the discharge of hydrogen ions from water. That reduces the cathode efficiency for nickel deposition from 100% to approximately 96% in an additive-free nickel electroplating solution. The discharged hydrogen atoms form bubbles of hydrogen gas at the cathode surface. Cathode efficiencies as low as 90% are characteristic of some bright nickel plating solutions that are formulated to give highly leveled, mirrorlike deposits rapidly, that is, at thicknesses below 12 μm [14]. An average cathode efficiency of 95.5% is commonly used to make estimates when precise values are not essential.

Because the anode and cathode efficiencies are not exactly equal, the nickel ion concentration and the pH of the solution will slowly increase as plating proceeds. The rate of increase in nickel ion concentration depends on the difference between cathode and anode efficiencies. Because cathode efficiencies may vary from 90 to 97%, whereas anode efficiency is almost always 100%, the rate of increase in nickel ion concentration depends on the cathode efficiency and the nature of the plating solution, not on the type of soluble nickel anode material that is used. The use of a special insoluble anode in combination with soluble anodes has been developed to help control the rate of increase of the nickel ion concentration [15].

3.2.2 Average Coating Thickness

An expression for calculating nickel thickness, *s* in micrometers, can be derived by dividing Eq. (3.1) by the product of the density of nickel, d (8.907 g cm^{-3}), and the surface area to be electroplated, *A*, and multiplying by 100 to obtain the thickness in micrometers:

$$s = \frac{m \times 100}{dA} = \frac{109.5 \times aIt}{8.097A} = \frac{12.294 \times aIt}{A} \quad (3.2)$$

The ratio *I/A* is the current density and thus the above expression shows that the coating thickness depends on the *current density* and time, whereas the amount or mass of nickel deposited, Eq. (3.1), depends on the *current* and time. Equation (3.2) is the basis for the electrodeposition data compiled in Table 3.1, which gives the time *in minutes* required to deposit a nickel coating of specified thickness at different values of current density. The expression above and Table 3.1 provide a means of estimating the *average* coating thickness.

3.2.3 Current and Metal Distribution

The *actual* thickness at any point on the surface of a shaped article is dependent on the current density at that point. The current density at any point is determined by how the current is apportioned over the surface of the article being electroplated. In nickel plating, the current distribution is largely determined by geometric factors, that is, by the shape of the part, the relative placement of the part with respect to the anode, how the parts are placed on plating racks, and the dimensions of the system. Because almost all except the simplest shapes to be electroplated have prominent surfaces that are nearer to the anode than recessed areas, a uniformly thick nickel coating is difficult to produce. The current density at prominences is greater due to the shorter anode-to-cathode distance and the lower resistance to current flow that implies. Conversely, recessed areas, being further away from the anode, will have a lower current density because of increased resistance to current flow. This inevitably means

TABLE 3.1 Nickel Electrodeposition Data

Deposit Thickness (μm)	Weight per Unit Area (g dm^{-2})	Ampere Hours per Unit (Ah dm^{-2})	Time (min) to Obtain Deposit at Various Current Densities (A dm^{-2})									
			0.5	1	1.5	2	3	4	5	6	8	10
2	0.18	0.17	20	10	6.8	5.1	3.4	2.6	2.0	1.7	1.3	1
4	0.36	0.34	41	20	14	10	6.8	5.1	4.1	3.4	2.6	2
6	0.53	0.51	61	31	20	15	10	7.7	6.1	5.1	3.8	3.1
8	0.71	0.68	82	41	27	20	13	10	8.2	6.8	5.1	4.1
10	0.89	0.85	100	51	34	26	17	13	10	8.5	6.4	S.I
12	1.1	1.0	120	61	41	31	20	15	12	10	7.7	6.1
14	1.2	1.2	140	71	48	36	24	18	14	12	8.9	7.1
16	1.4	1.4	160	82	54	41	27	20	16	14	10	8.2
18	1.6	1.5	180	92	61	46	31	23	18	15	11	*9.2*
20	1.8	1.7	200	100	68	51	34	26	20	17	13	10
40	3.6	3.4	410	200	140	100	68	51	41	34	26	20

Note: Based on 95.5% cathode efficiency.

that prominent areas will have thicker coatings than recessed ones.

Because geometric factors exert the greatest influence on current density at localized areas in the case of nickel plating, current distribution is virtually the same as metal distribution. Thus shields and auxiliary anodes can be used effectively to obtain acceptable thickness uniformity. Shields are made of nonconductive materials, and they may be placed on the anode, on the cathode, or between electrodes to block or control current flow. Auxiliary anodes may be either soluble or insoluble, and are placed closer to the cathode than principal anodes so as to direct the current to a recessed or relatively small area on the cathode. The analysis of geometric effects by computer modeling has received attention [16].

3.2.4 Throwing Power

In addition to the geometric factors, metal distribution is influenced by cathode polarization, the cathode efficiency–current density relationship, and the electrical conductivity of the solution [17]. The complex relationship between the factors that influence current distribution and hence metal distribution is called *throwing power*. A solution with a high throwing power is capable of depositing almost equal thicknesses on both recessed and prominent areas. For example, in copper cyanide solutions, high cathode polarization and the favorable cathode efficiency–current density relationship (cathode efficiency is lower at high than at low current densities) result in a solution with excellent throwing power. As already implied, cathode polarization and current efficiency do not significantly affect the throwing power of acid nickel plating solutions formulated with simple salts. The cathode polarization is low and the cathode efficiency is high and relatively constant above $1\,A\,dm^{-2}$.

Throwing power can be measured to give relative values [18]. Measurements indicate that the throwing power of nickel electroplating solutions can be somewhat improved by lowering the current density, increasing the electrical conductivity of the solution, increasing the distance between anode and cathode, and raising the pH and the temperature. Table 3.2 compares the throwing power of various plating solutions; it is based on the work of Watson, who applied a Hull cell to make the measurements. The nickel plating solution with the best throwing power contained a high concentration of anhydrous sodium sulfate; its composition is given in Table 3.3, which also indicates that throwing power decreases as the current density is increased [19].

3.2.5 Internal Stress

Internal stress refers to forces created within the deposit as a result of the electrocrystallization process and/or the co-deposition of impurities such as hydrogen, sulfur, and other elements [20]. Internal stress is either tensile (contractile) or

TABLE 3.2 Throwing Power of Various Electroplating Solutions

Solution	Average Current Density		Throwing Power (%) at Primary Current Density Ratios		
	$A\,dm^{-2}$	$A\,ft^{-2}$	5 : 1	12 : 1	25 : 1
Watts nickel	4.3	40	8	7	14
Sulfamate nickel	4.3	40	11	13	19
All-chloride nickel	4.3	40	18	18	27
Na/high sulfate	4.3	40	23	31	40
Mg/high sulfate	4.3	40	16	18	32
Proprietary bright nickel A	4.3	40	1	−12	−6
Proprietary bright nickel B	4.3	40	3	−12	−6
Acid copper	4.3	40	0	−29	−61
Rochelle copper	4.3	40	86	91	93
Conventional chromium	16	150	−42	−48	−100

Source: Watson [19].
Note: The 100% represents a uniform thickness over the cathode surface; −100 indicates the opposite extreme, where recessed areas are thinly plated and prominent areas are thickly plated.

compressive (expansive) in nature. In tensively stressed deposits, the average distance between nickel atoms in the lattice is greater than the equilibrium value, creating a force that tends to drive the atoms closer together. When a tensively stressed deposit is detached from its substrate, it contracts. In addition, if a thin cathode strip is electroplated on one side only (by painting the back and placing the bare side facing the anode), a deposit stressed in tension will cause the strip to bend or curl toward the anode. In compressively stressed deposits, the atoms are closer together and the force tends to drive them further apart. When detached from the substrate,

TABLE 3.3 Composition and Throwing Power at Various Current Densities of a High-Sulfate Solution

Average Current Density		Throwing Power (%) at Primary Current Density Ratios		
$A\,dm^{-2}$	$A\,ft^{-2}$	5 : 1	12 : 1	25 : 1
0.2	2	63	76	85
1.0	10	38	50	64
4.3	40	23	31	40

Source: Watson [19].
Note: Nickel sulfate, $30\,g\,L^{-1}$; nickel chloride, $38\,g\,L^{-1}$; boric acid, $25\,g\,L^{-1}$; sodium sulfate (anhydrous), $180\,g\,L^{-1}$. The 100% represents a uniform thickness over the cathode surface; −100 indicates the opposite extreme where recessed areas are thinly plated and prominent areas are thickly plated.

TABLE 3.4   Nickel Electroplating Solutions

	Electrolyte Composition[a] (g L^{-1})		
	Watts Nickel	Nickel Sulfamate	Basic Semibright Bath[b]
Nickel sulfate, NiSO$_4$ · 6H$_2$O	225–400		300
Nickel sulfamate, Ni(SO$_3$NH$_2$)$_2$		30–45	
Nickel chloride, NiCl$_2$ · 6H$_2$O	30–60	300–450	35
Boric acid, H$_3$BO$_3$	30–45	0–30	45
	Operating Conditions		
Temperature (°C)	44–66	32–60	54
Agitation	Air or mechanical	Air or mechanical	Air or mechanical
Cathode current density (A dm^{-2})	3–11	0.5–30	3–10
Anodes	Nickel	Nickel	Nickel
pH	2–4.5	3.5–5.0	3.5–4.5
	Mechanical Properties		
Tensile strength (MPa)	345–435	415–610	—
Elongation (%)	10–30	5–30	8–20
Vickers hardness (100 g load)	130–200	170–230	300–400
Internal stress (MPa)	125–185 (tensile)	0–55 (tensile)	35–150 (tensile)

[a] Antipitting agents formulated for nickel plating are added to control pitting.
[b] Organic additives available from plating supply houses are required for semibright nickel plating.
Note: Some typical properties of *fully-bright* nickel deposits are as follows: Elongation percentage, 2–5; Vickers hardness, 100 g load, 600–800; internal stress (MPa), 12–25 compressive.

compressively stressed deposits expand and a thin strip plated on one side only, as described, will bend away from the anode. Dislocation theory provides a logical explanation of the origins of internal stress in etectrodeposits [21, 22].

Stress in electrodeposited nickel can vary over a wide range depending on solution composition and operating conditions. In general, nickel electrodeposited from additive-free Watts solutions exhibits a tensile stress that is 125–185 MPa for the conditions given in Table 3.4. Deposits from sulfamate solutions display lower tensile stress within the range of 0–55 MPa. Compressively stressed nickel deposits are obtained from solutions that contain sulfur-containing organic additives similar to the carriers that are added to bright nickel plating solutions (discussed below). As far as is known, compressively stressed nickel deposits are almost always associated with the codeposition of sulfur. High deposit stress can be especially troublesome in electroforming where the adhesion between the electrodeposit and the mandrel is deliberately kept as low as possible to facilitate separation.

3.2.6   Adhesion

With the exception of electroforming, a high degree of adhesion between the deposit and the substrate is critical in all applications. Under favorable conditions, the crystal lattice of the substrate extends into the deposit (epitaxy). Epitaxial growth rarely occurs in commercial electroplating, however, where adhesion is due to cohesive forces between metal atoms.

Atoms of the electrodeposited metal align themselves in opposition to atoms of the substrate and are held to the surface by interatomic forces that result in the formation of metallic, covalent, ionic, polar, or other types of bonds. *Perfect* adhesion in electoplating is achieved when the bond strength is greater than the tensile strength of the weaker component; that is, in measuring adhesion by means of a quantitative test, failure occurs not at the interface but either within the deposit or within the substrate. In commercial electroplating, good adhesion is achieved by means of standard preparation methods that are described in American Society for Testing and Materials (ASTM) standards and elsewhere [23, 24].

3.2.7   Leveling and Microthrowing Power

The ability of an electroplating solution to fill in defects and scratches on the surface *preferentially* is called leveling. The deposit fills defects and tiny scratches, eventually covering them, and as a result the surface becomes smoother as the deposit increases in thickness. The semibright and bright nickel electroplating solutions described in the next section have excellent leveling properties. Organic additives in those solutions are adsorbed preferentially at micropeaks; the resulting increase in the local resistance to current flow increases the current density in microgrooves, thereby promoting leveling [25].

Microthrowing power refers to the ability of an electroplating solution to fill tiny crevices with deposits that follow

the contour of a defect or scratch without any leveling action whatsoever [26]. Additive-free nickel plating solutions have excellent microthrowing power but little leveling ability. In the absence of specifically adsorbed organic additives, the current density in micropeaks and microgrooves is uniform because of the low polarization and high cathode efficiency of most nickel electroplating solutions.

3.3   DECORATIVE ELECTROPLATING

The technology of decorative nickel electroplating has been improved continually over the years due to the development of bright and semibright nickel plating solutions, multilayer nickel coatings, and microdiscontinuous chromium. The major effect has been an increase in the corrosion resistance of decorative, electroplated nickel plus chromium coatings. In addition new and improved techniques for plating on plastics, aluminum alloys, and stainless steel have broadened the scope of decorative applications.

3.3.1   Bright Nickel Solutions

Modem bright nickel electroplating solutions employ combinations of additives carefully formulated to produce bright deposits over a wide range of current density. The deposits have excellent leveling or scratch-filling characteristics, fair ductility, and low internal stress. Modern processes produce bright deposits in areas of low current density, permit use of high average current densities and bath temperatures, are less sensitive to metallic contaminants than some of the solutions first commercialized, permit continuous purification of the plating solution by filtering through activated carbon, and produce breakdown products that can also be removed by activated carbon treatment and are not overly sensitive to anode effects. Bright nickel electroplating solutions have similar compositions as the Watts nickel electrolyte included in Table 3.4. Because the exact formulations of commercial processes are proprietary, the recommendations of the suppliers of decorative nickel plating processes should be followed.

The additives for bright nickel electroplating fall roughly into three categories: carriers, brighteners, and auxiliary brighteners. Those are the terms preferred by electroplaters, but the terminology is not standardized. To avoid confusion, alternative terms mentioned in the literature are shown in parentheses [6, pp. 96–103; 27].

Carriers (Brighteners of the First Class, Secondary Brighteners, Control Agents)   These are usually aromatic organic compounds. Examples are benzene sulfonic acid, 1,3,6-naphthalene sulfonic acid (sodium salt), p-toluene sufonamide, saccharin (o-benzoic sulfonimide), thiophen-2-sulfonic acid, benzene sulfinic acid, and allyl sulfonic acid. Carriers are the principal source of the sulfur codeposited with the nickel. Their main function is to refine grain size and provide deposits with increased luster compared with matte or dull deposits from baths without additives. When used by themselves, carriers do not produce mirror-bright deposits. Carriers are used in concentrations of about $1–25\,g\,L^{-1}$, the exact concentration depending on the specific compound. Carriers are not consumed rapidly by electrolysis, and consumption is primarily by dragout and by losses during activated carbon treatments. The stress-reducing property of carriers is increased if they contain amido or imido nitrogen. For example, saccharin is a most effective stress reducer and often helps to decrease or eliminate hazes.

Brighteners (Brigkteners of the Second Class, Primary Brighteners, Leveling Agents)   In combination with carriers and auxiliary brighteners, brighteners produce brilliant deposits having good ductility and leveling characteristics over a wide range of current densities. Some of these compounds include formaldehyde chloral hydrate, o-sulfobenzaldehyde, allyl sulfonic acid, coumarin; o-hydroxy cinnamic acid, diethyl maleate, 2-butyne-l,4-diol; 2-butyne-l,4-disulfonic acid; ethyl cyanohydrin, p-amino azo benzene, thiourea, and allyl thiourea and polyethylene glycols of various kinds. The best-known example in this class may be coumarin (1,2-benzopyrone), the leveling agent introduced by DuRose for producing semibright nickel deposits. Because they increase the internal stress and promote brittleness of nickel deposits, brightener concentrations are kept low and carefully controlled. Concentrations of $0.005–0.2\,g\,L^{-1}$ are generally used. The rates of consumption of these materials may vary within wide limits.

Auxiliary Brighteners   Auxiliary brighteners augment the luster attainable with carriers and brighteners and increase the rate of brightening and leveling. Some examples are sodium allyl sulfonate; zinc, cobalt, cadmium; and 1,4-butyne 2-diol. The concentration of these additives may vary from about 0.1 to $4\,g\,L^{-1}$ Sulfobetaines, such as pyridinium propyl sulfonate, are especially active sulfur-containing organic compounds that have a powerful effect on leveling in nickel deposits. However, because they introduce sulfur into the deposit, they cannot be used for semibright nickel plating [6, pp. 96–103]. They can be especially effective when added to bright nickel plating solutions in low, carefully controlled concentrations. The inorganic metallic ions—zinc cobalt, cadmium—are not often used anymore as auxiliary brighteners.

3.3.2   Electrocrystallization

The mechanism of nickel electrodeposition involves surface adsorption of species formed in the cathode film accompanied

by inhibition of growth of certain crystal faces. In the absence of organic additives, species like H_2, H_{ads}, and $Ni(OH)_2$, which form as a result of the reduction of hydrogen ions, determine most of the microstructural features of the nickel deposit [28, 29].

The mechanism by which *unsaturated* organic additives modify the electrocrystallization process to yield mirror-bright surfaces also involves adsorption, hydrogenation, and desorption. The organic molecule is adsorbed on the surface via the unsaturated bond, blocking certain sites on the nickel lattice and thus altering the growth rates of different crystal faces. The unsaturated bond reacts with hydrogen in the cathode film and the resulting reduction products are desorbed from the surface and/or incorporated into the deposit. The rates of those processes are influenced by the degree of unsaturation, the size and shape of the organic molecule, the functional groups present, aromatic rings, and other stereochemical factors.

That general mechanism has been confirmed and clarified by studying the effects of individual additives [30]. For example, the active group in a carrier like sodium benzene sulfonate is $=C-S$. Hydrogenolysis of the $=C-S$ bonds results in the formation of sulfur anions that are adsorbed on the (110) crystallization direction causing the [100] texture to predominate. The sulfur is incorporated into the deposit as the sulfide. Below 25 A dm^{-2} the active groups in saccharin, $=C-S$ and $S=O$, react with hydrogen to form sulfur anions that are also codeposited and suppress growth in the (110) direction, promoting the formation of the [100] texture and extending the [100] planes in the surface of the deposits, but above that current density, hydrogenation of adsorbed $C=C$ and $C\equiv C$ bonds also takes place. This promotes reduction of hydrogen ions and increases the pH in the cathode film with the consequent formation of a colloidal suspension of nickel hydroxide. The selective adsorption of colloidal nickel hydroxide inhibits growth in the (100) direction, favoring formation of [211], [211] + [111], and [111] textures. The active groups in sulfur-free brighteners include $C=C$, $C\equiv C$, $C\equiv N$, and others, and the mechanism by which these modify crystal growth also involves hydrogenation, increased alkalinity in the cathode film, and precipitation and inhibition of crystal growth by colloidal nickel hydroxide causing [211] and [111] textures to dominate crystallographic features. The two mechanisms by which sulfur-containing and sulfur-free organic addition agents influence crystal growth are thus distinctly different, and complex sulfur-containing compounds like saccharin apparently display features of both. The effect of pulsed reversed current in the presence of organic additives has also been studied [31].

Brightness is attained if the microstructural components of the surface form a plane from which they do not vary by distances greater than the wavelength of light [32]. The criterion for brightness is thus not simply the production of fine-grained deposits but the creation of *flat* crystals. Exactly

how a complex mixture of carriers, brighteners, and auxiliary brighteners act in concert to meet those criteria may need further elucidation, but the synergistic effects first described in the classical work of Edwards are probably involved [33].

3.3.3 Effects of Codeposited Sulfur

The incorporation of sulfur has several important effects. Sulfur increases the electrochemical reactivity of bright nickel compared to sulfur-free nickel, and that effect is applied in multilayer coatings to improve corrosion performance. Codeposition of sulfur changes the intrinsic internal stress of electrodeposited nickel from tensile (contractile) to compressive (expansive) and the incorporation of sulfide, an anion considerably larger than the nickel atom, must compress the nickel atoms in the crystal lattice. Carriers are thus useful for controlling internal stress. In addition, sulfur increases the hardness and lowers the elongation percentage of electrodeposited nickel (Table 3.4).

3.3.4 Semibright Nickel

Semibright nickel solutions contain nickel sulfate, nickel chloride, boric acid, and leveling agents. A typical composition is included in Table 3.4. Coumarin has, for the most part, been superseded by other organic compounds [34], notably the acetylenics that are now widely employed. Although the ability of coumarin to level nickel deposits is excellent, the acetylenics form reduction products that have little or no effect on the properties of the semibright nickel deposit, whereas the melilotic acid formed by the cathodic reduction of coumarin is incorporated in the deposit, lowering its ductility and raising its hardness, The effect of melilotic acid must be controlled by frequent treatments with activated carbon. Coumarin-free semibright nickel solutions need to be carbon treated less frequently, may be easier and more economical to maintain, and may produce deposits with consistent properties.

Semibright nickel plating processes yield smooth, sulfur-free deposits that are semilustrous with columnar structures similar to Watts nickel deposits, in contrast to full-bright nickel deposits that have banded (laminar) structures as a result of the periodicity of sulfur codeposition. The highly leveled surface is easy to polish and buff to a mirror finish. The good ductility of semibright nickel deposits is important in those applications where multilayer coatings are stressed in service. Semibright nickel deposits are an essential part of multilayer nickel coatings.

3.3.5 Multilayer Nickel Coatings

Single-layer bright nickel plus chromium coatings proved to be less resistant to corrosion than the polished Watts

nickel plus chromium coatings that they replaced. The lower resistance to corrosion was attributed to the activating effect of the sulfur incorporated in bright nickel electrodeposits. The search for coatings with improved corrosion resistance led, first, to the development of semibright nickel coatings. Semibright nickel deposits, being sulfur free, are equivalent in corrosion resistance to polished Watts nickel deposits and for a while (1945–1950) were applied as single-layer coatings in the production of automobile bumpers to obtain improved corrosion performance despite the disadvantage of having to polish the coatings after electroplating to achieve full brightness.

The idea of combining layers of bright and semibright nickel was conceived later as a means of eliminating the costly polishing operation [35]. The fact that decorative double-layer nickel coatings are much more resistant to corrosion than equivalent thicknesses of single-layer bright nickel was discovered as a result of studies conducted after the double-layer coatings were applied commercially. The introduction of triple-layer coatings occurred later [36]. Today single-layer bright nickel coatings are only specified for mild corrosion service with nickel thickness commonly in the range of 5–12 μm. For severe and very severe corrosion service, thicker, multilayered coatings are specified.

Double-layer nickel coatings have an undercoat of highly leveled, sulfur-free, semibright nickel covered with sufficient bright nickel to give a mirror finish without having to polish the coating. The excellent leveling characteristics of the semibright nickel layer also helps minimize the requirement for expensive mechanical finishing of the substrate. Because the undercoat of sulfur-free, semibright nickel is electrochemically more noble than bright nickel, corrosive attack, when it does occur, is preferentially directed toward the bright nickel and a flat-based pit is formed (Fig. 3.1). This effectively retards the pitting attack because, before the pit can penetrate the coating further, a considerable portion of the bright nickel layer must be removed. As a result double-layer coatings show a marked improvement in corrosion performance over single-layer coatings.

The electrochemical basis for the improved corrosion performance observed with double-layer coatings was provided by Flint and Melbourne, DuRose, Safranek, and others [37–39]. Petrocelli, Hospadaruk, and DiBari [40] constructed Evans-type corrosion diagrams from which the galvanic relationships between nickel and chromium in various test electrolytes were deduced. They showed that galvanically coupling semibright nickel to bright nickel caused the semibright nickel to become cathodically polarized, lowering its rate of corrosion, whereas the bright nickel became anodically polarized, increasing its rate of corrosion. When bright nickel, semibright nickel, and chromium were galvanically coupled in the same solution, chromium was
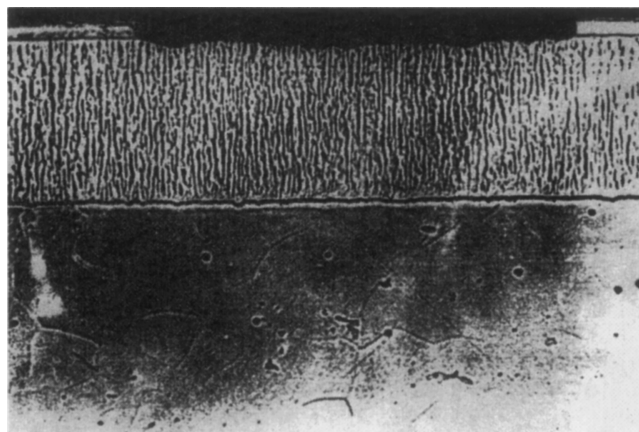

FIGURE 3.1   In double-layer nickel coatings, corrosion is initially confined to the top, full-bright nickel layer and penetration through the underlying semibright nickel layer is delayed (after 30 months exposure outdoors in an industrial atmoshpere).

cathodic to both the bright and the semibright nickel, and as a result coupling to chromium increased the rate of corrosion of both types of nickel.

During electrochemical studies of the behavior of various types of nickel deposits, it became clear that there were basically two types of proprietary bright nickel processes commercially available, one with a significantly higher reactivity than the other [41]. When equal areas of semibright nickel were coupled to each type, the highly reactive bright nickel provided greater protection of the semibright nickel than the low-reactivity type. The relative merits of using high-reactivity bright nickel in combination with semibright nickel was confirmed in outdoor stationary and mobile exposure programs performed with contoured panels [42]. Contoured panels have raised and recessed areas, and the thickness of the coating is greater on the relatively flat portion of the panel than in the recessed areas where the average thickness of the coating is 45% of the nominal value. The fact that recessed areas performed better with the high-reactivity bright nickel not only confirmed the observations made in the laboratory but also showed that the improvement in corrosion performance due to double-layer nickel coatings becomes more important as coating thickness is decreased. Snyder [43] refers to the two types as high- and low-potential bright nickel and states that the low-potential types may give better performance as single-layer coatings.

In triple-layer coatings, semibright and bright nickel layers are separated by a thin, highly active nickel layer containing about 0.15% sulfur deposited from a special solution [34, 44], The thickness of the very active nickel layer is of the order of 1.2–2.5 μm. The corrosion mechanism is similar to that of double-layer nickel coatings; once a corrosion pit reaches the very active nickel layer, corrosion proceeds laterally, the top layer of bright nickel becomes

cathodically polarized, and its rate of corrosion is decreased. Whether or not triple-layer nickel coatings give significantly better corrosion performance compared to double-layer nickel coatings of equal thickness over extended periods of time is still not completely settled, but certainly the appearance in the initial stages of corrosion is improved because much of the corrosion takes place beneath the top layer of bright nickel and is difficult to see. Double- and triple-layer nickel coatings delay penetration of corrosion to the substrate and are effective in improving corrosion performance of nickel plus chromium coatings.

3.3.6 Microdiscontinuous Chromium

On surfaces that are electroplated with nickel plus conventional chromium, corrosion of the nickel begins at a pore in the chromium coating. Because conventional electrodeposited chromium has relatively few discontinuities, any pore or crack is surrounded by a large cathodic area of chromium that draws current from a relatively small area of nickel, and as a result the rate of pit penetration through the nickel can be quite rapid. Corrosion may be under anodic control during the initial stages, but as the exposed nickel anode area increases, the rate of corrosion becomes cathodically controlled.

These observations led some investigators to conclude that a pore-free, electrodeposited chromium coating would lead to significant improvement in the corrosion performance of nickel plus chromium coatings. Crack-free chromium electroplating processes were introduced in the 1960s but quickly disappeared when it became apparent that crack-free chromium develops porosity in service, similar to the porosity of conventional chromium. (Crack-free chromium has a predominantly hexagonal close-packed structure, unlike conventional chromium, which is body-centered cubic. The very high wear rate of crack-free chromium was attributed to its different crystal structure [22].)

Saur was one of the first to establish that an inverse relationship exists between the number of pores in the chromium and the degree of substrate corrosion [45]. Based on his evaluation of test panels and parts that had been in service for up to 21 years, he concluded that "an increase in chromium discontinuities increases the area of nickel corrosion, the increase in exposed nickel is associated with an increase in basis metal protection, and a minimum chromium imperfection density is beneficial for corrosion protection of the substrate." Saur and his co-workers [46] at the General Motors Research Laboratory also developed the test described in ASTM Standard B 627 [23], Electrolytic Corrosion Testing (EC Test), which applies potentiostatic and galvanostatic polarization in a specified sequence to simulate anodic and cathodic corrosion control and permits a quantitative evaluation of the protectiveness of nickel plus chromium coatings to be made. Use of an interference microscope

made it possible to examine specimens subjected to that test; measure pit densities, radii, and depths; and correlate that data to basis metal protection and appearance in nickel chromium coating systems [47]. Saur's work and that of others led to the development of commercial processes for increasing the number of discontinuities in electrodeposited chromium [48].

Commercial processes for producing microdiscontinuous chromium result either in the creation of micropores that are essentially circular in shape or in microcracks that form a fine, invisible, continuous network of cracks over the entire surface. One of the most popular processes for producing microporous chromium requires the deposition of a thin layer of bright nickel, prior to chromium plating, from a solution that contains insoluble, extremely fine, nonmetallic particles dispersed throughout the tank. The resulting chromium deposit is completely microporous when applied over the special nickel layer. Methods that involve mild impingement with fine particles after the deposition of chromium are effective in producing microporous chromium [49].

The development of microcracked chromium began with dual chromium which had the requisite crack pattern [50] and the work of Safranek and others [51] who added selenium to conventional chromium plating solutions to induce microcracking; those methods are no longer in commercial use. Still in limited use is a method that requires the deposition of a thin, highly stressed nickel deposit from an all-chloride nickel plating solution, prior to chromium plating, which gives the desired crack pattern after plating with chromium. One difficulty with the latter process is controlling the crack pattern in low-current-density areas. The most popular processes for producing microdiscontinuous chromium then are those based on deposition of special nickel strikes *prior* to chromium plating or on particle impingement *after* electroplating with chromium.

The use of microdiscontinuous chromium in combination with decorative multilayer nickel coatings, with or without copper underlayers, has resulted in great improvement in outdoor corrosion performance under severely corrosive conditions. The effect of the microdiscontinuities is to distribute the corrosion current over many tiny cells. The current available at any cell or pit is small, and the rate at which a pit proceeds through the bright nickel layer is correspondingly small. As the defect area increases, the area of exposed nickel (the anode) increases while the area of chromium (the cathode) decreases. Because the corrosion reaction is under cathodic control, reducing the size of the cathode surrounding each pit reduces the rate of nickel corrosion. The mechanism is consistent with the principles of galvanic corrosion. The area of exposed nickel was estimated by assuming that pits are cylindrically shaped, with pit radii and densities described in the literature; at very high chromium defect densities, the exposed nickel area is

approximately 3.5% [42]. The rate of pitting of double-layer nickel coatings 40 μm thick electroplated with microdiscontinuous chromium appeared to be approximately 2 μm per year, and steel panels plated with those coatings did not rust in a moderately severe, outdoor marine exposure under static conditions for more than 15 years [52]. Similar results have been obtained in programs conducted by members of ASTM Committee B 8 and others [53–55].

3.3.7   The STEP Test

The focus on electrochemical aspects of corrosion culminated in the development of the STEP test by Harbulak [56]. The test made it possible to measure potential differences between various layers in a multilayer nickel coating on actual electroplated parts rather than on deposits detached from the substrate. STEP is an acronym for simultaneous thickness and electrode potential measurement. In the test, which is a simple but brilliant modification of the well-known coulometric method of thickness testing, the electrode potential is monitored continuously as the coating is dissolved anodically. This is made possible by placing a reference electrode in the form of a silver or platinum wire in the coulometric cell used for stripping the coating. (Silver is preferred because the silver–silver chloride electrode has a constant potential whereas the potential exhibited by platinum is sensitive to the exact surface state of the platinum.) By recording the changes in potential with time, the potential differences, as well as the thicknesses, of the individual nickel layers can be measured. Unpublished work on the precision of the STEP test by ASTM Committee B 8 members indicate that potential differences and thicknesses can be measured with a standard deviation of less than 5% on standard reference materials. The STEP test is described in ASTM Standard B 764 [23].

Although there are no universally accepted values for the optimum potential differences between nickel layers, ASTM Standard B 456 [23] provides the following guidelines: (1) The STEP potential difference between the semibright and bright nickel layer generally falls within the range of 100–200 mV and in all combinations the semibright nickel layer is more noble (more positive) than the bright nickel layer; (2) the STEP potential difference between the high-activity layer and the bright nickel layer in triple-layer coatings has a potential range of 15–35 mV, and the high-activity layer is more active (anodic) than the bright nickel layer; and (3) the STEP potential difference between the bright nickel and any thin layer applied just prior to chromium plating for producing microporous or microcracked chromium has a potential range of 0–30 mV, and the bright nickel layer is more active. The importance of the latter in minimizing the deterioration in surface appearance that may occur in severe outdoor conditions or during accelerated corrosion testing has been stressed by Tremmel [57].

3.3.8   Electroplating Plastics, Aluminum, and Stainless Steel

Electroplating on plastics, aluminum, and stainless steel has broadened the scope of decorative nickel plating.

Plastics   The discovery that ABS plastics can be chemically etched and rendered electrically conductive made it possible to deposit *decorative* nickel/chromium coatings onto injection-molded plastic parts with a level of adhesion not previously attainable [58]*. ABS is a terpolymer of acrylonitrile, butadiene, and styrene. When parts made of that material are immersed in strong chromic or chromic plus sulfuric acid solutions, the relatively soft, tiny butadiene rubber particles dispersed in the acrylonitrile–styrene matrix are chemically etched. The effectiveness of etching depends on how uniformly the butadiene particles are dispersed throughout the part and other factors related to injection-molding parameters. The physical bond achieved by the *keying* of the deposit into microscopic etch pits on the surface no doubt plays an important role in achieving adhesion, but the observation that the hexavalent chromium in the etching solution is reduced to trivalent chromium and must be periodically replenished led to speculation that the bonding might be chemical in nature [59]. Regardless of the exact mechanism, the adhesion (perhaps, 50–120 g mm^{-1} peel strength) is sufficient to prevent coatings from blistering at elevated temperatures on parts that are properly processed.

The traditional preparation sequence includes conditioning, etching, neutralizing, catalyzing, and autocatalytic deposition. Conditioning prior to etching can eliminate certain types of adhesion problems and may be done in a chromic/sulfuric acid solution or in an organic solvent (2,4-pentadione* and other ketones are sometimes used). The organic solvent softens and swells the plastic surface, making it more receptive to subsequent processing steps. Etchants are either chromic, chromic/sulfuric, or chromic/sulfuric/phosphoric acid types. The purpose of the neutralization step that follows etching is to remove all residual chromic acid from the surface of the parts, and this is accomplished by immersing them in acid or alkaline solutions that may contain complexing or reducing agents. After neutralization, catalyzing is commonly accomplished by immersing in a solution containing colloidal stannous/palladium chloride [60] and an excess of hydrochloric acid. Tiny amounts of palladium are deposited on the surface; the palladium acts as a catalyst for the autocatalytic (electroless) deposition of either copper or nickel. To pass thermal cycle tests, substantial thicknesses of ductile acid copper must be electroplated on top of the autocatalytically deposited metal, and it is expedient to use electroless copper rather than electroless nickel to avoid

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*See [6], Chapter 12, pp. 330–341 and 360–362 for bibliography on electroplating onto plastics.

*The use of 2, 4-pentadione is patented.

processing problems, such as immersion deposition of copper and bipolar effects [61]. In addition electroless nickel can sometimes corrode preferentially at the metal–plastic interface, causing blistering and lifting of the coating [62, 63]. (That is most likely due to low phosphorus in the electroless nickel. Small amounts of phosphorus activate nickel [64]; large amounts tend to passivate it [65].) Electroless copper followed by electroplating with bright acid copper is now common practice, although electroless nickel is also used successfully. This basic method for preparing plastics for electroplating is discussed in ASTM Standard B 727 and elsewhere [23, 66].

Efforts to simplify the traditional method have been made, including gas etching with sulfur dioxide and the use of permanganates to replace chromates [67] The activation of plastic surfaces by plasma and ozone etching are other ways to prepare plastics for electroplating [68].

Decorative nickel plus chromium coatings can be deposited on top of electroplated bright acid copper by established procedures. ASTM Standard B 604 [23] specifies the use of multilayer nickel coatings for the most severe corrosion conditions on the basis of the comprehensive corrosion performance program conducted in the 1970s by members of ASTM and the American Society for Electroplated Plastics (ASEP) that showed that copper underlayers corroded during mobile, static, and accelerated corrosion tests if the nickel deposit was too thin [69, 70], The coatings specified in the standard are intended to protect the underlying copper layer from corrosion for extended periods of time. The chromium layer should be either microcracked or microporous for severe and very severe corrosion service.

The original applications for electroplated plastics were established with ABS, but many polymers can be successfully electroplated, including polypropylene, polysulfone, polyphenylene oxide, polycarbonate, polyester, nylon, and others [6, pp. 341–344, 360]. In general, catalysis with palladium is common to most preparation sequences, but different etching solutions and etching times are required to process different plastics. Automotive applications for decorative electroplated plastics appear to be growing [71].

Aluminum Immersion deposition is the most widely used technique for preparing aluminum and its alloys for electroplating. Immersion deposition processes are either alkaline zincate or alkaline stannate solutions that strip the oxide film from the aluminum and deposit a thin film of zinc or tin, respectively, on the surface before the oxide film can re-form. Although immersion deposition films are generally nonadherent, their adhesion on aluminum and its alloys can be excellent; the bond strength can equal or exceed the tensile strength of the aluminum or aluminum alloy [72]. Traditionally, treatment in zincate would be followed by electroplating in a tartrate-type copper cyanide solution, but

methods for direct nickel deposition on the zinc surface have been introduced employing nickel glycolate [73] or autocatalytic (electroless) nickel strike [74]. A proprietary tin immersion/bronze strike is reportedly less susceptible to undercutting and blistering in corrosive environments than the zinc immersion/copper cyanide strike [75]. The preparation of aluminum for electroplating is discussed in detail in ASTM standard B 253 [23].

The performance of decorative, electroplated nickel plus chromium coatings on aluminum alloys was studied in connection with the development of lightweight automobile bumpers in the mid-1970s [76]. The effects on corrosion performance of various preparation methods, alloy type, nickel thickness, and type of chromium coatings were evaluated [77]. In reviewing the results, it was concluded that the use of microdiscontinuous chromium was probably the most important factor contributing to the improved corrosion performance of electroplated aluminum [78]. The experience gained during the development program has led to increased use of plated aluminum on truck bumpers and on styled aluminum wheels for trucks and passenger cars.

Stainless Steel Decorative nickel plus chromium plating of stainless steel is primarily applied in automotive applications and only to a limited extent. The justification for electroplating stainless steel is the cost and difficulty of achieving a mirror finish on the material by mechanical means and the need to color match bumper inserts and other components placed in proximity to nickel/chromium plated ones. The methods of preparing stainless steel for electroplating described in ASTM Standard B 254 [23] are suitable for decorative plating.

3.3.9 Standards and Coating Requirements

ASTM Standard B 456 [23] provides information on specific requirements for decorative nickel plus chromium coatings to achieve acceptable performance under different conditions of service. The standard classifies various coating systems according to their resistance to corrosion and recommends specific coatings for different service conditions. The thicknesses that are specified in most cases have been verified by corrosion performance studies conducted by members of the committee.

The requirements for double- and triple-layer nickel coatings included in the standard are summarized in Table 3.5. The sulfur contents are specified to identify the type of nickel and to control the electrochemical potentials between individual nickel layers. Coating classification numbers appropriate for each service condition are given in Table 3.6 for steel. The classification numbers for aluminum alloys given in Table 3.7 are adapted from the International Organization for Standardization (ISO) standard 1456 [79]. The ones for plastics in Table 3.8 are from ASTM Standard B 604 [23].

TABLE 3.5   Requirements for Double- and Triple-Layer Nickel Coatings

Layer (Type of Nickel Coating)	Specific Elongation (%)	Sulfur Content (%, mm^{-1})	Thickness Percentage of Total Nickel Thickness	
			Double Layer	Triple Layer
Bottom (s)	> 8	< 0.005	> 60 (but at least 75 for steel)	> 50 (but not more than 70)
Middle (b)	—	> 0.15	—	10 max
Top (b)	—	0.04–0.15	> 10 but < 40	≥ 30

Source: Adapted from ASTM Standard B 456.
Note: s designates the semibright nickel layer applied prior to bright nickel; b designates full-bright nickel that contains the amount of sulfur specified.

The service condition numbers grade the severity of corrosion environments in service as follows:

- *Service Condition No. SC 5 (Extended Very Severe)* Service conditions that include likely damage from denting, scratching, and abrasive wear in addition to corrosive environments where *long-time protection* of the substrate is required, for example, conditions encountered by some exterior components of automobiles.

- *Service Condition No. SC 4 (Very Severe)* Service conditions that include likely damage from denting, scratching, and abrasive wear in addition to exposure to corrosive environments, for example, conditions encountered by exterior components of automobiles and by boat fittings in salt water service.

- *Service Condition No. SC 3 (Severe)* Exposure that is likely to include frequent or occasional wetting by rain or dew or possibly strong cleaners and saline solutions, for example, conditions encountered by porch and lawn furniture, bicycle and perambulator parts, and hospital furniture and fixtures.

- *Service Condition No. SC 2 (Moderate)* Exposure indoors in places where condensation of moisture may occur, for example, in kitchens and bathrooms.

- *Service Condition No. SC 1 (Mild)* Exposure indoors in normally warm, dry atmospheres with coating subject to minimum wear or abrasion.

TABLE 3.6   Decorative Nickel Plus Chromium Coatings on Steel

Service Condition Number	Classification Number	Minimum Nickel Thickness (μm)
SC 5: extended very severe	Fe/Ni35d Cr mc	35
	Fe/Ni35d Cr mp	35
SC 4: very severe	Fe/Ni40d Cr r	40
	Fe/Ni30d Cr mp	30
	Fe/Ni30d Cr mc	30
SC 3: severe	Fe/Ni30d Cr r	30
	Fe/Ni25d Cr mp	25
	Fe/Ni25d Cr mc	25
	Fe/Ni40p Cr r	40
	Fe/Ni30p Cr mp	30
	Fe/Ni30p Cr mc	30
SC 2: moderate service	Fe/Ni20b Cr r	20
	Fe/Ni15b Cr mp	15
	Fe/Ni15b Cr mc	15
SC 1: mild	Fe/Ni10b Cr r	10

Source. Adapted from ASTM Standard B 456.

TABLE 3.7   Decorative Nickel Plus Chromium Coatings on Aluminum

Service Condition Number	Classification Number	Minimum Nickel Thickness (μrn)
SC 4: very severe	Al/Ni50d Cr r	50
	Al/Ni35d Cr mp	35
	Al/Ni35d Cr mc	35
SC 3: severe	Al/Ni30d Cr r	30
	Al/Ni25d Cr mp	25
	AI/Ni25d Cr mc	25
	Al/Ni35p Cr r	35
	Al/Ni30p Cr mp	30
	Al/Ni30p Cr mc	30
SC 2: moderate	AI/Ni20b Cr r	20
SC 1: mild	Al/Ni10b Cr r	10

Source: Adapted from ISO standard 1456.

TABLE 3.8   Decorative Nickel Plus Chromium Coatings on Plastics

Service Condition Number	Classification Number	Minimum Nickel Thickness (μm)
SC 5: extended very severe	Pl/Cul5a Ni30d Cr mc	30
	Pl/Cul5a Ni30d Cr mp	30
SC 4: very severe	PI/Cul5a Ni30d Cr r	30
	PI/Cul5a Ni25d Cr mp	25
	Pl/Cul5a Ni25d Cr mc	25
SC 3: severe	Pl/Cul5a Ni25d Cr r	25
	Pl/Cul5a Ni20d Cr mp	20
	Pl/Cul5a Ni20d Cr mc	20
SC 2: moderate service	Pl/Cul5a Ni15b Cr r	15
	Pl/Cul5a Ni10b Cr mp	10
	Pl/Cul5a Ni10b Cr mc	10
SC 1: mild	Pl/Cul5a Ni7b Cr r	7

Source: Adapted from ASTM Standard B 604.

The classification numbers are a way to specify the coatings that are appropriate for each service condition; for example, the classification number

Fe/Ni30d Cr mp

indicates that the coating is applied to steel (Fe), consists of 30 μm of double-layer nickel (d) with a top-layer of microporous chromium (mp) 0.3 μm thick. (The thickness of chromium is not included in the classification number unless it differs from 0.3 μm. If different, the number would appear immediately next to the symbol for chromium.)

The type of nickel is designated in the tables by the following symbols: b for electrodeposited bright nickel (single layer); d for double- or triple-layer nickel coatings; p for dull, satin, or semibright nickel that is not polished; s for polished dull or semibright nickel. The symbol a is used to designate ductile copper deposited from bright acid-type baths. The type of chromium is designated by the following symbols: r for regular or conventional chromium; mp for microporous chromium having a minimum of 10,000 pores cm^{-2}; mc for microcracked chromium having more than 300 cracks cm^{-1} in any direction over the entire surface.

ASTM standard B 456 [23] provides test methods for measuring coating requirements. It is a comprehensive guide to controlling the quality of decorative, electroplated nickel plus chromium coatings.

3.3.10   Decorative Applications and Market Size

Decorative applications may be placed into two categories: automotive and nonautomotive. The decline in decorative plating for automotive applications noted in the 1980s has abated as a result of the popularity and increased production of light trucks and recreational vehicles that have retained brightwork, the development of nickel chromium–plated steel and aluminum-styled wheels, and an increase in the number of automotive applications for plated plastics [1]. Nonautomotive decorative applications comprise a large number of consumer products, including furniture and building hardware, plumbing fixtures, housewares, hand tools, major appliances, wire goods, bicycles, mopeds, motorcycles, and others. These continue to expand with the growth of the global economy. Approximately 80% of the nickel consumed for electroplating annually is for decorative purposes. The balance, 20%, is consumed for functional electroplating and electroforming.

3.4   FUNCTIONAL ELECTROPLATING AND DEPOSIT PROPERTIES

Electrodeposited nickel coatings are applied in functional applications to modify or improve corrosion resistance, hardness, wear, magnetic, and other properties. Although the appearance of the coating is important and the plated surface should be defect free, the lustrous mirrorlike deposits described in the previous section are not required.

Typical formulations for Watts and sulfamate solutions, the two most popular ones for functional applications, have been included in Table 3.4 along with recommended operating conditions and representative mechanical properties of deposits from each solution. Although the table indicates that the maximum current density for depositing nickel from a Watts solution is 11 A dm^{-2}, higher deposition rates can be achieved with increased agitation and solution flowrates. Other nickel electroplating solutions (Table 3.9) have been applied in functional applications, and deposits from those solutions have useful properties.

3.4.1   Deposit Properties

The main constituents in Watts solutions affect the properties of electrodeposited nickel. Nickel sulfate improves conductivity and metal distribution and determines the limiting cathode current density for producing sound nickel deposits. Nickel chloride improves anode corrosion but also increases conductivity, throwing power, and uniformity of coating thickness distribution. In addition chlorides increase the internal stress of the deposits, and they tend to refine grain size and minimize formation of nodules and trees. Boric acid is added for buffering purposes and affects the appearance of the deposits. Deposits may be cracked and burnt at low boric acid concentrations. Anionic wetting agents or surfactants that lower the surface tension of the plating solution so that air and hydrogen bubbles do not cling to the parts being plated are almost always added to control pitting and, by eliminating porosity, have an indirect effect on corrosion performance.

Operating conditions, such as pH, temperature, current density and chloride content, affect the properties of deposits from Watts solutions [80]. In a Watts solution, hardness, tensile strength, and internal stress increase above pH 5.0 while the elongation percentage decreases (Fig. 3.2), The hardness increases rapidly at low values of current density (Fig. 3.3). Increasing the temperature of the plating solution causes hardness and tensile strength to reach minimum values at about 55°C, while the elongation percentage is a maximum at that temperature (Fig. 3.4). Increasing the chloride ion concentration affects the properties of deposits from Watts solutions; for example, the elongation percentage is at a maximum, and hardness and tensile strength are at minimum values when the solution contains 25% by weight nickel chloride (Fig. 3.5). In general, conditions that increase the hardness of a nickel deposit will increase its tensile strength and lower its ductility. Close control of the main constituents and the operating conditions is thus required to produce nickel electrodeposits with consistent and known properties.

TABLE 3.9   Other Nickel Plating Solutions and Some Properties of Deposits

Type	Composition[a] (g L^{-1})	pH	Temperature (°C)	Cathode Current Density (A dm^{-2})	Vickers Hardness, (100 g load)	Tensile Strength (MPa)	Elongation (%)	Internal Stress (MPa)
Fluborate	Nickel fluoborate, 225–300 Nickel chloride, 0–15 Boric acid, 15–30	2.5–4	38–70	3–30	125–300	380–600	5–30	90–200
Hard nickel	Nickel sulfate, 180 Ammonium chloride, 25 Boric acid, 30	5.6–5.9	43–60	2–10	350–500	990–1100	5–8	300
All chloride	Nickel chloride, 225–300 Boric acid, 30–35	1–4	50–70	2.5–10	230–260	620–930	4–20	275–340
All sulfate	Nickel sufate, 225–410 Boric acid, 30–45	1.5–4	38–70	1–10	180–275	410–480	20	120
Sulfate/chloride	Nickel sulfate, 150–225 Nickel chloride, 150–225 Boric acid, 30–45	1.5–2.5	43–52	2.5–15	150–280	480–720	5–25	210–280
High sulfate	Nickel sulfate, 75–110 Soidum sulfate, 75–110 Ammonium chloride, 15–35 Boric acid, 15	5.3–5.8	20–32	0.5–2.5				
Black nickel (sulfate bath)	Nickel sulfate, 75 Zinc sulfate, 30 Ammonium sulfate, 35 Sodium thiocyanate, 15	5.6	24–32	0.15				
Black nickel (chloride bath)	Nickel chloride, 75 Zinc chloride, 30 Ammonium chloride, 30 Sodium thiocyanate, 15	5.0	24–32	0.15–0.6				
Nickel phosphorus	Nickel sulfate, 170 or 330 Nickel chloride, 35–55 Boric acid, 0 or 4 Phosphoric acid, 50 or 0 Phosphorus acid, 2–40	0.5–3.0	60–95	2–5				

[a] The formulas of the compounds in the table are as follows: nickel fluoborate, $Ni(BF_4)_2$; nickel sulfate, $NiSO_4 \cdot 6H_2O$; nickel chloride, $NiCl_2 \cdot 6H_2O$; boric acid, H_3BO_3; ammonium chloride, NH_4CI; ammonium sulfate, $(NH_4)_2SO_4$; sodium sulfate, Na_2SO_4; phosphoric aicd, H_3PO_4; phosphorus acid, H_3PO_3; zinc sulfate, $ZnSO_4 \cdot 7H_2O$; zinc chloride, $ZnCl_2$; sodium thiocyanate, NaSCN.

The properties of deposits from Watts and sulfamate solutions are affected in different ways by changes in operating conditions, as illustrated qualitatively in Figure 3.6 [81], For example, internal stress is not significantly affected by increasing the temperature of a Watts bath, whereas increasing the temperature in a sulfamate solution reduces internal stress significantly. Cathode current density has a relatively small effect on the tensile strength of deposits from a Watts solution, but increasing current density reduces the tensile strength of deposits from a sulfamate solution.

The mechanical properties measured at temperatures from −195 to 870°C of nickel electrodeposited from Watts, sulfamate, and all-chloride solutions were determined and compared to the properties of wrought nickel by Knapp and Sample [82] (Fig. 3.7). At −195°C, chloride and sulfamate nickel had ultimate tensile strength in excess of 100 kg mm^{-2} compared to a value of 56 kg mm^{-2} for Watts and annealed wrought nickel. The reduction in the elongation percentage above 450°C for the three types of electrodeposited nickel was attributed to the presence of small amounts of sulfur in the electrodeposited nickel. Although wrought nickel has comparable levels of sulfur, it also contains small amounts of manganese that prevent sulfur from migrating to grain boundaries at elevated temperatures where it forms nickel sulfide, which reduces high-temperature ductility. The codeposition of small amounts of manganese with nickel has since been shown to improve high-temperature ductility [83]. Considerable information on the physical and mechanical properties of electrodeposited nickel, nickel alloys, and nickel composite coatings is available [84, 85].
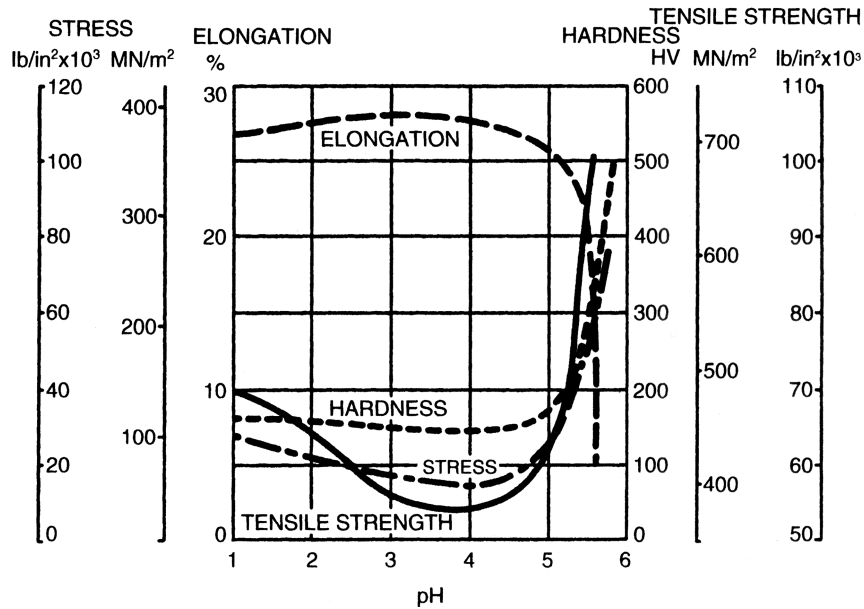
FIGURE 3.2 Influence of pH on the internal stress, tensile strength, ductility, and hardness of nickel electrodeposited from a Watts solution at 55°C and 5 A dm^{-2} [80].

3.4.2 Coating Requirements in Functional Applications

Corrosion performance in functional applications depends on nickel thickness and other factors, including the condition of the surface prior to plating. The thickness that should be applied depends on the specific application. For example, nickel thickness in optical and electronic applications where nickel is applied as an undercoat prior to electroplating with other metals may be 5 μm. To protect product purity, thickness may be 7 μm thick on processing equipment, such as ferrous containers. For drying cylinders and rolls for paper processing, for condenser and calender rolls for the textile industry, and for externally and internally plated pipe, fittings, and other components for chemical and nuclear plants, nickel coating thicknesses of 125 μm have been specified. Nickel coatings on automotive components, such as hydraulic rams, cylinder liners, and shock absorbers, may be 125 μm thick to provide corrosion and wear resistance. Coatings to prevent fretting corrosion and to enhance wear resistance are generally greater than 125 μm thick and have been used in the automotive and mining industries to coat pistons, cylinder
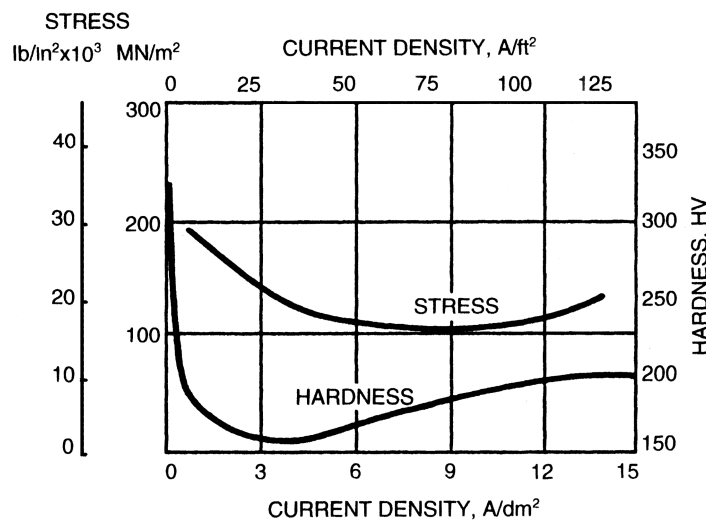

FIGURE 3.3 Influence of current density on the internal stress and hardness of nickel electrodeposited from a Watts solution at 55°C and pH 3.0 [80].
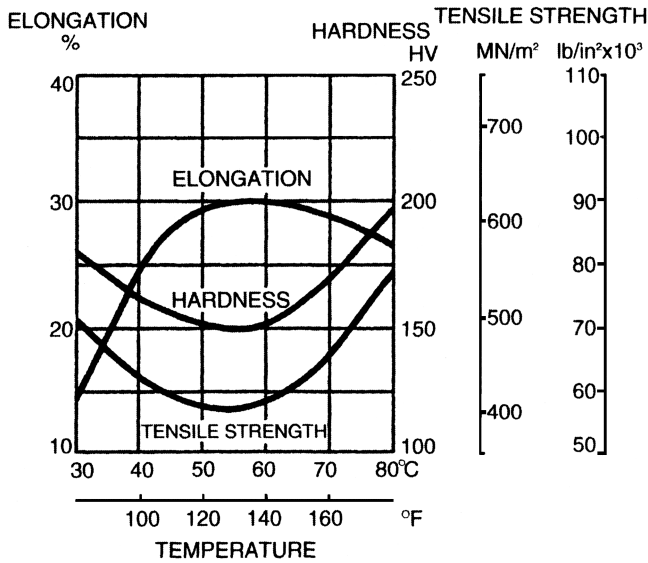
FIGURE 3.4 Influence of temperature on the elongation, tensile strength, and hardness of nickel electrodeposited from a Watts solution at pH 3.0 and 5 A dm^{-2} [80].

walls, rotary engine housings, gear shafts, drive shafts, pump rods, and hydraulic pistons. When nickel is applied to salvage worn or mismachined components, thickness is determined by the extent of the repair required. Other requirements for functional nickel coatings are discussed in ASTM Standard B 689 [23]. Nickel coatings used as diffusion barriers beneath precious metal deposits in electronic applications, nickel

electroplating of strip and hardware in the production of batteries, and nickel-electroplated steel coin blanks are a few examples of functional applications that have grown in importance.

3.4.3 Other Solutions

Other nickel plating solutions for functional applications are listed in Table 3.9, along with typical mechanical properties of the deposits. Many of these solutions were developed to meet specific engineering requirements; all are used to a lesser extent than Watts and nickel sulfamate solutions.

Fluoborate The fluoborate solution can be operated over a wide range of nickel concentrations, temperature, and current density and is relatively simple to control [86]. The fluoborate anion is corrosive, however, and some materials that contact the solution are chemically attacked. The mechanical and physical properties of deposits from a fluoborate bath are similar to those from Watts solutions. The major advantage is that electrodeposition from a nickel fluoborate solution can be performed at high current density.

Hard Nickel Developed especially for functional applications, this solution is applied where controlled hardness, improved abrasion resistance, greater tensile strength, and good ductility are required without using sulfur-containing organic addition agents [87]. Close control of pH, temperature, and current density is necessary for this bath
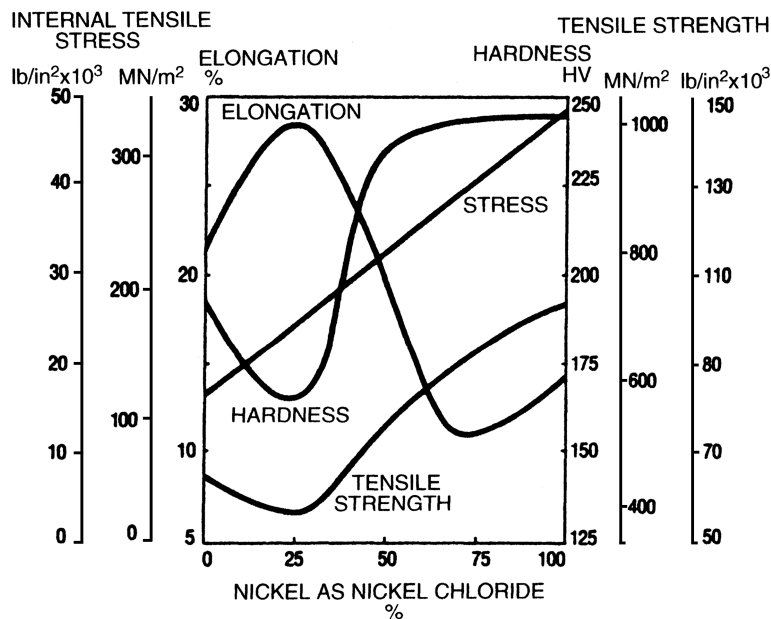

FIGURE 3.5 Influence of chloride concentration on the elongation, internal stress, hardness, and tensile strength of nickel electrodeposited from Watts-type solutions at pH 3.0, 55°C, and 5 A dm^{-2} [80].
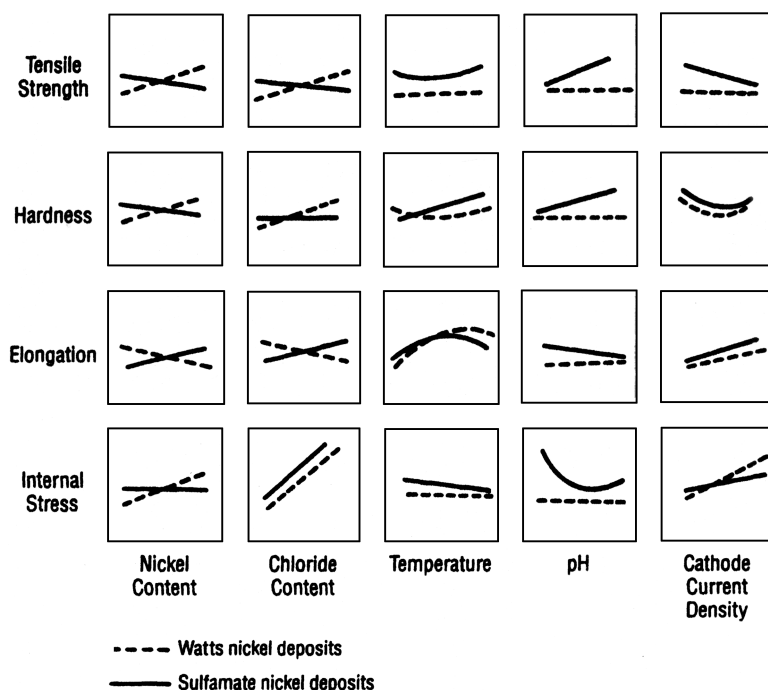
FIGURE 3.6　Qualitative effects of operating conditions on the properties of nickel electrodeposited from Watts and sulfamate solutions.

to give reproducible results. The internal stress is slightly higher than in deposits from Watts solutions. The disadvantages of the hard-nickel bath are its tendency to form nodules on edges and the low annealing temperature (230°C) of its deposits. Hard-nickel deposits are used primarily for buildup or salvage purposes. For optimum results, the ammonium ion concentration should be maintained at $8\,g\,L^{-1}$. In applications where the part being plated is not going to be exposed to elevated temperatures in service, it is easier to add organic compounds such as saccharin, *p*-toluene sulfonamide, and *p*-benzene sulfonamide to Watts or sulfamate solutions to achieve hardness without increased internal stress. Since these additives introduce 0.03% sulfur (or more), this approach must not be used for parts to be exposed to high temperatures where sulfur severely embrittles the nickel deposit. Leveling agents (brighteners) are effective in increasing the hardness of electrodeposited nickel without introducing sulfur, but they tend to raise internal stress [88].

All Chloride　The principal advantage of the all-chloride solution is its ability to operate effectively at high cathode current densities. Other advantages include its high conductivity, its slightly better throwing power, and a reduced tendency to form nodular growths on edges [89]. Deposits from this electrolyte are smoother, finer grained, harder, and stronger than those from Watts solutions and more highly stressed. Because of the partial solubility of lead chloride, lead cannot be used in contact with the all-chloride

solution, and mists from this solution are corrosive to the superstructure, vents, and other plant equipment if not well protected. The solution has been used for salvaging undersize or worn shafts and gears.

All Sulfate　This solution has been applied for electrodepositing nickel where the principal or auxiliary anodes are insoluble [90]. For example, insoluble auxiliary or conforming anodes may be required to plate the insides of steel pipes and fittings. Oxygen is evolved at insoluble anodes, and as a result the nickel concentration and pH decrease during plating. The pH is controlled and the nickel ion concentration is maintained by adding nickel carbonate. Another procedure that has been used in low-pH solutions replenishes the nickel electrolytically by employing a separate replenishment tank with nickel anodes; the current in the replenishment tank is periodically reversed to keep the nickel nodes actively dissolving in the absence of chlorides [90]. The insoluble anodes in all-sulfate solutions may be lead, carbon, graphite, or platinum. If a small anode area is required, solid platinum (in the form of wire) may be used. For large anode areas, platinum-plated or platinum-clad titanium is recommended; iridium-coated titanium is now in commercial use. In some forms, carbon and graphite are too fragile; lead has the disadvantage of forming loose oxide layers, especially if it is immersed in other solutions in the course of a plating cycle. In chloride-free solution, pure nickel is *almost* insoluble and may function as an internal anode if properly bagged.
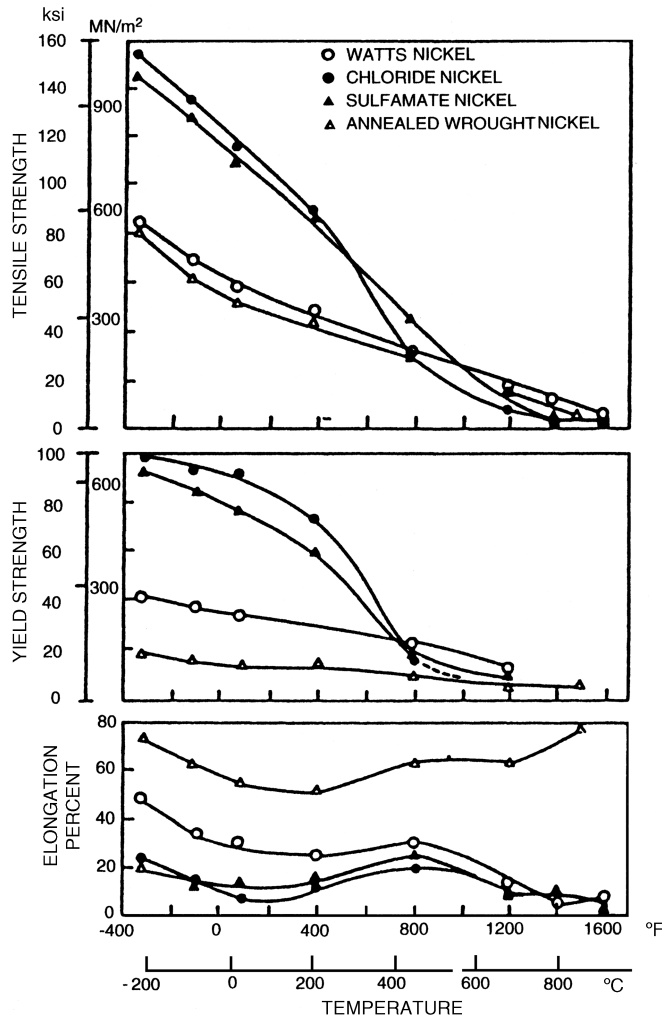
FIGURE 3.7 Effect of temperature on the tensile strength, yield strength, and elongation of dectrodeposited nickel.

the zinc. The deposits are less ductile and more highly stressed than nickel deposited from a Watts bath. In general, the deposition of copper from a cyanide solution directly on zinc-based die castings prior to the deposition of nickel is simpler and more reliable. Nickel glycolate and autocatalytic nickel solutions, as mentioned above, are preferred for depositing nickel directly on aluminum that has been given a zincate treatment.

Black Nickel There are at least two formulations for producing black nickel deposits; these incorporate zinc (Zn) and thiocyanate (CNS–) ions. Table 3.9 gives the [93] composition and operating conditions for sulfate and chloride black nickel plating baths [93]. The process was developed for decorative reasons: color matching and blending. The black nickel deposit has little wear or corrosion resistance and is usually deposited over a layer of nickel deposited from a bright or dull nickel plating solution. Black nickel deposit is still in commercial use, and the deposit is often protected with a clear lacquer coating.

Nickel–Phosphorus These solutions result in the electrodeposition of nickel–phosphorus alloys that are analogous to those deposited autocatalytically using sodium hypophosphite as the reducing agent [94]. The hardness of the electrolytic deposits can be increased by heat treatment in the same way that autocatalytic nickel deposits can with maximum hardness occurring at 400°C. The phosphorus content of the deposits is controlled by frequent additions of phosphite or phosphorus acid. The electrodeposition of nickel phosphorus alloys is receiving increased attention because deposits with greater than 10% phosphorus are amorphous and therefore have enhanced resistance to corrosion [95].

Sulfate–Choride The sulfate–chloride solution included in Table 3.9 has roughly equivalent amounts of nickel sulfate and nickel chloride and was developed to overcome some of the disadvantages of the all-chloride solution [91]. It has high conductivity and can be operated at high current densities. Although the internal stress of the deposits is higher than in deposits from Watts solutions, the stress is lower than in the all-chloride solution. The other properties are about midway between those for deposits from Watts and all-chloride solutions. Lead may not be used for equipment in contact with this solution because of the high chloride content.

High Sulfate The high-sulfate bath was developed for plating nickel directly on zinc-based die casting [92]. It has been used to plate nickel on aluminum that has been given a zincate or comparable surface preparation treatment. The high-sulfate and low-nickel contents, together with the high pH, provide good throwing power with little attack of

3.4.4 Fatigue Strength

Thick nickel deposits applied to steel substrates may cause significant reductions in composite fatigue strength when subjected to cyclical stress loading. The reduction in fatigue strength is influenced by the internal stress and thickness of the coating and by the hardness and tensile strength of the steel. The fatigue limit of nickel-plated steel is reduced almost proportionally to the amount of residual tensile stress in the nickel. Compressively stressed deposits have less of an effect on fatigue, and as a result, steel crankshafts have been nickel electroplated for resistance to wear and corrosion with low-stressed deposits from nickel sulfamate solutions. Specifying the thinnest coating consistent with design requirements is also beneficial for minimizing the effect on fatigue life. In some cases, specifying a steel with increased hardness and tensile strength may be necessary. Shot peening the steel prior to electroplating minimizes the reduction in fatigue strength; see ASTM Standard B 851 for details of the shot
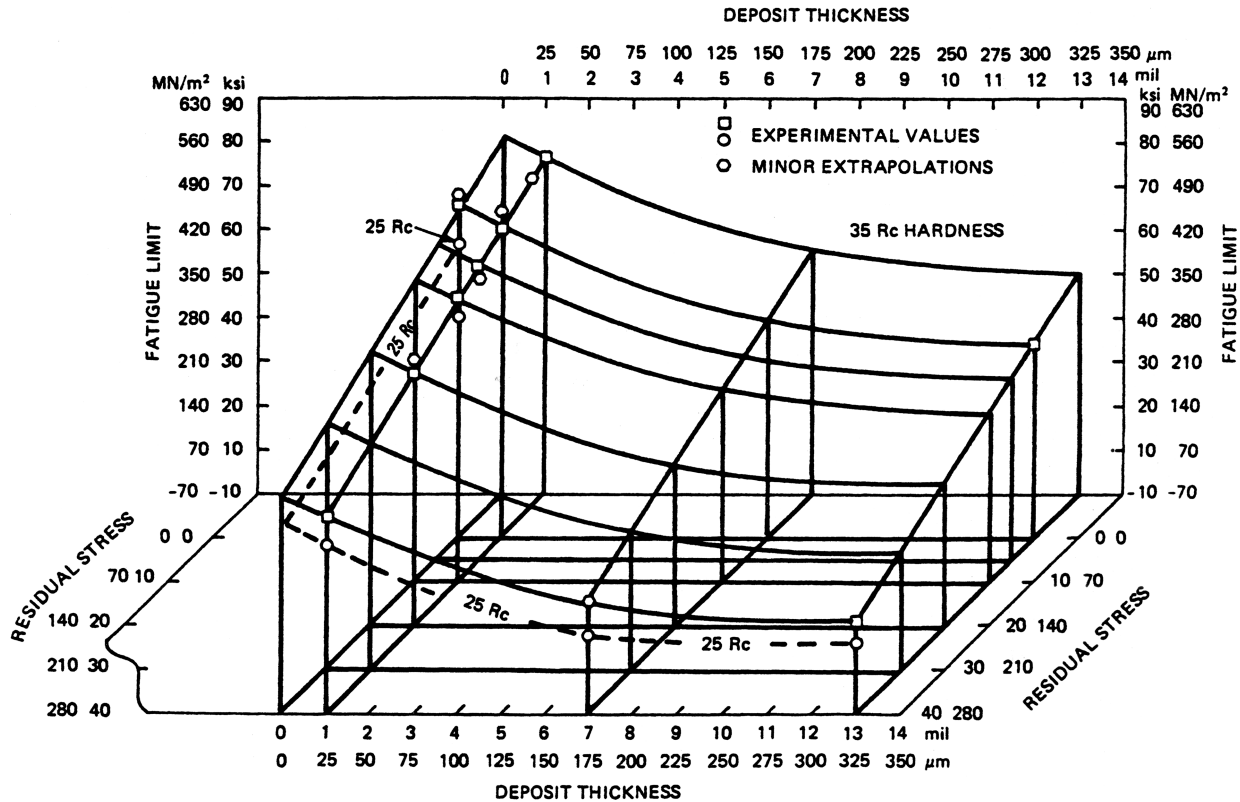
FIGURE 3.8   Effect of deposit thickness and internal stress on the 100 million cycle fatigue life of nickel-electroplated American Iron and Steel Institute (AISI) 4340 steel.

peening strength, process [23]. The effect of these variables on the fatigue limit of a nickel-plated high-strength steel is shown in Figure 3.8 [96].

3.4.5 Hydrogen Embrittlement

Highly stressed, high-strength steels are susceptible to hydrogen embrittlement during normal plating operations. Although nickel plating per se may not be the cause of embrittlement, the preparation of steels for electroplating involves exposures to acids and alkalis that are capable of introducing hydrogen into the steel. In general, parts made from steel with tensile strengths that are equal or greater than 1000 MPa should be heat treated after electroplating to avoid hydrogen embrittlement; depending on the state of the steel, stress relief prior to electroplating may be required to minimize hydrogen embrittlement susceptibility. Recommended treatments are given in ASTM Standards B 849 and B 850 [23].

3.5 NICKEL ELECTROFORMING

Electroforming with copper was conceived in 1838 by Jacobi of the Academy of Sciences, St. Peterburg, Russia [97].

Bottger reportedly electroformed nickel in 1843. Today nickel is utilized in the largest number of applications because it is strong, tough, and resistant to corrosion, erosion, and wear and because its mechanical properties can be varied and controlled by changing solution composition and operating conditions, by alloying, and by incorporating particles and fibers within the electrodeposited nickel matrix [98],

3.5.1 Electroforming and Electrofabrication

Electroforming is electroplating applied to the production of parts. In decorative and functional applications, good adhesion of the coating to its substrate is critical to its function. In electroforming, metal is deliberately electrodeposited nonadherently so that it can be separated from the substrate. The substrate in electroforming is a *mandrel or mold*, and the nickel that is separated from the mandrel becomes the final product. The mandrel is usually a negative or reverse replica of the product to be fabricated and is often recovered and reused. Electrofabrication also describes processes that result in the production of components and parts but that do not involve the use of traditional mandrels. In electrofabrication, the substrate often becomes an integral part of the component, and electrodeposition takes place selectively through masks or by means of specially designed cells [99, 100]. The

distinction between electroforming and electrofabrication lies in the nature of the mandrel and the role of the substrate.

3.5.2   Capabilities of Nickel Electroforming

Nickel electroforming processes can reproduce fine surfaces with great accuracy due to the excellent microthrowing power of nickel plating solutions. In the production of stampers for pressing compact audio and video discs, the accuracy of reproduction is within a fraction of a micrometer. An extension of this property is in the reproduction of complex surface finishes; for example, bright and semibright surfaces can be reproduced without the need for machining or polishing individual parts. The combination of electroforming and modern photolithographic techniques for generating patterns makes it possible to produce parts with extreme precision and fineness of detail on a microscopic scale. Parts can be reproduced in quantity with a high degree of dimensional accuracy. The mechanical and physical properties of nickel can be closely controlled by selecting the appropriate solution and the operating conditions. There is virtually no limitation to the size and thickness of the parts that can be electroformed. Shapes can be made that are impossible or too expensive to make any other way.

3.5.3   Mandrels

The ability to produce an electroformed part depends on the design and fabrication of the mandrel. A key consideration is to facilitate separation of the electroform. Rounding exterior angles, tapering the mandrel where possible, eliminating reentrant angles, controlling the mandrel's surface finish, and designing a fixture to assist in parting the electroform from the mandrel should be considered at the design stage. Mandrels may be manufactured by casting, machining, electroforming, and conventional pattern-making techniques, and they may be conductors or nonconductors of electricity and expendable or permanent. The nature of the material will determine how the mandrel is prepared for electroforming; in some cases there is a need to passivate the surface of the mandrel to prevent adhesion. Some of these details are discussed in ASTM standard B 832 [23].

3.5.4   Nickel Electroforming Solutions

Nickel sulfamate solutions (Table 3.4) are popular for electroforming because of the low internal stress of the deposits, the high rates of deposition possible, and the improved throwing power. Watts nickel solutions are utilized in a number of applications, but often with the addition of stress-reducing agents.

Nickel sulfamate is similar to nickel sulfate except that one of the hydroxyl groups is replaced by an amido group.

The formula of the normal crystallized form of nickel sulfamate may be written, $Ni(SO_3NH_2)_2 \cdot 4H_2O$. Crystallized forms are not readily available in the United States where prepurified concentrated liquid solutions are preferred. Nickel sulfamate can be prepared by reacting high-purity nickel powder or high-purity nickel carbonate with sulfamic acid under controlled conditions. Because of the high solubility of nickel sulfamate, higher nickel metal concentration is possible than in other nickel electrolytes, permitting higher plating rates. A small amount of nickel chloride is usually added to nickel sulfamate solutions to minimize anode passivity, especially at high current densities. If nickel chloride is not added, sulfur-containing nickel anode materials are required to avoid anodic oxidation of sulfamate anions (discussed below). Prolonged use of sulfamate solutions at temperatures above 70°C or at a pH of less than 3.0 can hydrolyze the nickel sulfamate to the less soluble form of nickel ammonium sulfate. Ammonium and sulfate ions increase the internal tensile stress and hardness of the deposits [101]. As far as is known, there is no *simple* way to remove ammonium ions from sulfamate solutions.

3.5.5   Anodic Oxidation of Sulfamate Anions and the Ni-Speed Process

A phenomenon that apparently occurs only in sulfamate solutions is anodic oxidation of sulfamate anions to form species that diffuse to the cathode where they can affect the internal stress and the composition of the deposit. This occurs at insoluble anodes operating at high potentials. At an insoluble platinum anode, a stress reducer forms which was identified as an azodisulfonate [102]; it reacts at the cathode, introduces sulfur into the deposit, especially at low current density, and lowers internal stress. The stress can be less than zero (compressive) depending on the amount of current flowing through the small insoluble platinum anode. A small auxiliary platinum anode that drew 1–2% of the total current passing through the electroplating cell was effective in controlling stress at compressive levels but resulted in the codeposition of small amounts of sulfur with the nickel [103], The codeposited sulfur affected the ductility and other mechanical properties of the deposit, and its tendency to become embrittled at elevated temperatures [104].

The concentrated nickel sulfamate process, *Ni-Speed*, was developed for electroforming at high current densities and low internal stress [105]. Because low- to zero-stress conditions can be achieved without organic addition agents, there is no incorporation of sulfur and the deposits do not become embrittled when heated above 200°C. The solution contains about 500–650 g L^{-1} of nickel sulfamate; 5–15g L^{-1} of nickel chloride hexahydrate, and 30–45 g L^{-1} boric acid. After purification with carbon and permanganate to remove all organic impurities, the solution is conditioned

electrolytically with a nonactivated anode material. When properly conditioned, a deposit prepared at 5 A dm^{-2} and at 60°C will be semilustrous and have a compressive stress. During operation, the solution is circulated through a separate conditioning tank where it is continuously electrolyzed at low current density; the conditioning tank has 10–20% of the capacity of the main tank and is operated with a nonactivated, sulfur-free anode material. The main electroforming tank is operated with an activated sulfur-containing anode material. Controlling the stress at or very close to zero depends on maintaining the solution temperature and current density at specified, *coupled* values; for example, internal stress is approximately zero at 50°C and 8 A dm^{-2}, at 60°C and 18 A dm^{-2}, or at 70°C and 32 A dm^{-2}.

The reaction that occurs at an insoluble platinum anode is apparently different from the reaction that occurs at the anode in the conditioning tank. The potential of a platinum anode in the nickel sulfamate solution is approximately $+1$ V versus the saturated calomel electrode (SCE). The potential of the nonactivated nickel anode material in the conditioning tank will be approximately $+0.2$ to $+0.4$ V versus SCE because of the presence of chlorides, whereas the activated anode in the electroforming tank will dissolve at -0.2 V versus SCE. It has been postulated that the oxidation reaction that occurs at the high potential is different from the reaction that occurs at intermediate potentials [106]. At an active anode dissolving at -0.2 V versus SCE, anodic oxidation of sulfamate anions does not occur. The existence of several oxidation species in sulfamate solutions has been reported [107]. The Ni-Speed process has been operated successfully in Europe where it has been used to electroform electrolytic nickel foil at low internal stress continuously on rotating drums at current densities as high as 40 A dm^{-2}. It has not been used to any great extent in North America where it is considered difficult to control and where its reproducibility has been questioned.

Zero stress can reportedly be maintained in conventional nickel sulfamate solutions by eliminating nickel chloride entirely using a sulfur-activated nickel anode material and continuously purifying the solution by means of an auxiliary tank similar to the conditioning tank described above.

3.5.6 Leveling Agents for Electroforming

The use of a leveling agent, for example, 2-butyne 1,4-diol, can improve metal distribution on the mandrel by suppressing the growth of nodules and by preventing the formation of planes of weakness when electroforming into comers [108]. Leveling agents increase internal stress, but the increase may be tolerable when the initial stress is at or close to zero. The breakdown products formed by butyne diol can be removed by continuous filtration of the solution through carbon and this helps control the effect on internal stress.

3.5.7 Postelectroforming Operations

After electrodeposition is complete operations such as machining and finishing, parting and separating from the mandrel, and backing the electroform are usually required [109].

3.5.8 Nickel Electroforming Applications

Products made by nickel electroforming include stampers for the production of phonograph records, compact discs, videodiscs, holograms, and information storage discs; textile printing screens; a wide assortment of molds and dies for processing plastics; abrasion strips for helicopter blades; seamless belts for photocopiers and facsimile machines; and porous nickel foam for making battery electrodes [110]. The electrofabrication of thin-film heads for magnetic recording, thin-film chip carriers, micromovable parts, and cooling channels in rocket thrust chambers involves the deposition of one or more layers of metal onto a substrate that becomes an integral part of the final product [111–113].

3.6 NICKEL ANODE MATERIALS

Most nickel plating processes are operated with soluble nickel anode materials. Nickel from the anode is converted into ions which enter the plating solution to replace those discharged at the cathode. In addition, the anode distributes current to the parts being electroplated and influences metal distribution. Commercially available nickel anode materials made to strict chemical specifications do not introduce impurities into the electroplating solution and influence quality only to the extent that they affect current and metal distribution.

The simplest way to satisfy anode requirements is to suspend an electrolytic nickel strip from hooks placed on an anode bar so that the nickel, not the hook, is immersed in the plating solution. Although significant quantities of the electrolytic nickel strip are still consumed for that purpose, it is the least satisfactory way to satisfy anode requirements. The electrolytic nickel strip dissolves preferentially at its bottom and its sides, which results in an ever-changing anode area accompanied by a corresponding increase in anode current density. The strip dissolves nonuniformly, becoming fragile and spongy and, as a result, tends to break and disintegrate before it is completely consumed, creating scrap that has to be discarded or recycled. Replacement of the electrolytic nickel strip usually requires interruption of the plating process and yields anode spears or stubs that have to be disposed of. The fact that the nickel strip is available in limited lengths is perhaps its greatest disadvantage. These limitations led to the development of wrought (rolled) products that dominated the market for many years and later to the development of improved primary forms of electrolytic nickel for titanium anode baskets.

3.6.1 Wrought Nickel Anode Materials

The first anode material developed intentionally to obtain improved performance was wrought depolarized nickel (ca. 1929). That material contains greater than 99% nickel, about 0.5% nickel oxide, and a minute amount of sulfur. In discussing the uniform dissolution and enhanced activity of wrought depolarized nickel, Wesley considered the effect of nickel oxide on sulfur distribution to be the key factor [114]; nickel oxide may prevent or interfere with the formation of nickel sulfide at grain boundaries where it would lead to nonuniform anode dissolution in wrought materials. Wrought depolarized nickel anodes form a brown film and metallic particles during dissolution, and they must be encased in anode bags to prevent those residues from entering the solution and causing roughness at the cathode. Although this anode material dissolves smoothly, it still has some of the disadvantages of the electrolytic nickel strip; that is, anode area and current density change during electroplating and operations usually have to be interrupted to replace anodes and anode bags. But because this material is made by hot rolling, there is no size limitation, and lengths suitable for large-scale electroplating in deep tanks are commercially available.

The wrought carbon anodes introduced in 1938 contain about 0.25% carbon and about 0.25% silicon. During dissolution, silicon is oxidized to silicic acid which, in combination with carbon, forms a thick, highly retentive, black film on the surface which keeps tiny metallic particles in contact with the anode long enough for them to dissolve [115]. Increased acidity of the anolyte due to the silicic acid is believed to promote uniform dissolution of this material. Rolled carbon anodes form little, if any, metallic residue, but they are nevertheless used with anode bags to keep carbon plus silicon residues out of solution. Because the silicon is oxidized, anode efficiency depends on the silicon content of the anode material, which is less than 100%. Work to develop an improved auxiliary anode material for use without anode bags indicated that lowering the carbon to 0.15% and increasing the silicon content to 1% or more was beneficial in eliminating roughness-producing metallic particles [116].

3.6.2 Anodic Behavior of Primary Nickel

The limitations of primary electrolytic nickel are related to its tendency to become passive when dissolved anodically. In nickel sulfate solutions, the anodic polarization curve for nickel obtained potentiostatically under *quasi-equilibrium* conditions exhibits distinct active, passive, and transpassive regions [117]. The departure of the active portion of the curve from linearity as E_{pp} is approached, as illustrated in Figure 3.9, is the point where an oxide film begins to form on the anode surface, where E_{pp} is the critical or principal passivation potential. The Flade potential, E_p, is the point
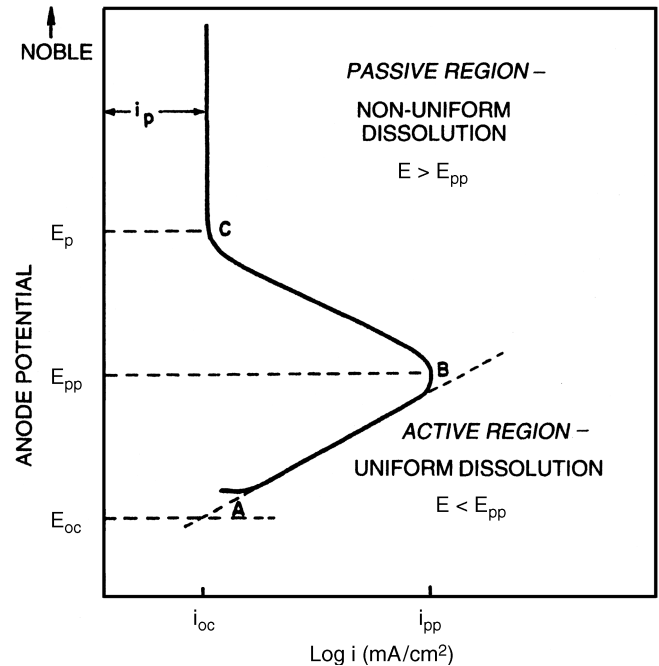

FIGURE 3.9 Idealized anodic polarization curve obtained potentiostatically for pure nickel in chloride-free nickel sulfate solutions [120]: E_{oc}, open-circuit potential; E_{pp}, principal or critical passivation potential; E_p, passivation potential; i_{oc}, corrosion current density; i_{pp}, principal passivation current density; i_p, current density in passive region. *AB* is the active region, *BC* the active-to-passive transition region, and *C* the beginning of the passive region.

where film formation is complete; that is, where an oxide film completely covers the surface and conducts electricity electronically rather than ionically. In the passive region, the nickel oxide film increases in thickness. In the transpassive region, the current density increases rapidly as a result of the oxidation of hydroxyl ions and the generation of oxygen. Because the value of the current density at E_{pp} is very low, pure electrolytic nickel cannot be used to replenish nickel ions in a nickel sulfate electroplating solution that does not contain chloride ions.

When *E–I* curves are measured *potentiodynamically*, the shapes of the curves are affected by the sweep rate and two peaks corresponding to the formation of NiO and NiO_2 appear at low and high potentials, respectively, as reported by Hart and by Chatfield and Shreir [118, 119]. Whether the higher oxides of nickel are formed under actual electroplating conditions is not known.

When nickel chloride (Fig. 3.10) is added to nickel sulfate solutions, the active-to-passive transition region is still observed, but at an applied potential of about $+0.2$ V versus SCE, the current on the anode rises rapidly [120]. Hart and co-workers confirmed that the transition from active to passive dissolution occurs even at very high chloride
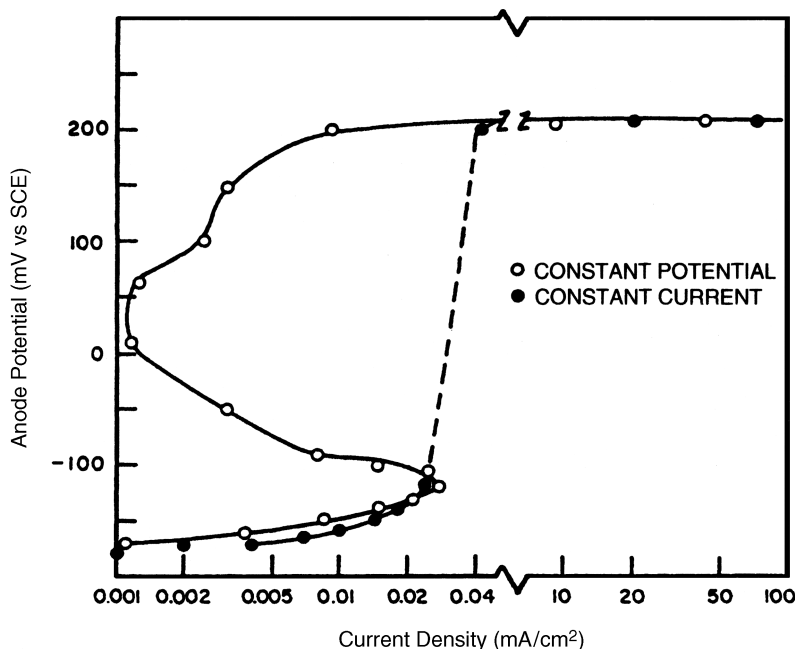
FIGURE 3.10 Anodic polarization of pure nickel in a Watts solution containing $14\,g\,L^{-1}$ of chloride at pH 4, 55°C, obtained potentiostatically (constant potential) and galvanostatically (constant current) from [120].

concentrations [121]. The persistence of the active-to-passive transition region suggests that an oxide film forms in the presence of chlorides but does not increase in thickness. Under practical plating conditions, pure electrolytic nickel dissolves at a constant potential, $+0.2\,V$ versus SCE, over a wide range of current density when chlorides are present, and the rate of dissolution is virtually independent of the anode potential [120].

The nonuniform dissolution of electrolytic nickel observed in most commercial nickel electroplating solutions, that is, its tendency to dissolve through pits on the surface and to become spongy at advanced stages of dissolution, is due to the oxide film on its surface, and a correlation between the electrochemical and the *physical* dissolution characteristics exists. That is, nickel dissolves nonuniformly when its dissolution potential exceeds the peak potential, E_{pp}, and uniformly below that potential [120].

It is unlikely that the reaction taking place in the active region is simply $Ni \rightarrow Ni^{2+} + 2e^-$. Active dissolution of nickel in a chloride-free nickel sulfate solution involves adsorbed hydroxyl ions and may proceed in three consecutive steps as follows [122].

1. $Ni + OH \rightarrow NiOH_{adsorbed} + e^-$
2. $NiOH_{adsorbed} \rightarrow NiOH^+ + e^-$
3. $NiOH^+ \rightarrow Ni^{2+} + OH^-$

The reactions responsible for the transition from active-to-passive behavior may be written

4. $NiOH_{adsorbed} + OH^- \rightarrow Ni(OH)_{2\downarrow} + e^-$
5. $Ni(OH)_{2\downarrow} \rightarrow NiO_\downarrow + H_2O$

The anodic polarization characteristics of nickel are the result of the competition among these reactions. The rate-determining step changes (from 3 to 2 to 1) as overvoltage is increased. At potentials where reactions 4 and 5 are possible, the percentage of the surface area covered with an oxide film increases, and accordingly, the current density gradually decreases in the transition region. In the presence of chlorides, species like $NiCl_{adsorbed}$ and $NiCl^+$ interfere with the formation of nickel hydroxide and thickening of the oxide film. This *chloride-assisted* dissolution increases anode efficiency to 100%, but dissolution is localized and occurs beneath or through the oxide film.

3.6.3 Titanium Anode Basket and Primary Forms of Nickel

The introduction of titanium anode baskets [123] transformed nickel anode practices and led to the development of special forms of primary nickel for electroplating.

Titanium Anode Baskets   Baskets for nickel electroplating are made of titanium mesh strengthened by solid strips of titanium at tops, bottoms, and edges. The baskets are encased in cloth anode bags, suspended on the anode bar by hooks that are an integral part of the baskets, and loaded with small

pieces of nickel. The mesh facilitates the free flow of plating solution. Baskets that incorporate hoppers at the tops facilitate basket loading and help prevent pieces of nickel from falling into the tank.

Titanium anode baskets were quickly accepted because of their many advantages [124]. The basket anode is large and unchanging, assuring that a uniform anode area gives constant current distribution and consistent thickness for repeat batches of the same work. Anode maintenance can be done without interfering with electroplating, and it involves topping up the load to keep the baskets filled. Conforming baskets are possible in virtually any size and shape. The anode-to-cathode distance is constant, contributing to good current distribution. Lowest cost, primary forms of nickel can be used to fill the baskets. Baskets can be semiautomatically or automatically filled with nickel, and that practice is growing in progressive electroplating shops. Anode bags last longer with anode baskets, and if the bags are tight fitting, less metallic residues are formed by electrolytic nickel anode materials.

Titanium can corrode in nickel plating solutions if it is not in contact with nickel metal (titanium is protected by the nickel), or if excessively large, solid areas of titanium are used to fabricate the baskets. Titanium cannot be used in concentrated fluoborate solutions or in solutions containing fluoride ions; small amounts of fluoride in solution activate titanium, causing it to corrode [125].

Sulfur-Containing Electrolytic Nickel   Work to develop an improved primary form of nickel for use in baskets focused on finding additives that would increase the activity of the metal in electroplating solutions. Sulfur, selenium, tellurium, phosphorus, carbon, and silicon were studied. The most effective additive proved to be sulfur [117, 120]. Sulfur lowers the dissolution potential by at least 0.4 V compared to pure electrolytic nickel and transforms the mode of dissolution from nonuniform to uniform. Sulfur-containing electrolytic nickel is the most active anode material commercially available, as indicated by the data in Figure 3.11. A black nickel sulfide film forms on the
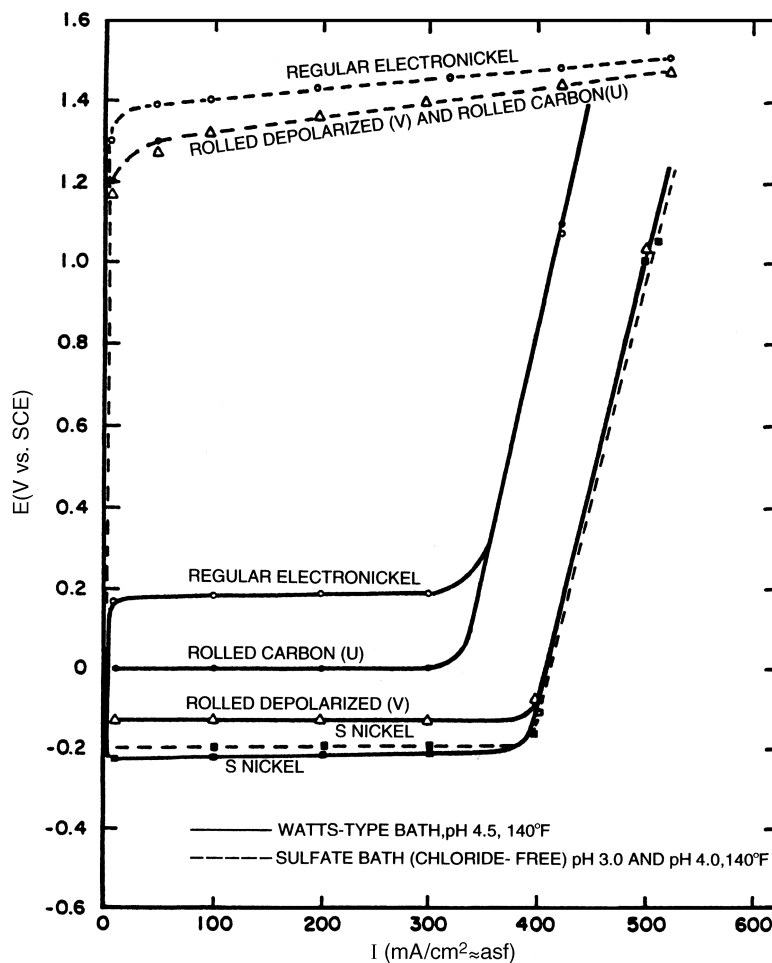

FIGURE 3.11   Anodic polarization under galvanostatic conditions of various nickel anode materials in a Watts and a chloride-free nickel sulfate solution.

surface as sulfur-activated nickel anode materials are dissolved. Because nickel sulfide is highly insoluble, sulfur in the anode material does not enter the solution but is retained in the anode bag as part of the residue. The amount of residue is less than 0.1% of the metal dissolved; that is, more than 99.9% of the nickel goes into solution. The lowering of the dissolution potential conserves energy and reduces power costs, as confirmed by tests conducted in the laboratory and in plating shops [126]. Sulfur-containing electrolytic nickel dissolves at 100% efficiency even in the absence of chloride ions, and this makes it possible to control deposit stress by eliminating chlorides from solution.

The mechanism by which sulfur depolarizes or activates electrolytic nickel has not been fully defined. Because the sulfur is present in the anode material as a sulfide and is electronegative, it may lower the effective concentration of hydroxyl ions in the anode film so that the nickel oxide film can only form at high anodic overvoltage *in the absence of chlorides*. Sulfur-containing electrolytic nickel does not appear to form an oxide film when chlorides are present in solution. DiBari and Petrocelli first suggested that adsorbed sulfur-containing anions might be responsible for the activation [117]; Morris and Fisher proposed that a tiny amount of the sulfur in the anode material is oxidized to form an anion, perhaps thiosulfate, that prevents oxide film formation by specific adsorption [127].

Electrolytic nickel containing a small amount of sulfur first became available in the form of sheared squares in 1963 [128]. Two forms of sulfur-containing nickel were introduced in 1972: a button-shaped material made by electro winning and a spherical form made by the decomposition of nickel carbonyl. Electroplaters quickly converted to the round and spherical forms because of their better settling characteristics compared to the electrolytic nickel squares that bridge and hang up at their corners.

Other Primary Forms of Nickel for Baskets Available forms of primary nickel for baskets include nonactivated, high-purity electrolytic nickel in buttonlike shapes [129] and screened nickel pellet made by the decomposition of nickel carbonyl. Electrolytic nickel squares about 25×25 mm and, to a less extent, squares that are 100×100 mm are used to fill baskets, but that practice is becoming obsolete except in some rapidly developing economies.

3.7 QUALITY CONTROL

Process quality control involves maintaining the concentrations of the main constituents within specified limits; controlling pH, temperature, and current density; and maintaining the purity of nickel electroplating solutions. Product quality control includes eliminating coating defects, properly preparing substrates prior to electroplating, as well as

TABLE 3.10 Nickel Electroplating Facts

Symbol	Ni	
Atomic weight	58.69	
Valency	2	
Specific gravity	8.90	
Plating rate, at 100% cathode efficiency	1.095 g Am-h^{-1} (0.039 oz Am-h^{-1})	
Nickel sulfate	NiSO$_4 \cdot$ 6H$_2$O	Contains 22.3% nickel
Nickel chloride	NiCl$_2 \cdot$ 6H$_2$O	Contains 24.7% nickel
Nickel sulfamate	Ni(NH$_2$SO$_3$)$_2$	Contains 23.2% nickel
Nickel carbonate	NiCO$_3$	Contains about 46% nickel

conducting tests to verify that specified product requirements have been met. The basic nickel electroplating facts in Table 3.10 and the conversion factors in Table 3.11 are often required for calculations related to quality control.

3.7.1 Process Control

Controlling the composition of the plating bath is one of the most important factors contributing to the quality of electrodeposited nickel. At the outset, the bath must be prepared to the specified composition, adjusted to the proper pH, and purified before use. Thereafter the composition and pH of the solution must be controlled within specified limits, and contamination by metallic, organic, and gaseous substances must be prevented.

Main Constituents The basic constituents of nickel electroplating solutions that are regularly controlled are the nickel metal content, the chloride concentration, the boric acid level, and the concentration of all addition agents. Nickel metal concentration is maintained between 60 and 80 g L^{-1} in most commercial applications. It is desirable to have a minimum of 25 g L^{-1} nickel chloride in the solution to promote anode corrosion except when sulfur-activated electrolytic nickel anode materials are used. Boric acid is the most commonly used buffering agent for nickel plating baths. Boric acid is effective in stabilizing the pH in the cathode film within the ranges normally required for best plating performance. It is available in a purified form and is inexpensive. Organic addition agents must be controlled within the limits specified by the suppliers of proprietary processes, and they must be replenished due to losses from drag-out, electrolytic consumption, and the effects of carbon filtration (or batch treatment).

Traditional procedures for chemical analysis of nickel, chloride, boric acid, and organic addition agents in nickel electroplating solutions exist that are based on titration, precipitation, and other wet chemical techniques, but these procedures have been supplanted in many cases by

TABLE 3.11   Units and Conversion Factors for Electroplating

Quantity	Traditional Unit (A)	SI Unit[a] (B)	To Convert from A to B Multiply by	To Convert from B to A Multiply by
Coating thickness	mil	μm	25.4	0.0394
	in.	mm	25.4	0.0394
Coating mass	mg in.$^{-2}$	g m^{-2}	1.55	0.645
(weight)	mg in.$^{-2}$	mg cm^{-2}	0.155	6.45
	oz in.$^{-2}$	kg m^{-2}	43.9	0.0228
	oz ft^{-2}	kg m^{-2}	0.305	3.28
Current density	A ft^{-2}	A m^{-2}	10.76	0.0929
	A ft^{-2}	A dm^{-2}	0.1076	9.29
	A in.$^{-2}$	A m^{-2}	1550	6.45×10^{-4}
	A in.$^{-2}$	A cm^{-2}	0.155	6.45
Plating rate	A-h ft^{-2}-mil	A-s m^{-2}-mm	1530	6.55×10^{-4}
Volume	gal	m^3	0.00379	264
	gal	L	3.79	0.264
	fl oz	mL	29.6	0.0338
Mass concentration	oz gal^{-1}	g L^{-1}	7.49	0.134
		kg m^{-3}	7.49	0.134
Volume concentration	fl oz gal^{-1}	M L^{-1}	7.81	0.128
		cm^3 L^{-1}	7.81	0.128
Force (internal stress)	1000 psi	MPa (Mn m^{-2})	6.89	0.145

instrumental techniques that are rapid and accurate. Suppliers of decorative nickel electroplating solutions usually provide methods for analyzing and controlling the specific organic additives in their processes. Liquid chromatography has become popular for controlling organic additives, and electroanalytical methods, like polarography, have been applied to the control of electroplating solutions [130, 131].

Controlling pH, Temperature, Current Density, and Water Quality   The pH of the nickel plating solution will rise during normal operation of the bath, necessitating regular additions of acid to maintain the pH within the prescribed limits. (A decrease in pH accompanied by a decrease in nickel ion concentration indicates that the process is not functioning properly.) In Watts solutions, sulfuric acid is added for pH adjustment; sulfamic acid is added to control the pH of nickel sulfamate solutions. The pH of nickel plating solutions should be measured frequently, and it is most often done by an electrometric method employing a glass electrode and a saturated calomel reference electrode.

The operating temperature has a significant effect on the properties of the deposits and should be maintained within specified limits ($\pm 2°$C) of the recommended value. In general, most commercial nickel plating baths are operated between 40 and 60°C.

The nickel plating process should be controlled by estimating the surface area of the parts to be electroplated and the ampere-hours required to deposit a specified thickness of nickel at a specified current density. The practice of operating the process at a fixed voltage is not recommended. Controlling cathode current density is important for meeting minimum coating thickness requirements and for producing deposits with consistent and predictable properties.

Since current density determines the rate of deposition, it must be as uniform as possible to achieve uniformly thick nickel deposits. Current distribution is controlled by proper rack design and proper placement of components on racks, by the use of nonconducting shields and baffles, and by the use of auxiliary anodes, when necessary. With care, relatively good thickness distribution can be achieved.

The quality of the water used in making up the bath and in replacing water lost by evaporation is important. Demineralized water should be used, especially if the local tap water has a high calcium content, greater than 200 ppm. Filtering the water before it is added to the plating tank is a useful precaution to eliminate particles that can cause rough deposits.

Controlling Impurities   Inorganic, organic, and gaseous impurities may be introduced into nickel plating solutions during normal operations. Continuing efforts to eliminate the sources of these impurities from the plating shop can improve the quality of the deposits as well as productivity and profitability. Inorganic contaminants arise from numerous sources, including nickel salts of technical grade, hard water, carry-over from acid dip tanks, airborne dust, bipolar attack of metallic immersion heaters, corrosion of the tank material through cracks in the lining, corrosion of anode bars, dirt

TABLE 3.12 Maximum Concentrations for Contaminants in Nickel Plating Solutions

Contaminant	Maximum Concentration (ppm)
Aluminum	60
Chromium	10
Copper	30
Iron	50
Lead	2
Zinc	20
Calcium	a

Note: The limits are different when several contaminants are present at the same time when complexing agents are part of the solution formulation.

[a] Calcium will precipitate at the saturation point, about $0.5\,g\,L^{-1}$, but the exact saturation point is dependent on solution pH.

from structures above the tank, and parts that fall into the solution and are not removed.

Table 3.12 lists maximum limits for inorganic, metallic impurities in nickel plating baths. The degree of contamination by many inorganic materials may be controlled by continuous filtration and low-current-density electrolysis at $0.2–0.5\,A\,dm^{-2}$. This may be accomplished on a batch basis or continuously by installing a compartment and overflow dam at one end of the electroplating tank. Solution from the filter is pumped into the bottom of the compartment, up past corrugated cathode sheets, over the dam, into the electroplating section of the tank, out through a bottom outlet at the far end of the tank, and back to the filter. Solid particles and soluble metallic impurities (e.g., copper, zinc, and lead) are removed simultaneously by this procedure. The effects of chromium, copper, iron, zinc, and lead impurities on some properties of nickel deposits were evaluated many years ago, and that information is still useful [132].

Organic contaminants may arise from many sources, including buffing compounds, lubricating oil dropped from overhead equipment, sizing from anode bags, waving lubricants on plastic anode bags, uncured rack coatings or stop-off lacquers, adhesives on certain types of masking tape, decomposition products from wetting agents, organic stabilizers in hydrogen peroxide, paint spray, and new or patched rubber tank linings.

Many organic contaminants can be effectively removed from nickel plating solutions by adsorption on activated carbon on either a batch or a continuous basis. On a batch basis, the solution is transferred to a spare tank, heated to 60–71°C, stirred for several hours with a slurry of $6\,g\,L^{-1}$ minimum of activated carbon, permitted to settle, and then filtered back into the plating tank. It is usually necessary to do a complete chemical analysis and adjust the composition of the solution after this type of treatment.

For solutions in which organic contamination is a recurring problem, continuous circulation of the solution through a filter, coated at frequent intervals with small amounts of fresh activated carbon, is recommended. When continuous carbon filtration is used, the wetting agent in the solution must be replenished and controlled more carefully to prevent pitting of the nickel deposits. In cases of severe organic contamination, it may be necessary to treat the solution with potassium permanganate prior to treating with carbon [133]. This should be used only as a last resort because of the difficulty of removing manganese dioxide and other precipitated solids; in the case of a proprietary solution, the supplier of the process should first be consulted.

Gaseous contamination of nickel plating solutions usually consists of dissolved air or carbon dioxide. Dissolved air in small amounts may lead to a type of pitting characterized by a teardrop pattern. Dissolved air in the plating solution usually can be traced to entrainment of air in the pumping system when the solution is circulated. If this occurs, circulating pump and valves should be checked and modified, if necessary. Nickel plating solutions can be purged of dissolved air by heating to a temperature at least 6°C higher than the normal operating temperature for several hours. The solution is cooled to the operating temperature before plating is resumed. Dissolved carbon dioxide in a nickel plating solution is usually found after nickel carbonate has been added to raise the pH and is liberated from warm nickel plating solutions after several hours. If solutions containing carbon dioxide are scheduled for immediate use, they should be purged by a combination of heating and air agitation for approximately 1 h at 6°C or more above the normal plating temperature.

Effects of Impurities on Bright Nickel Plating   Metallic and organic contaminants affect bright nickel electrodeposition in the following ways [134]:

- Aluminum and silicon produce hazes, generally in areas of medium-to-high current density, and they may also cause a fine roughness called salt and pepper, or stardust.
- Iron may produce roughness, particularly at high pH.
- Calcium contributes to needletike roughness as a result of the precipitation of calcium sulfate when calcium in solution exceeds the saturation point of $0.5\,g\,L^{-1}$ at 60°C.
- Chromium as chromate causes dark streaks, high-current-density gassing, and peeling. After reduction to the trivalent form by reaction with organic materials in the solution or at the cathode, chromium may produce hazing and roughness effects similar to those produced by iron, silicon, and aluminum.
- Copper, zinc, cadmium, and lead affect areas of low current density, producing hazes and dark-to-black deposits.

- Organic contaminants may also produce hazes or cloudiness on a bright deposit or result in a degradation of mechanical properties. Haze defects may occur over a broad or narrow current density range.
- Mechanical defects producing hairline cracks, called macrocracking, may be encountered if the coating is sufficiently stressed as a result of solution contamination. These cracks usually appear in areas of heavier plating thickness, but they are not necessarily confined to those areas.

Contamination by zinc, aluminum, and copper is most often caused by the dissolution of zinc-based die castings that have fallen from racks into the plating tank and been permitted to remain there. Inadequate rinsing before nickel plating increases the drag-in of metallics. The presence of cadmium and lead may be attributed to a number of sources, including lead-lined equipment and tanks, impure salts, and drag-in of other plating solutions on poorly rinsed racks. Chromium is almost always carried into the nickel solution on rack tips that have not been chromium stripped or on poorly maintained racks that have been used in the chromium tank and have trapped chromium plating solution in holes, pockets, and tears in the rack coating.

Purification Techniques and Starting Up a New Bath The following procedures can be used singly or in combination to purify nickel electroplating solutions:

- The high-pH treatment consists of adding nickel carbonate to the hot solution until a pH of 5.0–5.5 is obtained. This precipitates the hydroxides of metals such as iron, aluminum, and silicon, which in turn frequently absorb other impurities. Addition of hydrogen peroxide oxidizes iron to the ferric state, making it more easily precipitated at high pH, and frequently destroys organic impurities.
- Treatment with activated carbon removes organic impurities.
- Electrolytic purification removes many harmful metallic and organic impurities.

A complete purification procedure for a freshly prepared solution consists of the following steps:

1. Use a separate treatment tank (not the plating tank) to dissolve the nickel sulfate and nickel chloride in hot water at 38–49°C to about 80% of desired volume.
2. Add 1–$2\,\mathrm{M\,L^{-1}}$ of 30% hydrogen peroxide; agitate briefly and allow to settle for 1 h.
3. Add 1.2–$2.5\,\mathrm{g\,L^{-1}}$ activated carbon and agitate thoroughly.

4. Heat to 66°C, then add 1.2–$2.5\,\mathrm{g\,L^{-1}}$ of nickel carbonate to the solution, with agitation to adjust the pH to 5.2–5.5. More nickel carbonate may be required and the mixture should be stirred to assist the dissolution of the carbonate. Allow to settle 8–16 h.
5. Filter into the plating tank.
6. Add and dissolve boric acid; add water to bring bath up to its desired volume.
7. Electrolytically purify by using a large area of nickel-plated corrugated steel sheets as cathodes. The average cathode current density should be $0.5\,\mathrm{A\,dm^{-2}}$ and treatment should continue until 0.5–$1.5\,\mathrm{Ah\,L^{-1}}$ has passed through the solution. The solution should be agitated and the temperature held at 49–60°C. Prepare deposits at normal current densities at some point to check appearance, stress, and sulfur content; if not acceptable, continue the electrolytic purification until the properties are acceptable.
8. Remove the dummy cathodes and adjust the pH of the solution to the desired value.

3.7.2 Product Control

The nature of coating defects in parts that have been unsuccessfully electroplated may indicate the source of quality problems. Other aspects of product quality control include preparation of metals prior to electroplating and testing nickel electrodeposits.

Coating Defects Common defects include roughness, pitting, blistering, high stress and low ductility, discoloration, burning at high current density areas, and failure to meet thickness specifications [133].

- Roughness is usually caused by the incorporation of insoluble particles in the deposit. In bright nickel baths, chlorine generated at an auxiliary anode that is close to the cathode can react with organic additives to form insoluble particles. Insoluble particles may arise from incomplete polishing of the basis metal so that silvers of metal protrude from the surface, incomplete cleaning of the surface so that soil particles remain on the surface, detached flakes of deposit from improperly cleaned racks, dust carried into the tank from metal-polishing operations and other activities, insoluble salts, and metallic residues from the anode material.
- Roughness from incomplete polishing, cleaning, and inadequate rack maintenance is avoided by good housekeeping and regular inspection and control. Roughness caused by dust can be controlled by isolating surface preparation and metal-polishing operations from the plating area, by providing a supply of clean air, and by removing dirt from areas near and above the tanks.

Roughness caused by the precipitation of calcium sulfate can be avoided by using de-mineralized water. Continuous filtration of the plating solution so as to turn over the solution at least once an hour is important for minimizing roughness problems. Anode residues must be retained within anode bags, and care should be taken not to damage the bags or allow the solution level to rise above the tops of the bags.

- Pitting is caused by many factors, including adhesion of air or hydrogen bubbles to the parts being plated. Air should be expelled, as already mentioned. Pitting from adherent hydrogen bubbles can result from a solution that is chemically out of balance, at too low a pH, or is inadequately agitated. Incorrect racking of complicated components, too low a concentration of wetting or antipitting agents, use of incompatible wetting agents, the presence of organic contaminants, the presence of copper ions and other inorganic impurities, incomplete cleaning of the basis material, incomplete dissolution of organic additives that may form oily globules can all result in pitting. Pitting is therefore avoided by maintaining the composition of the plating solution within specified limits, by controlling the pH and temperature, and by preventing impurities of all kinds from entering the solution.

- Blistering is generally due to poor adhesion as a result of poor or incorrect surface preparation prior to plating (see next section). Blistering may also be related to incomplete removal of grease, dirt, or oxides; formation of metal soaps from polishing compounds; or silica films from cleaning solutions. In the case of zinc-based die castings or aluminum castings, blistering during or immediately after plating may be due to surface porosity and imperfections that trap plating solution under the coating.

- High stress and low ductility usually occur when organic addition agents are out of balance and also because of the presence of impurities.

- Discoloration in low-current-density areas is most likely the consequence of metallic contamination of the plating solution. The effects can be evaluated systematically by plating over a reproducible range of current densities on a Hull cell cathode. Hull cells are available from plating supply houses and are shaped so that nickel can be deposited onto a standard panel over a predictable range of current densities. The variation in current density over the face of the panel is achieved by placing the panel at a specified angle to the anode. Bent panels that are L shaped and that are plated with the recessed area facing the anode can also be used to assess discoloration at low-current-density areas, and they may provide information on roughness problems.

- Burning at high current densities can be caused by applying the full load on the rectifier to the lowest parts on a rack as it is lowered into the tank. This can be controlled by applying a reduced load or ramping the current during immersion of the rack. Burning is sometimes related to the presence of phosphates in solution introduced via contaminated activated carbon. Incorrect levels of organic additives can cause burning.

- Failure to meet thickness specifications is most frequently due to the application of too low a current and/or too short a plating time. This can be avoided by measuring the area of the parts to be plated, then calculating the total current required for a specified current density, and plating for the appropriate time. Another major cause of failure to meet thickness requirements is nonuniform distribution of current leading to insufficient deposit in low-current-density areas. Poor electrical contacts and stray currents can also cause thin deposits. Anode and cathode bars, hooks, and contacts should be kept clean.

Preparation Prior to Plating Nickel can be deposited adherently on most metals and alloys, plastics, and other materials by following standard methods of preparation and activation, including proper use of intermediate deposits such as cyanide copper, acid copper, and acid (Wood's) nickel chloride strikes. Standard procedures for the preparation of materials prior to electroplating can be found in handbooks and in ASTM standards [23, 24].

Controlling and Testing Deposits Properties The requirements for testing electrodeposited nickel coatings vary depending on the application. In decorative applications the appearance and the thickness of the deposit should be controlled and monitored on a regular basis. The plated surface must be free of defects such as blisters, roughness, pits, cracks, discoloration, stains, and unplated areas. It must also have the required finish: bright, satin, or semibright. In the case of decorative multilayered coatings, the sulfur contents of the deposits, the relative thicknesses of individual layers, the ductility of the semibright nickel layer, and the differences in electrochemical potentials between individual layers should be controlled. Requirements for corrosion performance and adhesion may also be specified and may require additional testing. In functional and electroforming applications, it may be necessary to monitor hardness, ductility, and internal stress in addition to thickness and appearance. Some test methods are briefly reviewed below:

- *Thickness* The coulometric method described in ISO Standard 2177 [79] and ASTM Standard B 504 [23] can be used to measure the chromium and nickel

thicknesses as well as the thickness of copper undercoats, if present. The coulometric method measures the quantity of electrical energy required to deplate a small, carefully defined area of the component under test. A cell is sealed to the test surface and filled with the appropriate electrolyte; then a cathode is inserted. The component is made the anode, and the circuit is connected to the power supply via an electronic coulometer. By integrating time in seconds with the current passing, the electronic coulometer provides a direct reading in coulombs; modern instruments provide a direct reading of thickness. The completion of the deplating is shown by a marked change in the applied voltage. For routine control of production, it is convenient to monitor nickel thickness nondestructively by means of a magnetic gauge, calibrating the gauge at intervals with standard samples. Instruments for measuring thickness by beta backscatter, X-ray spectrometry, and eddy current techniques are also available. The traditional method of measuring thickness by microscopic examination of a metallographically prepared cross section of the plated part is still employed, but it is time consuming, expensive, and destructive. ASTM Standard B 659 [23] is a general guide to the measurement of thickness of electrodeposited coatings on different substrates.

- *STEP Test*   This test was developed to measure potential differences between individual layers of nickel in decorative nickel coatings on production parts. It is similar to the coulometric method just described. By including a reference electrode in the circuit, however, it is possible to measure the potential of the material being dissolved at the same time that the thickness of the individual layers is being measured. With a double-layer nickel coating, a relatively large change in potential occurs when the bright nickel layer has dissolved and the semibright nickel layer begins to be attacked. The potential difference is related to overall corrosion resistance and should be greater than 100 mV. Details can be found in ASTM Standard Test Method B-764 [23].

- *Corrosion Testing*   When corrosion performance is specified, the electroplater may be required to perform accelerated corrosion tests on a specified number of production parts. Three accelerated corrosion tests are recognized internationally. They are the copper-accelerated acetic acid salt spray (CASS), the Corrodkote, and the acetic acid salt spray tests. The CASS and Corrodkote tests were developed when conventional chromium was the only type of chromium available; when used to evaluate microdiscontinuous chromium coatings, the surface appearance deteriorates more rapidly than in real-world environments. Details of these three tests can be found in ISO Standard

1456 [79] as well as in ASTM Standards B 368 (CASS) and B 380 {Corrodkote) [23]. CASS and other corrosion test requirements are specified in ASTM Standard Specification B 456 [23] for nickel-plus-chromium coatings applied to steel, zinc alloys, or copper alloys. Similar information for nickel-plus-chromium coatings on plastics is given in ASTM Standard Specification B 604 [23].

- *Thermal Cycle Testing*   Thermal cycle testing is specified for controlling the quality of decorative nickel/chromium-electroplated plastics and involves exposure of electroplated parts to low and high temperatures under controlled conditions. Thermal cycle testing may be combined with accelerated corrosion testing. Test procedures are described in ASTM Standard B 604 [23].

- *Ductility*   The ductility of the semibright nickel layer in a multilayered nickel coating is specified to control the properties of the deposit and to check that the solution is in good working condition. The simple test described in ISO Standard 1456 [79] and in ASTM B 489 [23] is based on bending a test strip of the deposit over a mandrel of specified diameter until the two ends of the strip are parallel. A semibright nickel deposit that meets the requirements of the bend test has an elongation percentage greater than 8. Other tests based on hydraulic or mechanical bulge testing are available [135]. The elongation percentage can also be determined by machining a test sample from relatively thick electroformed nickel and subjecting it to the conventional tensile test. Difficulties with conventional tensile testing as applied to electrodeposited coatings and films have been discussed, and improved techniques have been described [136]. Since ductility is affected by the thickness of the coating, ductility should be measured at the actual thickness specified in a specific end use [80,104, 136].

- *Adhesion*   Qualitative tests for adhesion are frequently used in the electroplating shop because quantitative tests are considered costly and time consuming. The tests described in ASTM B 571 [23] include bend, burnish, chisel, file, and others that are qualitative in nature. The method for determining the peel strength of metal-electroplated plastics (ASTM Standard B 533 [23]) is quantitative and provides an average value of the bond strength when a universal tensile test machine is used in making the measurements; a less rigorous variation of the test is often applied for process control. Quantitative results can also be obtained by conical head and ring shear tensile testing and by ultrasonic, centrifuge, and flyer plate methods, which have been described in the literature [137].

- *Internal Stress Measurements*   There are many ways that the internal stress of electrodeposits can be

measured, but the one most frequently applied in production is the spiral contractometer method (ASTM standard B 636 [23]). The method is based on electrodepositing nickel on the outside of a helix formed by winding a strip of metal around a cylinder followed by annealing. During the measurement of stress, one end of the helix is fixed in the contractometer and the free end is attached to an indicating needle that moves as stress develops. Internal stress can be calculated from the degree of needle deflection on the circular dial. Contractometers and precoated helices to prevent internal electroplating are commercially available. Modifications of the contractometer method, including measuring the needle deflection electronically, have been made [138]. Rigid and flexible strip methods are alternative techniques that give reliable results [139] (see also [21, 37]). The strain gage method permits stress to be monitored and controlled throughout the electrodeposition process, and the method has been applied in the production of electroformed optical parts having dimensional accuracies of 0.15 μm [140]. The dilatometer method also allows stress to be monitored continuously [141].

- *Microhardness Testing*   The hardness of electrodeposited coatings can be determined by the methods described in ASTM Standard B 578 [23] and E 384. Measurements are made on the cross section of a deposit of specified thickness using a specified load on the Knoop indenter.

3.8   POLLUTION PREVENTION

Regulations to prevent pollution and to protect health and safety in the workplace have affected nickel and chromium electroplating technically and commercially. Technically, a great deal of the research effort over the past 25 years has been devoted to finding substitutes for hazardous materials and making process changes to comply with government regulations. For example, trivalent chromium to replace hexavalent chromium, zinc–nickel alloy deposits to replace cadmium, substitution of permanganates for chromates in the preparation of plastics, elimination of coumarin from nickel electroplating processes, and development of alkaline cyanide-free copper electrolytes have been driven by pollution prevention considerations to a great extent. Commercially, pollution control has increased electroplating costs and some shops that were only marginally profitable have gone out of business. The number of nickel plating shops has declined in the United States and Europe, but continues to increase in China, India, and Southeast Asia.

Although there was great resistance to plating pollution prevention and control in the early 1970s, most electroplaters in the United States and many other parts of the world are complying with existing regulations. In some cases the recycling and recovery of salts and metals coupled with the conservation of water and energy have led to economies that partially offset the cost of compliance. Efforts to minimize waste generation in an electroplating plant require good housekeeping and operating practices that tend to improve overall quality.

Strict environmental regulations have been imposed on the electroplating industry to prevent nickel and other metallic ions from entering the environment via plant effluents. Conventional processes for wastewater treatment include precipitation of nickel and other metals as hydroxides (or sulfides). If hexavalent chromium is present, it must first be reduced to the trivalent form before being precipitated. Cyanides are commonly removed by alkaline chlorination using sodium hypochlorite, but ozonation and electrochemical, thermal, and precipitation methods are known. The solid wastes generated in conventional processes for wastewater treatment are then disposed of in landfills. Because disposal of the solid waste is expensive and wasteful, the recovery of metal values by reverse osmosis, ion exchange, electrowinning, and other methods is becoming important and economically feasible [142]. Nickel producers accept nickel-containing sludges for recycling through smelters or special plants, and companies that collect and recycle electroplating wastes have grown in number.

The adoption and enforcement of strict environmental regulations arise from concern with the possible effects of metal contaminants on human health. Although the general perception is that these health effects are completely understood, the reality is that our knowledge is extremely limited. It is only when metals are present in high concentrations and in very specific forms that they may be toxic.

In a nickel electroplating shop, three types of exposure are possible: nickel and its compounds may be inadvertently ingested, nickel-containing solutions may be allowed to remain on the skin for long periods of time, and nickel and its compounds may be taken into the body by breathing [143]. Nickel and its inorganic compounds are not highly toxic substances and exposure to small amounts does not present serious health risks. Nevertheless, it is advisable to avoid ingesting even small amounts of these substances by taking some simple precautions in the workplace—wearing work gloves, washing one's hands before eating, and not eating in the workplace. Only one compound, gaseous nickel carbonyl, is known to be acutely toxic. This compound forms under special conditions in the few nickel refineries that produce high-purity nickel using nickel carbonyl as a process intermediate. It is not present or formed in the electroplating shop.

People who have become skin sensitized should avoid contact with nickel and its compounds. To avoid *becoming* sensitized, one must limit contact with nickel and its compounds. In electroplating, this may mean wearing work gloves and washing one's hands immediately after coming

in contact with nickel electroplating solutions. The risk of cancer appears to be limited to the inhalation of high concentrations of dusts containing nickel subsulfides and oxides under conditions previously existing in certain nickel refineries. Similar health problems have not been observed in electroplating and other workplaces where nickel is found. Airborne nickel in the workplace should be kept below regulatory or other acceptable exposure limits.

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