Nickel Electroplating*

Contents

Overview

The nickel plating process is used extensively for *decorative, engineering and electroforming* purposes because the appearance and other properties of electrodeposited nickel can be varied over wide ranges by controlling the composition and the operating parameters of the plating solution. Decorative applications account for about 80% of the nickel consumed in plating; 20% is consumed for engineering and electroforming purposes. Autocatalytic (electroless) nickel plating
processes are commercially important, but are outside the scope of this article. The annual worldwide consumption of nickel for electroplating, including nickel consumed as plating salts, is approximately 180 million pounds (81,700 metric tons), and accounts for 11 to 12 percent of world nickel consumption.

Decorative Plating

Modern decorative nickel plating solutions contain organic additives that modify the electrocrystallization process so that mirror-bright, highly-leveled nickel coatings are deposited *directly* from solution. Prior to the introduction of the "organic" baths, decorative nickel coatings were produced by polishing nickel-plated parts mechanically, a practice that continued from 1870 to about 1945. Thin layers of chromium were electrodeposited over polished nickel coatings for the first time in 1927 to prevent the "yellowing" or tarnishing of nickel in outdoor atmospheres, and that practice continues with the as-deposited bright nickel coatings now available. An effort to develop improved decorative, electroplated nickel coatings began in the late 1940's and led to the development of multilayer nickel coatings (early 1950's) and microdiscontinuous chromium coatings (mid-to-late 1960's). Modern multilayer nickel coatings in combination with microdiscontinuous chromium are capable of protecting and enhancing the appearance of most metals and alloys, plateable plastics and other materials for extended periods of time.

Engineering Plating

The engineering applications of nickel plating include those where a fully-bright appearance is not required. Engineering nickel deposits are usually sulfur-free, and matte in appearance. These deposits may be specified to improve corrosion and wear resistance, to salvage or build-up worn or undersized parts, to modify magnetic properties, to prepare surfaces for enameling or for organic coating, to function as diffusion barriers in electronic applications and for other purposes. Engineering applications exist in the chemical, nuclear, telecommunications, consumer electronics and computer industries.

Electroforming

Nickel *electroforming* is electrodeposition applied to the manufacture of nickel products of various kinds and differs from electroplating in one major respect. In electroplating, the coating is metallurgically bonded to the substrate and is an integral part of the surface. In electroforming, nickel is deposited onto a mandrel or mold *non-adherently* so that the nickel can be separated from the mandrel when it is removed from the plating solution. Electroforming applications include the fabrication of molds and dies, mesh and other products that are indispensable to operations in the textile, aerospace, communication, electronics, automotive, photocopying and entertainment industries.

Basics

Before describing decorative, engineering and electroforming plating processes, some basic facts are reviewed that make it possible to control the nickel plating process, predict the amount of nickel deposited and estimate nickel coating thickness.

The Basic Process

Nickel plating is similar to other electroplating processes that employ soluble metal anodes. It requires the passage of direct current between two electrodes that are 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^+). 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 replenished by those formed at the anode.

Hydrogen Evolution and Cathode Efficiency

The discharge of nickel ions is not the only reaction that can occur at the cathode; a small percentage of the current is consumed in the discharge of hydrogen ions from water. This reduces the cathode efficiency for nickel deposition from 100 per cent to 92 to 97 per cent depending on the nature of the electrolyte. The discharged hydrogen atoms form bubbles of hydrogen gas at the cathode surface.

Anode Efficiency

Under normal conditions the efficiency of dissolution at the anode is 100 per cent and no hydroxyl ions are discharged from the water. If the pH of the solution is too high, however, hydroxyl ions may be discharged in preference to the dissolution of nickel, and oxygen will be evolved. Under those conditions, the nickel anode becomes passive and ceases to dissolve nickel. Activated nickel anode materials are available commercially that resist the onset of passivity and replenish the solution with nickel ions over a wide range of plating conditions.

Nickel Ion and pH Changes

Under normal operating conditions, 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 92 to 97 per cent, whereas anode efficiency is always 100 per cent, the rate of increase in nickel ion concentration depends on the nature of the plating solution and not on the type of soluble nickel anode material that is used.

Faraday's Law for 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 (Faraday's Law). The proportionality constant is equal to M divided by nF, where M is the molecular weight, n is the number of electrons involved in the electrochemical reaction, and F is Faraday's constant, equal to 96,500

coulombs (ampere-seconds). For nickel, the constant is 1.095 grams per ampere-hour. That constant may be expressed in various units (see Tables 1A and 1B for useful facts and conversion factors for electroplating). The constant for nickel deposition is calculated assuming that cathode efficiency is 100%; since a small part of the current goes to discharge hydrogen, the constant must be adjusted by multiplying by the cathode efficiency; (for example, 1.095 x 0.955 = 1.046).

Faraday's Law for nickel may be expressed as follows:

$$m = 1.095 \, (a) \, (I) \, (t)$$

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 for the reaction of interest. In almost all cases, the anode efficiency is 100% (**a** = 1). The cathode efficiency may vary from 92 to 97% and accordingly, **a** will vary from 0.92 to 0.97.

Table 1A - Nickel electroplating facts

Nickel	Symbol Atomic Weight - Valency - Specific Gravity - Plating Rate, at 100% cathode efficiency -	Ni 58.69 2 8.90 1.095 g/Ampere-hour (0.039 oz./Ampere-hour)
Nickel Sulfate	$NiSO_4 \cdot 6H_2O$	Contains 22.3% nickel.
Nickel Chloride	$NiCl_2 \cdot 6H_2O$	Contains 24.7% nickel.
Nickel Sulfamate	$Ni(NH_2SO_3)_2$	Contains 23.2% nickel.
Nickel Carbonate	$NiCO_3$	Contains about 46% nickel.

Table 1B – Units and conversion factors for nickel electroplating

Quantity	A Traditional Unit	B SI Unit	To Convert from A to B Multiply by	To Convert from B to A Multiply by
Coating Thickness	Mil	$?m$	25.4	0.0394
	Inch	mm	25.4	0.0394
Coating Mass (Weight)	mg/in^2	g/m^2	1.55	0.645
	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	$A\text{-}hr/ft^2\text{-}mil$	$A\text{-}s/m^2\text{-}?m$	1530	6.55×10^{-4}
Volume	Gal	m^3	0.00379	264
	Gal	Liter(L)	3.79	0.264
	fl oz	Ml	29.6	0.0338
Mass Concentration	oz/gal	g/L	7.49	0.134
		kg/m^3	7.49	0.134
Volume Concentration	fl oz/gal	ml/L	7.81	0.128
		cm^3/L	7.81	0.128
Force (Internal Stress)	1000 psi	$MPa (Mn/m^2)$	6.89	0.145

Average Nickel Thickness

The nickel electrodeposition data compiled in Table 2 has been calculated on the assumption that cathode efficiency is 95.5%, which approximates the case for most nickel plating solutions. From the table, one can estimate the time required to deposit a specified thickness of nickel at a specified current density. If the plating process is operated at 5 A/dm^2, for example, it takes about 20 minutes to deposit a nickel coating with an average thickness of 20 ?m.

The data in the table provides a means of estimating the **average** coating thickness. The actual thickness on an individual part may be different depending on the uniformity of current density distribution. Under practical plating conditions, the thickness of the nickel on a batch of parts is measured in one or more trials and adjustments made, if necessary, as to how the parts are placed in the tank relative to the anode and how they are positioned on the plating racks. In some cases, shields and auxiliary anodes may be required to obtain acceptable thickness uniformity. Shields are made of non-conductive materials, and 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 current to a recessed or relatively small area on the cathode. With care, current density distribution and coating thickness can be made reasonably uniform and predictable.

Table 2 – Nickel electrodeposition data - Based on 95.5% cathode efficiency)

Deposit Thick-ness	Weight per unit area	Amp Hours Per Unit	Time, in minutes, To obtain deposit at various current densities									
			Current Density, A/dm^2									
? m	G/dm^2	Ah/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	5.1
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

The Watts Solution and Deposit Properties

The nickel plating solution described by Watts (1916) eventually replaced all others in use up to that time. It remains the basis of most decorative nickel plating processes, and is used for engineering applications and for electroforming. It is operated at elevated temperatures and is capable of being used with high current densities.

The composition of the modern Watts bath is included in Table 3. The constituents of the Watts bath have several functions.

?? *Nickel sulfate* is available in commercially pure forms, is relatively inexpensive, and is the major source of the nickel ions in solution; a high nickel sulfate concentration is used when high current densities are required.

?? *Nickel chloride* serves primarily to improve anode corrosion, but also increases conductivity and uniformity of coating thickness distribution. Excessive amounts of chloride increase the corrosivity of the solution and the internal stress of the deposits. (Internal stress refers to forces created within the deposit as a result of the electrocrystallization process and/or the codeposition of impurities such as hydrogen, sulfur and other elements. Internal stress is either tensile (contractile), or compressive (expansive), and may cause plating problems if excessively high.)

?? *Boric acid* is used in nickel plating solutions for buffering purposes; its concentration may affect the appearance of the deposits. The deposit may first become frosty in high current density areas at 30 g/L (4 oz/gal) of boric acid, and then as the boric acid concentration approaches 15 to 23 g/L (2 to 3 oz/gal), the deposit may be burnt and cracked. No effect on appearance is observed at high boric acid concentrations up to saturation (45 g/L or 6 oz/gal). *Wetting agents or surfactants*, formulated specifically for nickel plating solutions, are almost always added to control pitting; their function is to lower the surface tension of the plating solution so that air and hydrogen bubbles do not cling to the parts being plated.

Good quality nickel deposits can be produced within the ranges of solution pH, temperature and current density given in Table 3. Although the maximum current density given in the table is 11 A/dm^2, higher rates of plating are possible with increased solution agitation and flow rates. The physical and mechanical properties of nickel deposited from Watts solutions are affected by the operating conditions and chloride content of the solution. Maximum ductility and softest deposits are produced when 25% of the nickel in solution is present as nickel chloride. (A comprehensive source of mechanical property data for electrodeposited nickel, nickel alloys and nickel composite coatings is *The Properties of Electrodeposited Alloys - A Handbook*, by William H. Safranek, Second Edition, published by the American Electroplaters and Surface Finishers Society, 126-44 Research Parkway, Orlando, FLA 32826.)

The nickel plating processes used for decorative, engineering and electroforming purposes are discussed in the following sections.

Decorative Nickel Plating and Multilayer Coatings

The technology of decorative nickel plating has been improved continuously over the years. Prime examples include: development of the "organic" bright nickel solutions, introduction of semi-bright nickel plating processes, development of multilayer nickel coatings and the use of microdiscontinuous chromium in combination with multilayer nickel. The major result of these developments has been a remarkable improvement in the corrosion performance of decorative nickel plus chromium coatings *without the need to increase deposit thickness.*

Bright Nickel Solutions

Bright nickel plating solutions are modifications of the Watts formulation given in Table 3, but contain organic and other additives that act to produce a fully bright finish suitable for immediate chromium plating without mechanical finishing.   Portions of the addition agent molecules may be incorporated into the deposit, resulting in a hard, fine-grained coating that contains incorporated sulfur. The sulfur causes the deposit to be electrochemically more reactive than sulfur-free matte, polished or semi-bright nickel deposits. Decomposition products of the additives accumulate in solution with time and are removed by purification with activated carbon. In modern solutions, continuous filtration through active carbon removes deleterious decomposition products without significant removal of the addition agents themselves.

Table 3 - Nickel electroplating solutions

	Electrolyte Composition[1], g/L		
	Watts Nickel	Nickel Sulfamate	Typical Semi-Bright Bath[2]
Nickel Sulfate, $NiSO_4 \cdot 6H_2O$	225 to 400		300
Nickel Sulfamate, $Ni(SO_3NH_2)_2$		300 to 450	
Nickel Chloride, $NiCl_2 \cdot 6H_2O$	30 to 60	0 to 30	35
Boric Acid, H_3BO_3	30 to 45	30 to 45	45
	Operating Conditions		
Temperature, ^0C	44 to 66	32 to 60	54
Agitation	Air or mechanical	Air of mechanical	Air or mechanical
Cathode Current Density, A/dm^2	3 to 11	0.5 to 30	3 to 10
Anodes	Nickel	Nickel	nickel
PH	2 to 4.5	3.5 to 5.0	3.5 to 4.5
	Mechanical Properties		
Tensile Strength, Mpa	345 to 485	415 to 610	-
Elongation, %	10 to 30	5 to 30	8 to 20
Vickers Hardness, 100 gram load	130 to 200	170 to 230	300 to 400
Internal Stress, Mpa	125 to 185 (tensile)	0 to 55 (tensile)	35 to 150 (tensile)

NOTE 1 Anti-pitting agents formulated for nickel plating are added to control pitting.

NOTE 2 Organic additives available from plating supply houses are required for semibright nickel plating.

NOTE 3 Typical properties of *bright* nickel deposits are as follows: Elongation, % - 2 to 5 Vickers Hardness,100 gram load - 600 to 800; Internal Stress, MPa - 12 to 25 compressive.

Several substances---organic and inorganic---are used at appropriate concentrations to achieve brightness, leveling and control of internal stress. (Leveling is the ability of the deposit to become smoother than the surface on which it is deposited as the thickness of the nickel is increased.)

The substances used as additives in bright nickel plating solutions may be described by the following three terms: carriers, auxiliary brighteners and brighteners. The terminology is not standardized, however, and alternative terms mentioned in the literature are shown in parentheses.

Carriers (brighteners of the first class, secondary brighteners, control agents, ductilizers) are usually aromatic organic compounds. They are the principal source of the sulfur codeposited with the nickel. Their main function is to refine grain structure and provide deposits with increased luster compared with matte or dull deposits from baths without additives. Some of these additives can be used in Watts solution or high-chloride versions of the Watts solution (for example, solutions with 115 g/L nickel chloride). This class of brightener widens the bright range

when used in combination with the auxiliary brighteners and brighteners discussed below. Some examples of carriers are: saccharin (o-sulfobenzoic imide); paratoluene sulfonamide; benzene sulfonamide; benzene monosulfonate (sodium salt); ortho sulfobenzaldehyde (sodium salt); and naphthalene 1, 3, 6-trisulfonate (sodium salt). Carriers are used in concentrations of about 1 to 25 g/L (0.1 to 3 oz/gal), either singly or in combination. They are not consumed rapidly by electrolysis, and consumption is primarily by dragout and by losses during batch carbon treatment. (Batch treatment involves interrupting production, transferring the plating solution to a separate treatment tank where it is treated with activated carbon, filtered and returned to the main tank.) 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. It is generally used as sodium saccharin at a concentration of 0.5 to 4.0 g/L (0.07 to 0.5 oz/gal).

Auxiliary brighteners may be either organic or inorganic. Their function is to augment the luster attainable with the carriers and brighteners, and to increase the rate of brightening and leveling. Some examples are: sodium allyl sulfonate; zinc, cobalt, cadmium (for rack and barrel plating); 1, 4-butyne 2-diol. The concentration of these additives may vary from about 0.1 to 4 g/L (0.01 to 0.5 oz/gal). The rate of consumption depends on the type of compound and may vary widely. These compounds may be of aromatic or aliphatic types and usually are heterocyclic or unsaturated. The inorganic metallic ions - zinc, cobalt, cadmium - are not often used anymore as auxiliary brighteners.

Brighteners (brighteners of the second class, primary brighteners, leveling agents) when used in combination with carriers and auxiliary brighteners, produce bright-to-brilliant deposits having good ductility and leveling characteristics over a wide range of current densities. Some of the compounds used as brighteners include: reduced fuchsin; phenosafranin; thiourea; 1, 4-butyne diol; n-allylquinolinium bromide; and 5-aminobenzimidazolethiol-2. Materials of this type generally are used in concentrations of 0.005 to 0.2 g/L (0.0006 to 0.02 oz/gal); an excess of brighteners may cause serious embrittlement. The rates of consumption of these materials may vary within wide limits.

Modern bright nickel plating solutions employ combinations of additives similar to those described and are formulated to produce bright deposits over a wide range of current density. The deposits have excellent leveling or scratch-filling characteristics; produce deposits with fair ductility and low internal stress; 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 use of activated carbon on filters; produce breakdown products that can be removed by activated carbon, and are not overly sensitive to anode effects.

Multilayer Decorative Plating

The single-layer bright nickel coatings produced from solutions containing organic additives are less resistant to corrosion than polished nickel coatings. The lower corrosion resistance is due to the presence of small amounts of sulfur that originate from the organic additives present in solution. The amount of sulfur that is incorporated depends on exactly how the process is formulated and controlled. Single-layer bright nickel coatings are suitable for use in mildly corrosive service using a nickel thickness of 10 to 20 mm. For severe and very severe conditions of exposure, especially where longtime resistance to corrosion is required, multilayer nickel coatings with microdiscontinuous chromium are used. The principal types are *double- and triple-layer* coatings.

Double-layer coatings involve the electrodeposition of two layers of nickel, one semibright and one bright, before application of chromium. The first layer (semibright) is deposited from a Watts-type formulation containing one or more sulfur-free organic additives. Semibright nickel deposits contain less than 0.005 mass percent sulfur, and are semi-lustrous, smooth, and fine-grained over a wide current density range. The deposits have a columnar structure and good ductility. The typical composition and operating conditions for a semibright nickel plating bath are given in Table 3. Deposit internal stress increases with increasing nickel chloride content; deposits also tend to be nonuniform in color and leveling at high chloride levels.   The concentrations of the organic additives for semibright nickel solutions are usually fairly low, from 0.05 to 0.5 g/L (0.006 to 0.06 oz/gal). Examples of these additives are: 1, 4-butyne diol (or other aliphatic compounds with olefinic or acetylenic unsaturation); formaldehyde; coumarin or ethylene cyanohydrin. There are two families of semi-bright nickel plating processes that are usually referred to as *coumarin* and *non-coumarin* types. The latter were introduced more recently and offer advantages. Semi-bright nickel plating solutions usually contain anionic surfactants and antipitting agents, singly or in combination.

The bright nickel layer deposited on top of the semibright one may range in thickness from 5 to 8 mm (0.2 to 0.3 mil), or about 20 to 35% of the total nickel thickness. Ideally, it should be plated from a bath that is compatible with the semibright additive, or additives, because in most double-layer systems the semibright additive functions as either a brightener or an auxiliary brightener in the bright nickel bath.

Triple-layer coatings are similar to double-layer coatings except that a thin, high-sulfur containing layer is deposited between the semi-bright and bright layers. The thin layer must contain greater than 0.15 mass percent sulfur. Some of the requirements for double-and triple-layer nickel coatings are summarized in Table 4. The reasons why multilayer coatings improve corrosion performance are discussed below (see Corrosion Performance).

Table 4 - Requirements for double- and triple-layer nickel coatings

Layer (Type of Nickel Coating)	Specific Elongation, %	Sulfur Content, % (m/m)	Thickness, As a Per Cent of Total Nickel Thickness	
			Double-layer	Triple-layer
Bottom (s – semibright)	greater than 8	Less than 0.005	Greater than 60 (but at least 75 for steel)	greater than 50 (but not more than 70)
Middle (b - high-sulfur bright)	-	Greater than 0.15	-	10 max
Top (b - bright)	-	Between 0.04 and 0.15	greater than 10, but less than 40	equal to or greater than 30

NOTE   *s* designates the semi-bright nickel layer that is applied prior to bright nickel; *b* designates the fully-bright nickel layer that contains the amount of sulfur specified.

Microdiscontinuous Chromium

Decorative, electrodeposited nickel coatings whether single- or multi-layer are most often used in combination with electrodeposited chromium. The thin layer of chromium, initially applied over nickel to prevent tarnishing, now provides added resistance to corrosion because of the developments discussed in this and the next section.

Conventional or regular chromium deposits are low-porosity coatings, whereas microdiscontinuous chromium deposits have a high, controlled degree of microporosity or microcracking. Controlled microporosity or microcracking in the chromium is achieved by depositing a special nickel strike on top of the bright nickel layer just prior to chromium plating.

When it is plated over with chromium, the thin layer of nickel, usually about 1 to 2 mm (0.04 to 0.08 mils), helps create microcracks or micropores in the chromium. Microporosity may also be achieved without the use of a special nickel layer by means of the PIXIE process; this is a patented process that involves post-plating treatment of the chromium to increase porosity on a microscopic scale. Traditionally, the chromium is deposited from conventional hexavalent type processes, but within the last ten years, trivalent chromium plating processes have grown in popularity.

Microcracked chromium is produced by depositing the thin layer of nickel from a special bath formulated to produce nickel with a high internal tensile stress. When it is chromium-plated, the thin nickel and the chromium will crack. Varying the conditions under which the nickel layer is deposited can provide variations in the crack density over a range of from 30 cracks/mm (750 cracks per inch) to 80 cracks/mm (2000 cracks per inch). The nickel bath usually consists of a basic nickel chloride electrolyte with additives that provide additional stress such as the ammonium ion. Boric acid is not used, but other buffers such as the acetate ion may be added. Proprietary organic additives are also used to enhance the brightness and the ability of the deposit to crack, especially in the low current density areas. Temperature and pH are controlled to vary the crack density; low temperature, 23^0C (73^0F) and high pH 4.5 favor higher crack densities; high temperature, 36^0C (97^0F) and low pH (3.5) favor lower crack densities. Cracking of the chromium deposit must occur subsequent to chromium plating. Aging or the use of a hot water dip may be necessary to promote the formation of all microcracks.

Microporous chromium is produced from Watts-type nickel baths using air agitation and containing very fine inert particles, usually inorganic, containing also the normal additives used for bright nickel plating. Chromium, plated over the resulting nickel particle matrix, deposits around the particles creating pores. The nickel baths are operated much like bright nickel solutions with the exception that filtration cannot be performed. In some instances, auxiliary additives permit reduction of the particle concentration in the plating bath and still provide high pore densities. Pore densities can vary according to the concentration of particles, agitation rates and additives. Generally, a minimum pore density of 100 pores/mm^2 (64,000 pores/in^2) is specified. In either case, chromium thicknesses should not be allowed to exceed about 0.5 mm (0.02 mil) or the cracks/pores will start to heal.

Microcracked chromium deposits can also be produced directly from chromium baths by increasing thickness, or by depositing chromium over chromium. The latter, dual layer chromium technique is no longer popular.

Corrosion Performance

The improved performance of multilayer nickel coatings is due to the combination of layers of nickel having different electrochemical reactivities. If one measures the corrosion potentials of various nickel deposits in the same electrolyte, one finds that the bright nickel deposits display more active dissolution potentials than do the semi-bright nickels. If bright and semi-bright nickel deposits (for example, in the form of foils separated from the substrate) are electrically connected in the electrolyte, electrons will flow from the bright nickel to the semi-bright nickel. The result is that the rate of corrosion of the bright nickel is increased, whereas the rate of corrosion of the semi-bright nickel is decreased. In a composite coating consisting of bright nickel over semi-bright nickel, this is manifested by enhanced lateral corrosion of the bright nickel layer and delayed penetration of the semibright nickel layer.

The extent to which bright nickel protects the underlying semibright nickel layer by sacrificial action is dependent on the difference between the corrosion potentials of the semi-bright and

bright nickel. The difference should be at least 100 millivolts (as measured by the STEP Test described below), and there is evidence that larger differences in potential are beneficial, especially in low current density areas of complicated parts. If the difference becomes too great, appearance suffers because of the accelerated corrosion of the bright nickel layer; that is, there is an optimum value that represents a compromise between preventing basis metal attack and controlling superficial corrosion. The result is that penetration of the coating and exposure of the underlying substrate occur slowly.   Multilayer nickel coatings are, thus, more protective than single-layer bright nickel coatings of equal thickness.

The rate of pit penetration through the nickel layers varies inversely with the number of microdiscontinuities in the chromium layer. Pit penetration may occur rapidly with low-porosity, conventional chromium. When corrosion takes place at a pore in conventional chromium, the large cathodic area of chromium surrounding the pore accelerates the corrosion of the nickel and pitting may occur rapidly.   With microdiscontinuous chromium, a large number of microscopic pores or cracks are deliberately induced in the chromium deposit so that corrosion can start at many sites. The available corrosion current has to be spread over a myriad number of tiny corrosion cells, so that the rate of corrosion of the nickel is greatly reduced. For example, the approximate depth of pitting of nickel after 16 hours of CASS testing (see ASTM Standard B 368, Copper-Accelerated Acetic Acid Salt Spray (Fog) Testing) was 10 to 20 micrometers with conventional chromium, and 1 to 6 micrometers with microdiscontinuous chromium.

Table 5 - Coating systems on steel giving best performance after 15 years of outdoor marine exposure and 96 hours of CASS testing

Type and Thickness of Coating, ?m			ASTM Performance Ratings[1]	
Copper	Nickel	Chromium	Outdoor Marine, 15 years	CASS, 96 hours
-	38d[3]	1.5 mc[2]	10/8	10/8
12	26d	1.5 mc	10/9	10/8
-	38d	0.25 mp	10/7	10/7
12	26d	0.25 mp	10/9	10/7

NOTE 1 A two-number system has been adopted by ASTM for rating panels after corrosion testing. The first, the protection number, is based on the per cent defective area due to corrosion of the basis metal; a rating of 10 on steel indicates the panel did not rust. The second, the appearance number, is similarly based on per cent defective area, but rates the extent to which corrosion of the basis metal, as well as superficial corrosion, detract from the overall cosmetic appearance. Appearance ratings of 7, 8 and 9 indicate 0.25 to 0.5 %, 0.1 to 0.25 %, and 0 to 0.1 %, of the area is defective due to superficial staining and corrosion, respectively.

NOTE 2 The type of microcracked chromium used in this study is based on the addition of selenium compounds to a conventional chromium bath to obtain microcracking; consistent crack patterns were obtained at the chromium thickness given in the table.

NOTE 3 The double-layer nickel coatings in the program differed in reactivity. See G.A. DiBari and F.X. Carlin, *Decorative Nickel/Chromium Electrodeposits On Steel-15 Years Corrosion Performance Data*, Plating and Surface Finishing, May 1985, page 128, for details.

Corrosion studies conducted by plating suppliers, nickel producers and groups such as ASTM Committee B 8 have confirmed that multilayer nickel coatings are significantly more protective than single-layer bright nickel coatings; microdiscontinuous chromium coatings provide more protection than conventional chromium coatings; and the corrosion protection of decorative, electroplated nickel plus chromium coatings is directly proportional to nickel thickness, and to the ratio of semi-bright and bright nickel in multilayer coatings.

Table 5 is based on the results of an Inco study conducted at the LaQue Center for Corrosion Technology, Wrightsville Beach, NC, and summarizes the types of coatings that protected standard panels from corrosion for more than 15 years outdoors in a severe marine atmosphere.

Standards and Recommended Thicknesses

ASTM Standard Specification B 456 provides information on specific requirements for decorative nickel plus chromium coatings to achieve acceptable performance under five different conditions of service. (Individual copies of ASTM Standards can be obtained from AESF, 12644 Research Parkway, Orlando, FL 32826 and ASTM, 1916 Race Street, Philadelphia, PA 19103-1187.) The ASTM Standard defines several classes of coatings that differ in thickness and type, and classifies the various coating systems according to their resistance to corrosion. The standard specifies the requirements for double- and triple-layer nickel coatings (see Table 4), and gives the classification numbers of coatings appropriate for each service condition number. For example, Table 6 specifies decorative nickel plus chromium coatings on steel.

Table 6 - Decorative nickel plus chromium coatings on steel

Service Condition Number (Typical Applications)	Classification Number[1,2,3]	Minimum Nickel Thickness, ?m
SC 5 – Extended very severe (exterior automotive where long-time corrosion protection is a requirement).	Fe/Ni35d Cr mc Fe/Ni35d Cr mp	35 35
SC 4 – Very severe (exterior automotive, boat fittings).	Fe/Ni40d Cr r Fe/Ni30d Cr mp Fe/Ni30d Cr mc	40 30 30
SC 3 – Severe (patio and lawn furniture, bicycles, hospital furniture and cabinets).	Fe/Ni30d Cr r Fe/Ni25d Cr mp Fe/Ni25d Cr mc Fe/Ni40p Cr r Fe/Ni30p Cr mp Fe/Ni30p Cr mc	30 25 25 40 30 30
SC 2 – Moderate service (stove tops, oven liners, office furniture, golf club shafts, plumbing fixtures and bathroom accessories).	Fe/Ni20b Cr r Fe/Ni15b Cr mp Fe/Ni15b Cr mc	20 15 15
SC 1 – Mild (toaster bodies, interior automotive accessories, trim for major appliances, fans, light fixtures).	Fe/Ni10b Cr r	10

NOTE 1   Results of several test programs indicate there is some doubt whether the coating systems described by the classification numbers involving regular chromium are satisfactory for SC 4 & SC 3.

NOTE 2   When permitted by the purchaser, copper may be used as an undercoat for nickel but is not substitutable for any of the part of the nickel specified.

NOTE 3   The symbols in this column have the following meanings: **b** for electrodeposited single-layer bright nickel; **d** for double- or multilayer nickel coatings; **r** for regular or conventional chromium; **mp** for microporous chromium; and **mc** for microcracked chromium.

The service condition number characterizes the severity of the corrosion environment: 5 being the most severe; 1 being the least severe. The classification number is a way to specify the details of the coating in an abbreviated fashion; for example, the classification number:

indicates that the coating is applied to steel (Fe); consists of 30 micrometers of double-layer nickel (d) with a top-layer of microporous (mp) chromium that is 0.3 micrometers thick. (The thickness value of the chromium is not included in the classification number unless its thickness is different from 0.3 micrometer.)

ASTM Standard Specification B 456 provides other details and information necessary to produce decorative nickel plus chromium coatings of highest quality.

Engineering and Electroforming Processes

Electrodeposited nickel coatings are applied in engineering applications to modify or improve surface properties such as corrosion resistance, hardness, wear and magnetic properties. Although the appearance of the coating is important and the plated surface should be defect-free, the lustrous, mirror-like deposits described in previous sections are not usually required. Nickel electroforming is the specialized use of the nickel plating process to produce or reproduce articles by electroplating onto a mandrel which is subsequently separated from the deposit.

Watts and Nickel Sulfamate Processes

The two most popular solutions for depositing engineering nickel coatings and for electroforming, Watts nickel and nickel sulfamate, have been included in Table 3. The table summarizes the chemical composition, the operating conditions and typical mechanical property data for deposits from these solutions. The Watts solution is relatively inexpensive, and easy to control; it has already been discussed. The sulfamate solution has distinct advantages and is described further.

Nickel sulfamate solutions are widely used for electroforming because of the low internal stress of the deposits, high rates of deposition, and superior throwing power. Throwing power is the relationship between current distribution and uniformity of coating thickness as influenced by geometric factors (the shape and relative positioning of anode and cathode), and by the electrochemical characteristics of the solution (conductivity, cathode polarization and cathode efficiency). Throwing power is a measure of the extent to which a solution will produce deposits that are more uniform than those that would be produced in the absence of cathode polarization and cathode efficiency effects. Because of the very high solubility of nickel sulfamate, a higher nickel metal concentration is possible than in other nickel electrolytes, permitting lower operating temperatures and 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 with about 0.02% sulfur, Inco S-Rounds and S-Nickel pellets, are essential to avoid anodic oxidation of the sulfamate ion that can result in the uncontrolled and unpredictable production of sulfur-containing compounds that act as stress reducers and that cannot easily be removed from solution. Bromide ions, instead of chloride, are sometimes added to nickel sulfamate solutions to promote anode dissolution.

Nickel sulfamate is so soluble that it cannot be readily recrystallized from solution. It is commercially available as a concentrated solution usually prepared by reacting high-purity nickel powder with sulfamic acid under controlled conditions. Nickel sulfamate plating solutions are more expensive than those based on commercial grades of nickel sulfate and nickel chloride. The extra cost of using solutions that are as pure as possible is more than offset by savings in the preliminary purification procedures necessary otherwise.

Prolonged use of sulfamate solutions at temperatures above 70^0C (140^0F) or at a pH less than 3 can hydrolyze the nickel sulfamate to the less soluble form of nickel ammonium sulfate. The ammonium and sulfate ions produced from the hydrolysis increase the internal tensile stress and hardness of the deposits.

Nickel electrodeposited from a well-purified sulfamate bath containing no stress-reducing agent and operated at 46^0C (115^0F), a pH of 4.0, and a current density of 2.0 A/dm^2 (20 A/ft^2) has a residual tensile stress varying from 15 to 40 MPa (2 to 6 ksi). The stress in a deposit produced from a similarly operated Watts bath would be about 170 MPa (25 ksi).

Sulfamate nickel plating baths are especially useful for applications requiring low residual stress in the electrodeposited nickel, such as in electroforming, and for coating objects that are susceptible to fatigue cracking. Steel crankshafts that are nickel plated for resistance to corrosion and wear should be coated with a low-stress nickel deposit, such as sulfamate nickel, to minimize loss of fatigue strength. The fatigue limit of nickel plated steel is reduced almost proportionally to the amount of residual tensile stress in the nickel plate and the use of compressively stressed deposits provides additional benefits.

Other Solutions for Engineering Applications

Other nickel plating solutions for engineering applications are listed in Table 7, along with available mechanical properties of the deposits. Many of these solutions were developed to meet specific engineering requirements; all are used to a much lesser extent than Watts and nickel sulfamate solutions.

?? *Fluoborate*. The fluoborate solution in Table 7 can be operated over a wide range of nickel concentrations, temperature, and current density. The fluoborate anion is aggressive and some materials that contact the solution are chemically attacked. Silica filter aids cannot be used on a continuous basis, although cellulose filters are satisfactory. Lead, titanium, and high silicon cast iron are readily attacked. Stainless steels containing 20% chromium, 25 to 30% nickel, and 2 to 3% molybdenum are resistant. Anode materials can be encased in Vinyon, polypropylene, or Orlon anode bags to prevent insoluble particles and anode residues from entering the plating solution; nylon bags are unsuitable. Only sleeve-type glass electrodes for pH measurement should be used because of the formation of relatively insoluble potassium fluoborate with permanent junction types. The mechanical and physical properties of deposits produced by the fluoborate bath are similar to those from Watts solutions. The nickel fluoborate solution has been used primarily for high-speed deposition of thick nickel.

?? *Hard Nickel*. Developed especially for engineering applications, this solution is applied where controlled hardness, improved abrasion resistance, greater tensile strength, and good ductility are required (without the use of sulfur-containing organic addition agents). Close control of pH, temperature and current density is necessary for this bath to maintain the desired hardness values. The tensile strength increases and the ductility decreases with an increase in pH and a decrease in temperature. 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 of 230^0C (450^0F) 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 (1.1 oz/gal). (In those applications where the part being plated is not going to be exposed to elevated temperatures in service, it is simpler to add organic compounds such as saccharin, p-

toluene sulfonamide, p-benzene sulfonamide or other "carriers" to Watts or sulfamate solutions to achieve hardness without increased internal stress. Since the additives introduce 0.03% sulfur (or more), this approach can not be used for parts to be exposed to high temperatures where sulfur severely embrittles the nickel deposit.)

?? *All-Chloride.* The principal advantage of the all-chloride bath (Table 7) 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. 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 to some extent 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. For example, insoluble auxiliary or conforming anodes may be required to plate the insides of steel pipes and fittings. To prevent pitting, hydrogen peroxide may be added to all-sulfate solutions, provided they contain no wetting agents or organic stress-reducers. Oxygen is evolved at insoluble anodes in the all-sulfate solution and as a result, the nickel concentration and pH decrease during plating. The pH is controlled and the nickel ion concentration maintained by adding nickel carbonate. Another procedure that has been used in low-pH solutions replenishes the nickel electrolytically by employing a replenishment tank with nickel anodes; the current in the replenishment tank is periodically reversed to keep the nickel anodes actively dissolving in the absence of chlorides. 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. 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.

?? *Sulfate/Chloride.* The sulfate/chloride solution given in Table 7 has roughly equivalent amounts of nickel sulfate and nickel chloride, and was developed to overcome some of the disadvantages of the all-chloride solution. 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-base die castings. It may, also, be 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 the zinc. The deposits are less ductile and more highly stressed than nickel deposited from a Watts bath. For this reason, high sulfate nickel is sometimes used as a thin undercoating for more ductile nickel. (In general, the deposition of copper from a cyanide solution directly on zinc-base die castings prior to the deposition of nickel is simpler and more reliable.)

Table 7 - Other nickel plating solutions and some properties of the deposits

Composition[1], g/L	pH	^{0}C	Current Density, A/dm^2	Vickers Hardness, 100 g Load	Tensile Strength, MPa	Elongation per cent	Internal Stress, MPa
Fluoborate - 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 sulfate, 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 Sodium sulfate, 75-110 Ammonium chloride, 25 Boric acid, 15	5.3-5.8	20-32	0.5-2.5				
Black nickel (sulfate) - Nickel sulfate, 75 Zinc sulfate, 30 Ammonium sulfate, 35 Sodium thiocyanate, 15	5.6	24-32	0.15				
Black nickel (chloride) - 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 Phosphorous acid, 2-40	0.5-3.0	60-95	2-5				

NOTE   The formulas of the compounds in the table are as follows: nickel fluoborate, Ni(BF$_4$)$_2$; nickel sulfate, NiSO$_4$·6H$_2$O; nickel chloride,NiCl$_2$·6H$_2$O; boric acid, H$_3$BO$_3$; ammonium chloride, NH$_4$Cl; ammonium sulfate, (NH$_4$)$_2$SO$_4$; sodium sulfate, Na$_2$SO$_4$; phosphoric acid, H$_3$PO$_4$; phosphorous acid, H$_3$PO$_3$; zinc sulfate, ZnSO$_4$·7H$_2$O; zinc chloride, ZnCl$_2$; sodium thiocyanate, NaSCN.

?? *Black Nickel*. There are at least two formulations for producing black nickel deposits; these incorporate zinc (Zn) and thiocyanate (CNS-) ions. Table 7 gives the composition and operating conditions for a sulfate and a chloride black nickel plating bath. 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. It is in commercial use, but limited in its applications.

?? *Nickel Phosphorus.* These solutions result in the electrodeposition of nickel-phosphorus alloys that are analogous to those deposited "electrolessly" using sodium hypophosphite as the reducing agent. The hardness of the electrolytic deposits can be increased by heat treatment in the same way that electroless nickel deposits can with maximum hardness

occurring at 400^0C (750^0F). The phosphorus content of the deposits is best controlled by frequent additions of phosphite or phosphorous 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.

Nickel Alloy Plating and Composites

Although discussion of alloy plating is beyond the scope of this article, nickel alloy plating processes of commercial importance include nickel-iron (without brighteners), nickel-cobalt, nickel-palladium and tin-nickel. An alloy plating process that is growing in importance is zinc-nickel containing 8 to 12 per cent nickel. In addition, the incorporation of inert particles within a nickel matrix is possible and coatings that incorporate silicon carbide, diamonds, mica, PTFE and other materials are being applied for engineering purposes.

Quality Control

Achieving high quality involves controlling the bath composition, the purity of the plating solution, and the thickness and uniformity of the deposits. Eliminating rejects, troubleshooting, and the testing of deposits are important aspects of process and product control.

Control Solution Composition

Control of the composition of the plating bath is one of the most important factors contributing to the quality of nickel deposits. 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 and organic substances must be prevented.

Purification Techniques and Starting Up a New Bath

Before any freshly prepared nickel plating bath is used, contaminants such as iron, copper, zinc, and organics present in trace quantities in commercial salts must be removed to obtain the best results. The following treatments are available for purifying a freshly prepared nickel plating solution:

?? *High-pH treatment* consists of adding nickel carbonate to the hot solution until a pH of 5.0 to 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 most of the harmful metallic and organic impurities.

A complete purification procedure for a Watts solution would comprise 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 to 49^0C (100 to 120^0F) to about 80% of desired volume;
2. Add 1 to 2 m/L (0.8 to 1.6 pints/100 gal) of 30% hydrogen peroxide; agitate briefly and allow to settle for one hour;
3. Add 1.2 to 2.4 g/L (1 to 2 lb/100 gal) activated carbon and agitate thoroughly;
4. Heat to 66^0C (150^0F), then add 1.2 to 2.4 g/L (1 to 2 lb/ 100 gal) of nickel carbonate to the solution, with agitation to adjust the pH to 5.2 to 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 to 16 hours;

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 A/dm^2 (5 A/ft^2) and treatment should continue until 0.5 to 1.3 A-h/L (2 to 5 A-h/gal) have passed through the solution. The solution should be agitated and the temperature held at 49 to 60^{0}C (120 to 140^{0}F); it is useful to prepare deposits at normal current densities at some point to check appearance, stress and sulfur content; if not acceptable, continue dummying until the properties are acceptable;
8. Remove the dummy cathodes and adjust the pH of the solution to the desired value.

Controlling the Main Constituents

The following basic constituents of nickel plating baths must be regularly controlled: (a) the nickel metal content; (b) the chloride concentration; (c) the boric acid; and (d) any organic addition agents. Nickel metal concentration is maintained between 60 and 80 g/L (8.0 and 10.5 oz/gal) in most commercial applications. It is desirable to have a minimum of 23 g/L (3 oz/gal) of nickel chloride in the solution to promote anode corrosion. (The chloride content is not critical for anode corrosion when sulfur-activated 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 must be replenished due to losses from dragout, electrolytic consumption and the effects of carbon filtration (or batch treatment).

Procedures exist for chemical analysis of nickel, chloride, boric acid and organic addition agents in nickel plating solutions, and modern instrumental techniques are available to monitor the main ingredients on a regular basis with improved precision; high-performance liquid-chromatography is one of the improved techniques for controlling organics that is growing in popularity.

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 the process is not functioning properly.)

The operating temperature may have a significant effect on the properties of the deposits and should be maintained within specified limits (plus or minus 2^{0}C) of the recommended value. In general, most commercial nickel plating baths are operated between 38 to 60^{0}C (100 to 140^{0}F).

The nickel plating process should be operated at specified current densities by estimating the surface area of the parts and calculating the total current required. The practice of operating the process at a fixed voltage is not recommended. Controlling cathode current density is essential for accurately predicting average nickel thickness, for achieving uniform coating thickness on complicated shapes, 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. The nickel plating solution has an electrical resistance

and almost all components to be plated have prominent surfaces that are nearer the anode than recessed areas. The current density is greater at the prominences because the anode-to-cathode distance is shorter and therefore has less electrical resistance. The apportioning of the current in this way is called "current distribution". This means that the recessed areas receive a thinner nickel deposit than the prominent ones. Current distribution is controlled by proper rack design and proper placement of components on those 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. The presence of small quantities of inorganic or organic contamination may result in plating defects.

Table 8 - Maximum allowable concentration of metallic contaminants In nickel plating baths

Contaminant	Maximum Concentration, ppm
Aluminum	60
Chromium	10
Copper	30
Iron	50
Lead	2
Zinc	20
Calcium	pH dependent; will precipitate at the saturation point.

NOTE   The   limits   may   be   different   when   several contaminants are present at the same time, and complexing agents are a part of the solution formulation.

   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 from structures above the tank, from parts that fall into the solution and are not removed, etc. Table 8 lists maximum limits for metallic impurities in nickel plating baths. The degree of contamination by many inorganic materials may be controlled by continuous filtration and dummying; that is, electrolysis of the plating solution at 0.2 to 0.5 A/dm (2 to 5 A/ft^2). This may be accomplished on a batch basis or continuously by installing a dummy compartment and overflow dam at one end of the plating tank. Solution from the filter is pumped into the bottom of the dummy compartment, up past the corrugated cathode sheets, over the dam, into the plating 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 (for example, copper, zinc, lead) are removed simultaneously by this procedure.

Organic contaminants may arise from many sources including: buffing compounds; lubricating oil dropped from overhead equipment; sizing from anode bags; weaving 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 to 71^0C (140 to 160^0F), stirred for several hours with a slurry of 6 g/L (5 lb/100 gal) 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.

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 6^0C (10^0F) 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 6^0C (10^0F) or more above the normal plating temperature.

Effects of Impurities on Bright Nickel Plating

The presence of impurities is especially troublesome in decorative nickel plating. 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. Metallic contaminants affect bright nickel deposition in the following ways:

?? Aluminum and silicon produce hazes, generally in areas of medium-to-high current density. Aluminum and silicon may also cause a fine roughness called salt and pepper or stardust.

?? Iron produces various degrees of roughness, particularly at high pH.

?? Calcium contributes to needle-like roughness as a result of the precipitation of calcium sulfate when calcium in solution exceeds the saturation point of 0.5 g/L (0.06 oz/gal) at 60^0C (140^0F).

?? Chromium as chromate causes dark streaks, high current density gassing, and may cause 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 appear at any current density area, or they may be confined to narrow current density ranges.

?? 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 (higher current density), but are not necessarily confined to those areas.

Eliminating Rejects/Troubleshooting

The production of defective plated parts or rejects may be associated with the presence in solution of soluble and insoluble impurities. The nature of the coating defect is often an indication of the source of the problem. Common defects include roughness, pitting, blistering (often associated with poor preparation of the surface prior to plating), high stress and low ductility, discoloration, burning at high current density areas, and failure to meet thickness specifications.

?? *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 an insoluble material that is incorporated in the deposit. Insoluble particles may enter the solution from many sources and may be the result of incomplete polishing of the basis metal so that slivers 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, among others.

?? Roughness from incomplete polishing, cleaning and inadequate rack maintenance is avoided by good housekeeping, 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 demineralized 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; has too low a pH; or is inadequately agitated. Incorrect racking of complicated components; too low a concentration of wetting or anti-pitting agents; the 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* may be associated with poor adhesion resulting from poor or incorrect surface 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 the proper use of intermediate deposits such as cyanide copper, acid copper and acid nickel chloride strikes. Standard procedures for the preparation of materials prior to electroplating can be found in handbooks and in the *Annual Book of ASTM Standards*, Volume 02.05, published annually by the American Society for Testing and Materials, Philadelphia, PA. 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-base 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 organic and inorganic impurities. Solutions must be maintained in a high state of purity.

?? *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 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 can be caused by exceeding the recommended maximum cathode current density, and 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 (see Table 2). Another major cause of failure to meet thickness requirements is non-uniform distribution of current leading to insufficient deposit in low current density areas. Poor electrical contacts and stray currents can also cause thin deposits, and anode and cathode bars, hooks and contacts should be kept clean.

Controlling and Testing Deposit Properties

The requirements for testing electrodeposited nickel coatings may vary significantly depending on the application. In almost all 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. Quality can only be maintained by checking the thickness of a specified number of plated parts. In decorative, electrodeposited multilayer coatings, it is also important to control the sulfur contents of the deposits, the relative thicknesses of individual layers, the ductility of the semibright nickel layer, and the difference in the electrochemical potentials between individual layers. Requirements for corrosion performance and adhesion may also be specified and may require additional testing.

   In engineering and electroforming applications, it may be necessary to monitor the mechanical properties including hardness, tensile strength, ductility and internal stress, as well as wear resistance and other properties. Some of the more important test methods are briefly outlined below. Additional details can be found in the standard test methods collected in the *Annual Book of ASTM Standards*.

   ?? *Thickness* may be measured by a variety of techniques. The coulometric method described in ISO Standard 2177 and ASTM Standard B 504 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 de-plate a small, carefully defined area of the component under test. A cell is sealed to the test surface, filled with the appropriate electrolyte, and a cathode inserted. The component is made the anode and the circuit 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 de-plating is shown by a marked change in the applied voltage. For routine control of production, it is convenient to monitor nickel thickness non-destructively 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 is time-consuming, expensive and destructive.

   ?? *The "STEP" Test* was developed to measure the difference in electrochemical potential between semi- and bright nickel layers in multilayer nickel deposits on parts that are plated in production. It is similar to the coulometric method just described. By including a reference electrode in the circuit, however, it is possible to measure the electrochemical potential of the material being dissolved at the same time that the thickness of the individual layers is being measured. For example, 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 the overall corrosion resistance of the double-layer coating, and should be greater than 100 millivolts. Details can be found in ASTM Standard Test Method B-764 (*Annual Book of ASTM Standards*, Volume 02.05).

   ?? *Corrosion testing* may be specified and may require the plater to perform accelerated corrosion tests on a specified number of production parts as an overall quality assurance requirement. 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 test is the one most widely used. The CASS and Corrodkote tests were developed when conventional chromium was the only type of chromium available; when the accelerated tests are 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, as well as in ASTM Standards. The

salt spray tests involve the application of the corrosive solution in the form of a spray or fog inside a fog cabinet or room made or lined with glass, rubber or resistant plastics. The Corrodkote test involves applying a corrosive slurry to parts and exposing them to high, controlled humidity in a suitable chamber or cabinet; the slurry is formulated to simulate road mud containing corrosive salts. The CASS and Corrodkote tests were developed to control the quality of decorative, electrodeposited nickel chromium plated parts for exterior automotive use under severe conditions of corrosion and abrasion. CASS and other corrosion test requirements are specified in ASTM Standard Specification B 456 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.

?? *Ductility* testing is used in decorative nickel plating to test that the percent elongation of semibright nickel deposits is greater than 8, and to check that bright nickel solutions are in good working condition. The simple test described in ISO Standard 1456 and in ASTM B 489 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. Other tests based on hydraulic or mechanical bulge testing are available. The per cent elongation can also be determined by traditional mechanical testing by machining a test sample from relatively thick electroformed nickel and subjecting it to a tensile test. Since ductility is affected by the thickness of the coating, ductility should be measured at the actual thickness specified in a specific end-use.

?? Other useful tests described in ASTM Standards, include: adhesion (B 571); internal stress measurements with the spiral contractometer (B 636); microhardness testing (B 578), among others.

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 plated and influences metal distribution.

The simplest way to satisfy anode requirements is to suspend nickel bars from hooks placed on an anode bar, so that the nickel, not the hook, is immersed in the plating solution. Nickel anode materials are encased in cloth anode bags to prevent insoluble anode residues from entering the solution and causing roughness at the cathode. The use of bars or electrolytic nickel strip is still practiced, but has been supplanted in most regions of the world by the use of titanium anode baskets. The baskets used in nickel plating are generally 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. The basket anode is large and unchanging assuring a uniform anode area giving constant current distribution and consistent thickness for repeat batches of the same work. Anode maintenance 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 semi-automatically or automatically filled with nickel and that practice is growing in progressive plating shops. (One limitation is that titanium can not be used in concentrated

fluoborate solutions or those containing fluoride ions; small amounts of fluoride in solution activates titanium causing it to corrode.)

The available forms of nickel for titanium baskets include Inco high-purity electrolytic nickel squares about 25 x 25 mm; Inco R-Rounds electrolytic nickel 22 mm in diameter; and Inco S-Rounds electrolytic 25 mm in diameter. Other popular forms of nickel for plating with baskets are made in spherical shapes. Nickel Pellets for Electroplating (screened) are sulfur-free and S-Nickel pellets are sulfur-containing grades.

The sulfur-activated forms dissolve uniformly at high current densities and at 100% anode efficiency even in the absence of chloride ions, whereas sulfur-free forms dissolve non-uniformly and require the presence of chloride ions in solution to dissolve efficiently. The need for chloride ions is due to the tendency for pure nickel to become passive in nickel sulfate solutions. Although the tendency for passivity persists even in the presence of chlorides, the chloride ion attacks the passive oxide film that forms when current flows through the anode, and nickel can be dissolved through pits on the surface. The sulfur-containing materials do not form oxide films and dissolve at low anode potentials. The small amount of sulfur in the nickel lowers the resistance to current flow, the practical effect being to reduce power costs. The unique advantage of the spherical forms of nickel is product flowability which facilitates automatic basket-loading and filling of conforming, semi-cylindrical and other complicated basket shapes.

The anode affects the quality of nickel primarily through its effect on current distribution and thickness uniformity. Inco nickel anode materials are made to strict specifications of purity and are unlikely to introduce significant amounts of impurities into the plating process.

Environmental, Health and Safety

Strict environmental regulations are being imposed on the plating industry throughout the world. The major problem facing nickel platers is to prevent nickel and other metallic ions from entering the environment via plant effluents. The most widely used method of removing metallics from effluents is to precipitate nickel and other metals in sludges as hydroxides or sulfides. The solid waste is then disposed of in landfills. As the number of landfill sites is limited, and because disposal of solid waste is expensive and wasteful, the recovery of metal values by applying reverse osmosis, ion exchange, electrowinning and other methods is economically appealing. Nickel producers accept nickel-containing sludges for recycling through smelters or special plants. The recovery of metal values is technically possible and will become important in the future.

The environmental regulations are not uniform and vary from state to state. Platers need to become familiar with all applicable local regulations and comply with them. Although there was great resistance to compliance in the early seventies, most electroplaters in the United States 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 in plating operations that partially offset the cost of compliance.

The adoption and enforcement of strict environmental regulations arises 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 the nickel plating 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.

Although nickel and its compounds are not considered acutely toxic, it is advisable to avoid ingesting even small amounts of these substances by taking some simple precautions - wearing work gloves, washing one's hands before eating, and by not eating in the workplace. Some workers may develop a skin rash or dermatitis after persistent contact with nickel and its salts. People who have become so-sensitized should avoid contact with nickel and its compounds. To avoid *becoming* sensitized, one should limit skin contact with nickel and its compounds; in the plating shop, this may mean wearing work gloves and washing one's hands immediately after coming in contact with nickel plating solutions. On the basis of available information, enhanced risk of cancer appears to be confined to the inhalation of high concentrations of dusts containing nickel subsulfides and oxides under conditions previously existing in certain nickel refineries. Although similar health problems have not been observed in plating shops and other workplaces where nickel is found, it is recommended that precautions be taken to avoid dispersing nickel-containing dusts or sprays into the air. Airborne concentrations of nickel should be kept below the permissible exposure limits established by law. It is not only the law, but good common sense. Simple, basic, good housekeeping and personal hygienne can help prevent the release of toxic substances to the environment and minimize the possible effects of metallic contaminants on human health.