3.1 Introduction

Nickel is one of the most important metals applied by electrodeposition. The plate is used principally as a bright coating underneath a much thinner chromium electroplate to provide a highly lustrous and corrosion-protective finish for articles of steel, brass, zinc die castings, chemically metalized plastics, and, to a much smaller extent, for coatings on aluminum and magnesium alloys. The protection of the underlying metal depends primarily on the nickel plate, with the thin chromium overlay conferring a permanently nontarnishing, hard, wear-resistant surface. To a far lesser extent, and only for mild exposures, thin gold or brass electroplate with a clear lacquer finish is used as a decorative coating on thin bright nickel deposits. Nickel coatings alone are also used industrially to afford corrosion protection to prevent contamination of a product. Because of favorable mechanical properties, nickel electrodeposits are used for electroforming of printing plates, phonograph record stampers, foil, tubes, screens, and many other articles [1].

The history of the electrodeposition of nickel goes back more than 125 years [2]. It began in 1843 when R. Bottger described the first apparently sound nickel plate, which he obtained from a bath containing nickel and ammonium sulfates. Following the lead of Roseleur in 1849, Adams [3] in 1869 was probably the first to do nickel plating on a truly commercial basis. He, too, used double salt baths, including both sulfate and chloride, and was probably the first to recognize the importance of impurities [4] in the plating bath. He employed cast soluble anodes which contained silicon, iron, and carbon [5]. Remington [6] was the next to commercialize nickel plating. Believing that nickel could not be cast into anodes, he patented an anode basket of platinum wire to hold the cubes of nickel which were then available. Another claim of his patent involved electroformed nickel anodes. Up to 1913 many bath compositions were proposed [7]. The only early developments that have survived, however, are Weston’s introduction of boric acid into the bath [8], the use of chlorides by Bancroft [9] and others to promote anode corrosion, and the discovery about 1912 in the Elkington plant of Birmingham, England, that cadmium salts act as brighteners. Electrolytic nickel refining profited by the experience of the nickel plater and has made use of warm nickel sulfate-boric acid solutions since 1894.
Since 1915, the rate of development has been quite rapid. Among the mileposts the following should be mentioned: high-speed plating, begun by Watts with his famous "Watts bath" [10]; control of quality of deposits, first emphasized by Watts and DeVerter [11] and finally maturing into ASTM-American Electroplaters' Society specifications in 1935; accurate pH control, introduced by Thompson [12]; low-pH baths, suggested by Phillips [13]; commercial introduction of modern bright nickel plating begun by Schloetter [14] and the many major improvements of it; design of automatic plating equipment for high production rates; development of baths for the deposition of ductile, low-stress, high-leveling semibright and bright nickel coatings; the use of combination plates of sulfur-free semibright nickel followed by sulfur-containing bright nickel to give greatly improved outdoor corrosion protection; the use of highly porous bright chromium on these double-layered nickel deposits to give outstanding outdoor corrosion protection with minimum thicknesses of total plate.

3.2 Principles

The fundamentals of plating discussed in Chapter 1, together with the chemistry of the Watts bath [15], are essential to understanding the effects on the deposit and the relationship of such variables as bath temperature, nickel concentration, current density, pH, and agitation. The Watts bath opened the way for rapid plating of ductile nickel at elevated bath temperatures with high cathode and anode efficiencies. The modern Watts formula is more concentrated than the original, and it can be represented reasonably well by Nickel sulfate (NiSO4 • 6H20) 240-340 g/l; Nickel chloride (NiCl2 • 6H20) 30-60 g/l; Boric acid (H3B03) 30-40 g/l

3.2 FUNCTIONS OF CONSTITUENTS: THE WATTS BATH

3.2.1 NICKEL SULFATE

Most of the nickel ion content is contributed by nickel sulfate. This salt is used because it is the least expensive salt of nickel with a stable anion that is not reduced at the cathode, oxidized at the anode, or volatilized. It is also highly soluble and readily available commercially. The limiting cathode current density for sound nickel deposits is a function of the nickel ion concentration in the cathode film, which in turn depends on the metal ion concentration of the bath itself. The larger amount of nickel sulfate now used in the Watts bath not only raises the limiting cathode current density but also lowers the resistivity, thus improving plate distribution.
3.2.2 CHLORIDE ION

A principal function of the chloride ion is to improve anode dissolution by reducing polarization. It also increases the conductivity of the bath and has marked effects at the cathode. It increases throwing power as a result of increasing cathode efficiency, electrolyte conductivity, and slope of the cathode potential curve [16]. These effects are at a maximum in the all-chloride bath studied in detail by Wesley and Carey [17], and to a lesser degree in the high-speed bath developed by Pinner and Kinnaman [18] which contains chloride and sulfate in about equal normalities. The interesting effects of chloride ion in the cathode film have been studied [19] though more needs to be done with brighteners present.

3.2.3 BORIC ACID

Boric acid serves as a weak buffer in a nickel plating solution. Its principal effect is that of controlling the pH in the cathode film. In the absence of a buffer, nickel deposits at ordinary temperatures tend to be hard, cracked, and pitted, as shown by Macnaughtan [20]. Nevertheless, Blum and Kasper [21] produced excellent heavy deposits from unbuffered boiling electrolytes. Boric acid is obtainable in a very pure and inexpensive form, is nonvolatile and stable, produces whiter deposits, is helpful in its smoothing action on the deposit, and is unique in its cooperative effect with leveling addition agents. Its concentration is not critical in the Watts bath.

3.2.4 ANTIPITTING AGENTS

The cathode efficiency for nickel deposition is high in the Watts bath; nevertheless sufficient hydrogen ions are discharged that pitted plate results from slowly forming hydrogen gas bubbles clinging to the growing cathode deposit. To prevent pitted deposits, certain anionic wetting agents which do not appreciably affect the ductility or stress of the plate are used. Before the advent of bright plating using organic additives to produce bright deposits, hydrogen peroxide was used in the plain baths to prevent pitting, and is still used in some cases. When it is carefully used, dull nickel plate of very high ductility is obtained [22]. It functions by depolarization of the cathode with respect to hydrogen evolution, and by oxidation of traces of organic contaminants in the bath. The usual recommendation for a Watts bath is an addition, once a day, of 0.5 ml of 30% hydrogen peroxide per liter of solution. A grade free of organic and metallic stabilizers should be used, and localized additions next to the cathode should be avoided. An excess of hydrogen peroxide seriously
increases the tensile stress and causes burning, a decrease in the limiting current density for
the given plating conditions, and embrittlement of the plate. For this reason, the use of a
proper wetting agent should always be given first consideration (see the section on wetting
agents).

It is essential that oil, grease, and other undesirable organic contaminants be prevented from
entering the bath as these contaminants may make the peroxide as well as the wetting agent
ineffective.

Fractional percentages of cobalt derived from anodes or salts have no significant effect on the
properties of nickel deposits [23]. The effects of appreciable additions of cobalt have received
much study [23], and in general, the alloy plate is harder and more highly tensile stressed than
nickel (see Chapter 6). The effects of cobalt in semibright and bright nickel are discussed
under these headings.

3.2.5 COMPOSITION RANGES

The foregoing discussion of the functions of the ingredients of a Watts bath shows that
their concentrations can be varied over rather wide ranges. The typical formula is excellent
for an average cathode current density of 5 A/dm at a temperature of 50°C. Under such
conditions local, current densities of one-half or twice this value will still result in excellent
deposits. For plating at a lower average current density, for example 2 A/dm², the nickel
sulfate and nickel chloride contents may be halved. For higher current densities than normal,
their concentrations can be increased, but the practical difficulty of excessive dragout losses
and crystallization sets a limit to such changes. Current densities higher than 10 A/dm² are
better achieved by increase in agitation, temperature, and ratio of chloride to sulfate.

3.3 EFFECTS OF OTHER CONTROLLABLE VARIABLES

Other factors also influence the nature of the cathode film and thereby the quality of the
deposit. They are current density, temperature, pH, and degree of agitation or relative motion
of cathode and solution. These are all interrelated; if a variable such as current density is
altered considerably without the other factors being altered at the same time, adverse effects
on the deposit may be noted. For example, the typical modern Watts bath can be operated at
55°C and pH 2.0 to give sound, ductile, gray deposits at 6 A/dm² with a moderate degree of
agitation. If the current density is lowered to 0.2 A/dm² without reduction of the temperature
or increase of the pH, bright, brittle deposits will be obtained.
Phillips [13] showed that the range of permissible current densities is greatly extended at low pH, where smoother deposits are obtained mainly because of less tendency for the precipitation of ferric hydroxide from traces of dissolved iron. With good filtration, the difference in smoothness is negligible for baths of pH 2 to 4.5. This is especially true for decorative plate obtained at pH 3.5 to 4.5. Disadvantages of lowering the pH too far appear in the later discussion of current efficiency and throwing power. A bath operated in the pH range 3.5 to 2.0 is sometimes used for an original flash nickel coating on steel for producing a smooth, adherent, rather lustrous base plate for further plating of nickel from baths of pH 2.5 to 4.5, or of copper from acidic baths.

3.3.1 METAL DISTRIBUTION (THROWING POWER)

As discussed in Chapter 1, the electrochemical properties which determine metal distribution over a cathode of a given shape are cathode polarization, solution conductivity, and cathode efficiency. A steep slope of the cathode potential-current density curve, a small or negative slope of the cathode current efficiency-current density curve, and a low specific resistivity of the electrolyte favor more uniform metal distribution or higher throwing power. How these characteristics of a Watts bath are affected by changes in the plating variables indicates their probable effect on throwing power.

The specific resistivity of the Watts bath is about 11 ohm-cm at 60°C, and it decreases in the usual way with increase in temperature [24]. It also decreases with increasing total concentration [24] and increasing chloride ion concentration [17]. It is but little affected by pH within the range 2.0 to 5.5 [16].

Like the cathode efficiency of all nickel plating baths, that of the Watts bath rises with increase in current density until the limiting current density is reached. It also rises with increase in temperature and with total concentration [24, 25]. Increase in chloride ion concentration has a more markedly beneficial effect, but the effect of pH is the most pronounced: The current efficiency decreases rapidly with a fall in pH [16, 24]. Typical cathode efficiency curves for nickel plating baths are given in Figure 1 taken from Wesley and Roehl [16], who also studied the variation of cathode potential with current density.

Fig. 1 Typical cathode efficiency-current density curves according to Wesley and Roehl [16]. A, hard bath; B, Watts, pH 5.5; C, Watts, pH 2.0; D, chloride bath.

The throwing power of the Watts bath is slightly improved by an increase in pH, temperature, and nickel and chloride contents [24, 25]. At high current densities, the low-pH Watts bath is only slightly inferior to other Current density, A/dm2 nickel baths in throwing
power, and can be made superior by sufficient increase in its chloride content [16]. High throwing power in acidic nickel baths can be obtained by using low nickel salt concentration, for example, 100 to 120 g/l NiSO4 • 6H2O, and high sodium chloride concentration of 160 g/l, with 30 g/l boric acid, pH of 4, 50 to 60°C, and no agitation [212]. However, the average cathode current density that can be used without burning is about 2 A/dm2. Agitation greatly diminishes the throwing power of such baths. This bath can be made to produce bright, stress-free, high throwing power, leveling nickel plate by the use of class I together with class II addition agents (see the section on bright nickel).

Harr [24] noted that hydrogen peroxide reduced the throwing power of the low-pH bath, but the effect did not last long after the addition had been made. He found that iron(III) sulfate is very detrimental to throwing power, but iron(II) sulfate is not. Watson [211] has shown that the throwing power of nickel plating solutions can be accurately determined using a Hull cell with proper techniques.

3.3.2 STRUCTURE AND MECHANICAL PROPERTIES OF DEPOSITS

Roehl [26], Brenner et al. [23], and Heussner et al. [27] reported a wealth of data on the effects of pH, temperature, current density, and solution composition on the metallographic structure and mechanical properties of nickel deposits from the modern Watts bath. These effects can be summarized in a general way as follows.

When plated at 55°C and pH 2.0, deposits show a columnar or conical structure which grows coarser with increasing thickness. Grain refinement occurs as the pH or the chloride content is increased or the temperature is decreased. The effect of current density varies with conditions. The hardness, tensile strength, and ductility of nickel deposits are almost always consistently related; that is, an increase in hardness is accompanied by an increase in tensile strength and a decrease in ductility.

Soft, ductile deposits are obtained at pH 4.5 or lower. For example, a tensile strength of 35 kg/m m2, an elongation of 37%, and a Vickers diamond pyramid hardness (10-kg load) of 100 were observed by Roehl [26] in nickel deposited at pH 4.5. As pH was decreased below 3 the hardness rose slowly, but as pH was increased above 5 it rose rapidly, with a corresponding increase in tensile strength and reduction in ductility.

Current densities over the range 1 to 5 A/dm had little effect on the mechanical properties of the deposit from the low-pH bath, but at pH 5.0 there appeared to be some decrease in hardness and tensile strength with increasing current density in this range. Brenner and Jennings [28] obtained a Knoop hardness (200-g load) of 175 in a bath at pH 3.0 and a low current density of 1 A/dm z. They found that the hardness reached a minimum of 135 at
4 A/dm² and then increased slowly with further rise in current density. An increase, in
temperature of the electrolyte had the expected effect of decreasing hardness and tensile
strength and increasing ductility.

The increase in hardness and strength of nickel deposits produced at high pH has been
shown by Macnaughtan et al. [29] to be related to the amount of occluded basic compounds
of nickel. These are believed to be codeposited in a finely divided or colloidal form dispersed
through the nickel lattice in such a way as to interfere with slip.

Nickel can be deposited with a wide variety of metallographic structures and with
controlled physical and mechanical properties over a wide range of values. When other than a
soft, ductile nickel is required, additives or bath compositions quite different from the Watts
solution are employed (see the section on heavy nickel plating).

3.3.3 STRESS

An important, complex, and not very well understood characteristic of nickel deposits
is that all are deposited in a condition of internal contractile (tensile) stress. Class I and Class
II addition agents (see the section on bright nickel) greatly affect the stress. The internal stress
in nickel plate has received extensive study [35, 37, 38], more than for any other plated metal.

The stress that arises independently of the substrate is called the intrinsic stress. It is
superimposed on an extrinsic stress induced by the substrate, though the effect of the latter is
only in the first thin layers of the deposit. The stress of primary interest to electroplaters is the
elastic tensile or compressive stress which can be measured by mechanical means, and this is
what is generally meant when the word stress is used in electroplating. This stress is also
referred to as macrostress or type I stress [38]. Its magnitude is important since excessive
tensile stress in nickel deposits can not only lead to gross cracking of the plate but also can
cause distortion of electroforms. These problems accelerated the development of methods to
measure such stresses quantitatively [28, 32-37]. Measurements were primarily based on the
amount of bending of a strip, nickel plated only on one side.

Besides the elastic macrostress, there are microstresses which have been classified as
types II and III stresses [38]. Microstresses do not cause macroscopic deformation and can be
determined only by methods such as measurement of X-ray line widening. In the theoretical
work of Hoar and Arrowsmith, Kroner, Popereka and others, on the origins of internal stress,
the theory of dislocations in metals has been used as the basis for an overall theory [37, 38].
For example, the movement of dislocations to the grain boundaries may be the cause of tensile stress according to Popereka [37]. The regulated incorporation of the sulfide anion, which is larger than the nickel cation, appears to be an important factor in the origin of compressive stress in nickel. The larger size of the sulfide anion and its effect on increasing the rate of nucleation would favor expansion at the grain boundaries [38]. The extensive literature on the origins of stress in electrodeposits and the methods of measurement has been reviewed by Weil [38].

3.3.4 Effect of Bath Variables.

Regardless of the mechanism, the practical plater wants to know how the major plating variables influence internal stress in nickel deposits. The preponderance of evidence supports the following conclusions:

1. Tensile stress increases with increase in chloride content of the bath.
2. 2. The effect of bath temperature on stress is not consistent; it varies with the composition of the bath (principally the chloride content) and the current density.
3. 3. The effect of pH varies with composition of the electrolyte; however, for a Watts bath it is definitely advisable to keep the pH below 5, not only because deposits with lower stress are obtained but also because the harmful effects of some impurities on stress may be much more pronounced at pH 5 or above.
4. 4. The effect of current density is not marked over the range 1 to 5 A/dm2 but is usually in the direction of an increasing tensile stress with increasing current density.
5. 5. Superimposing alternating current on the direct plating current tends to reduce stress, other conditions remaining the same.
6. 6. Agitation has little effect in purified plain Watts baths. In bright plating baths containing excessive concentrations of class II brighteners or harmful impurities, decreased agitation (decreased diffusion rate) will result in decreased tensile stress.
7. 7. Hydrogen peroxide, dissolved inorganic impurities such as lead, zinc, iron, chromium, aluminum, and phosphate, organic impurities such as sizing from
unwashed anode bags, amines from improperly cured rubber linings, and excessive concentrations of class II brighteners can all act to increase the tensile stress seriously.

8. Fluorides and fluoborates tend to reduce tensile stress slightly. Class I brighteners can decrease the tensile (contractile) stress to zero and then with increasing concentrations, reverse the direction so as to make the nickel expand or be under compression if restrained from expanding. These organic sulfon compounds add sulfur as sulfide to the nickel deposit, increasing the hardness of the deposit and its tensile strength, but decreasing its ductility and making the plate very brittle (sulfur embrittlement) when heated to temperatures above about 370°C [42]. Adhesion to steel is not lost, however.

9. Stress may be induced into the first thin layers of a plate that is deposited on a structurally different substrate with different lattice spacing or on a substrate that has a high internal stress in the surface. Highly tensile stressed nickel plate can cause the usual thin, highly tensile stressed decorative chromium plate to stress crack at the same time as the nickel stress cracks from the added tensile stress of the chromium plate.

3.3.4 Effect of Bath Variables.

It is important to differentiate between the deleterious effects of high stress and lack of ductility. There are no predictable relationships between hardness, brittleness, and stress. Relatively soft deposits from the Watts bath may be highly stressed in tension and show good ductility, whereas nickel deposited in the presence of sodium naphthalene trisulfonate can show zero stress with a Vickers hardness of 540 and a low ductility [35].

3.3.5 EARLY NICKEL PLATING PROBLEMS

Nickel plating had about a 50-year history in the plating of polished brass and steel articles before the advent of commercial chromium plating in 1924. The nickel plate was comparatively pore free and protected the underlying metal very well. It was deposited from plain inorganic baths and the dull plate was polished. With the introduction of chromium plating, it was first thought that this thin, hard, nontarnishing plate would replace nickel plating, but it was soon found that thin chromium deposited directly on brass plumbing goods
became discolored from green corrosion products formed from the brass through minute pores in the thin chromium plate. A galvanic couple forms under moist conditions with the passive chromium surface becoming the cathode, and brass exposed in the pores of the chromium plate the anode, of the corrosion cell, and with the unfavorable condition of large cathodic areas and small anodic areas, pitting corrosion results. The corrosion proceeds with undercutting of the chromium plate, resulting in flaking off of pieces of the hard, brittle chromium and the accumulation of unsightly greenish brass corrosion products. Even to this day, brass plumbing goods are sometimes directly plated with chromium, especially in times of nickel shortages, or when manufacturers do not have plating specifications. It was soon realized that applying the very thin chromium plate on top of nickel plate solved the tarnishing problem with nickel, and the poor corrosion protection with thin bright chromium plate alone. With an undercoat of 3 to 9 Asm of nickel, nickel-chromium plate on brass plumbing goods will last the life of the fixtures, whereas without the nickel undercoat, the brass goods look unsightly in about a year or less.

The cost of buffing the dull nickel plate to a high luster, and the problem of cutthroughs stimulated the search for addition agents to produce bright ductile plate directly from the plating bath.

3.3.6 THE BRIGHT NICKEL BATHS

The nickel baths to which brighteners, mainly bath-soluble organic compounds, are added, are mostly of the Watts type but with widely varying proportions of chloride and sulfate. Boric acid is always present, usually not less than 35 g/l. Conditions in the cathode film must be favorable not only for the deposition of nickel but also for the functioning of the brighteners. The most important brighteners function best at pH values of about 3 to 5 and bath temperatures of about 50 to 65°C.

The unique decorative and corrosion-resistant coating that can be obtained with nickel plate underneath a thin, hard, wear-resistant, and non-tarnishing chromium plate was responsible for the intensive research that led to the development of modern bright nickel plating. These brighteners have received more attention than those for any other plating bath, owing to the economic importance of eliminating the expensive polishing of dull nickel deposits, and the fact that the organic brighteners for nickel were definite compounds and therefore their mode of action could be more accurately studied.

The nickel brighteners fall into two distinct classes. Aromatic sulfonic acids, sulfonamides, and sulfonimides have been designated class I nickel brighteners. The aromatic rings to which
the sulfon group is attached are generally benzene and naphthalene rings. These brighteners produce almost bright or cloudy bright plate on buffed surfaces but are unable to build higher luster with continued plating. Class I aromatic sulfon brighteners have no critical upper concentrations and are used in relatively high concentrations (1-10 g/l) without significantly affecting the adhesion and the limiting current density. They decrease the tensile stress of the deposit and can with increasing concentrations endow the plate with compressive stress. Sulfur is introduced into the plate, about 0.03% at pH values of 3 to 5 when the class I compounds are used in warm baths without class II brighteners. The sulfur is present as sulfide, and the plate is harder and of higher tensile strength, but less ductile than the normal dull Watts nickel plate. Nevertheless, the plate is surprisingly ductile considering its hardness. Class I brighteners are often used in the electroforming of intricately shaped articles because with control, a very low or zero stress in the resulting nickel deposits is possible.

The brighteners designated as class II nickel brighteners are used together with class I brighteners to obtain a brilliant leveling deposit of increasing luster with continued plating to the point of highest luster. Class II brighteners are principally unsaturated compounds [43] which produce the leveling and increased luster of the deposit when used in conjunction with class I brighteners. They introduce carbonaceous material into the plate [30, 44]. Most class II brighteners cannot be successfully used alone to obtain bright plate because they produce excessive brittleness and tensile stress, and inferior adhesion to the substrate. A certain few class II compounds, especially coumarin, which are used to obtain ductile, semibright, sulfur-free nickel plate do make possible ductile, bright, or almost bright plate but with decreased leveling when extremely high rates of solution agitation are used, unlike the case of normal use with the usual agitation which aids leveling. It is also true that higher concentrations of coumarin above the optimum cause brighter plate but with decreased leveling.

3.3.7 CLASS I NICKEL BRIGHTENERS

The first brighteners of this class were the alkyl naphthalene sulfonic acids proposed by Lutz and Westbrook [45]. The commercial grades of these compounds were impure. The impurities resulted from the synthetic methods used in their large-scale preparation, and the materials as such caused brittle plate and were never used in practical nickel plating. These compounds were wetting agents and the plates obtained were free from pitting. Schlotter [14] introduced benzene and naphthalene di- and trisulfonic acids, without substituent groups, and these were successfully used commercially. They were far better than materials such as gum tragacanath and similar critical materials that only could be used for very thin deposits; otherwise the internal stress in the plate together with its brittleness would cause cracked,
peeled plate. Schlotter's sulfonic acids were not critical in concentration and did not cause poor adhesion or cracked plate with thick deposits; however, good brightness could only be obtained on buffed surfaces and even then it left much to be desired. Waite [46, 47] used zinc sulfate in small concentrations in conjunction with naphthalene sulfonic acids; Harshaw and Long [48] used selenious oxide and Lind et al. [68] used dyes in conjunction with naphthalene sulfonic acids to obtain greatly improved brightness and moderate leveling, and these baths, especially Lind's, came into extensive use in the American automobile industry in 1937-1939. Brown [49] introduced the use of the benzene sulfonamides and sulfonimides including saccharin, and indicated the prime importance of the unsaturation of the benzene ring, in that cyclohexyl sulfonic acid or sulfonamide as well as other pure saturated sulfon compounds such as methyl, ethyl, propyl, or butyl sulfonic acids were not nickel brighteners [50, 51]. Based on this work [49] the unsaturated aliphatic sulfon compounds, vinyl and allyl sulfonamides, and sulfonic acids [50, 51] were developed. These compounds are generally classified as class I nickel brighteners because they are sulfon compounds which like the plain aromatic sulfon compounds decrease tensile stress and introduce similar concentrations of sulfide sulfur into the plate. However, they also introduce carbonaceous material into the plate and give improved brightness. Later, propargyl sulfonic acid and 2-butyne-1,4-disulfonic acid [52] were developed. Meanwhile, Hoffman [53, 54] had added styrene ti-sulfonic acid and Freed [55] had added benzaldehyde o-sulfonic acid (o-sulfobenzalde-hyde). Shenk added diaryl sulfonimides [56].

The unsaturated aliphatic sulfonic acids listed above as well as o-benzoyl sulfimide, ortho- or metasulfobenzaldehyde, p-vinyl benzene sulfonic acid [57], and pyridine-3-sulfonic acid [58] give bright nickel plate in the presence of high concentrations of chloride (over 150 g/l NiC12 • 6H2O). Plain benzene and naphthalene sulfonic acids do not give bright plate in these high-chloride baths.

Benzene sulfinic acids [58] are more effective than the benzene or naphthalene sulfonic acids and benzene sulfonamides or sulfonimides in increasing the tolerance of the bath, Watts or high chloride, to excess of inorganic impurities, or excess of class II brighteners that cause poorly adherent, peeled, or dark plate or misplating in low-current-density areas. The sulfinic acids undergo oxidation by air to the sulfonic acids.

All of these class I nickel brighteners undergo hydrogenolysis at the nickel cathode; for example, naphthalene sulfonic acid yields naphthalene at the cathode at the same time sulfide is incorporated into the plate [43, 49, 60, 61]. It appears that the benzene and naphthalene sulfonic acids are hydrogenolyzed to benzene and naphthalene, respectively, plus the bisulfite anion; the latter is then reduced at the cathode to sulfide which is incorporated into the plate
The benzene or naphthalene rings are not hydrogenated [60] and carbon or carbonaceous material, as far as can be ascertained, is not added to the plate [30]. With more complex class I compounds such as o-benzoyl sulfimide, the benzene ring is also not hydrogenated [61]. The incorporation of sulfur into the plate follows an exponential curve of the form of an adsorption curve. Sulfur incorporation increase; with increasing concentration of class I sulfon brightener and reaches a maximum for a given pH at a given bath temperature [40], for example, about 0.04% at 30°C and about 0.03% at 60°C and pH of 3. Further increases in concentration of the class I brightener produce no appreciable increase in sulfur content of the plate. In order for hydrogenolysis or hydrogenation to occur, it must be assumed that the compounds are adsorbed on the freshly forming nickel surface, and a freshly forming nickel surface would be an excellent hydrogenation catalyst similar to Raney nickel.

With the α- and ω-unsaturated aliphatic sulfonic acids, about 90% of the compounds are hydrogenated to the saturated sulfonic acids. The remaining 10% undergoes hydrogenolysis with incorporation of nickel sulfide into the plate, and also with incorporation of carbonaceous material as shown by Beacom and Riley [62]. The incorporation of carbonaceous material apparently results from the irreversible adsorption of some of the unsaturated aliphatic remnant after the hydrogenolysis. The unsaturated aliphatic sulfonic acids are not brighteners when the nickel baths have pH values of about 3.5 or lower. Under these conditions, practically the entire cathodic reaction is rapid hydrogenation of the unsaturated linkage without hydrogenolysis of the sulfonic group and without appreciable incorporation of sulfur into the deposits. This is unlike the benzene and naphthalene sulfon compounds which still function as brighteners at these low pH values, and in fact incorporate about twice as much sulfur in the plate as when bath pH values are 3 to 5 [63]. This difference between the unsaturated aliphatic and the aromatic sulfon compounds is that while the aromatic ring may be adsorbed on the nickel cathode, it is not hydrogenated, and in this sense it is reversibly adsorbed. With the unsaturated aliphatic sulfon compounds, it is evidently easier to hydrogenate the unsaturated linkage than to fission by hydrogenolysis the carbon-to-sulfur bond.

If the unsaturated linkage in the unsaturated aliphatic sulfonic acids is in the 7 position to the sulfon group, instead of in the α or ω position as in the aliphatic sulfon compounds discussed above, then the compounds introduce practically no sulfur into the nickel plate and thus turn out to be not class I but class II nickel brighteners [52, 112]. The 7 -unsaturated linkage is hydrogenated, but the carbon-to-sulfur linkage does not undergo apprecia-ble hydrogenolysis at the nickel cathode because there is practically no electronic inductive effect extending over two carbon atoms from an unsaturated bond. For these reactions, at the nickel cathode the ionic mechanism of hydrogenation and hydrogenolysis appears logical [58]. Incorporation of
sulfur into the nickel plate [227] is not the sole criterion for class I nickel brighteners. The essential group in the sulfon compound is C=C—SO₂—, C—C—SO₂—, or CE—C—C—SO₂—. If the —SO₂— group is part of an ester linkage as in organic sulfates, there is also no incorporation of sulfur into the nickel plate, and the compounds are not class I nickel brighteners. It is interesting that saturated sulfinic acids such as methyl sulfinic acid, CH₃SO—OH, cause sulfur incorporation. For example, 0.3 g/l of methyl sulfinic acid causes the incorporation of about 0.05% sulfur into the nickel plate; nevertheless, it is not a brightener used either alone in the Watts bath or in conjunction with class II brighteners [58].

Unsaturation, aromatic or aliphatic, is a necessary qualification for the anionic sulfon and sulfinic class I nickel brighteners [43]. If certain substituent groups such as aldehydo or halogen are present on class I compounds, improved brightness may sometimes be obtained, whereas if amino or nitro groups or alkyl chains are present on the benzene ring of class I compounds, the compounds may not even function as class I brighteners and may even be harmful to the plate. In the latter cases, the harmful substituent groups seriously change the adsorption characteristics of the compound [64].

3.3.8 BRIGHTENER REACTIONS AT THE CATHODE

Henricks _ [65] early noted that class I brighteners were anionic compounds, that is, the active portion was an anion, and that many of the class II addition agents were cationic; he suggested that they function by an adsorption mechanism similar to that for corrosion inhibitors. He also suggested that the banding in bright nickel plate was similar to Liesegang phenomena, and that the brightening mechanism usually involved an organic addition agent working in conjunction with an inorganic colloid (nickel hydroxide in this case), forming in the cathode film. More recently, polarization and cathodic impedance studies have shown that the electrocrystallization of nickel apparently occurs in several steps, and that an adsorbed species of nickel hydroxide is formed as an intermediate and is consumed during electrodeposition [80, 217]. Addition agents appear to modify the rates of the electron transfer reactions involving the adsorbed species of nickel hydroxide [80].

The growth rates of the various crystal faces of the deposit from plain acidic nickel baths are unequal and the columnar structure grows progressively coarser with continued plating on smooth polycrystalline surfaces [31, 80]. With the use of brightener additives, the change in electrocrystallization is dramatic. The striking effects produced by small concentrations of brighteners indicate their adsorption on growth sites, on points and edges of crystals, dislocations, and possibly preferentially on certain crystal faces, producing an inhibiting effect on the most active growing sites [161, 162, 206].
The adsorption of the unsaturated addition agents on the nickel and their subsequent desorption after hydrogenation [93] is not necessarily the essential reaction for their functioning. Very important are the irreversible steps which also occur with the inclusion of the brightener, or a hydrogenolyzed portion of it, as in case of class I brighteners [40, 58, 64]. With most class II brighteners, the exact nature of the inclusions is not clearly established except for the case of some cationic compounds [30, 64, 66] and the large cationic aniline dye, fuchsin, which is included as such [67, 68].

With class I nickel brighteners, the key factor appears to be the adsorption on the nickel cathode through an unsaturated linkage, aromatic, or aliphatic in a or i3 position to the sulfon group, as the necessary step for hydrogenolysis of the carbon-to-sulfur bond. The subsequent further reduction of the resulting bisulfite ion with its positive sulfur of oxidation number two less than the maximum results in the controlled incorporation of sulfur into the nickel deposit [40, 58]. Edwards [40] has deduced that there are only a certain number of effective sites available for the class I compounds, which, however, may be increased by the presence of other additives, especially by amine nitrogen containing class II nickel brighteners that have critical concentration ranges in the bath. In some cases, the number of adsorption sites available to class I compounds is not increased but may even be slightly decreased by the presence of certain class II nickel brighteners that have practically noncritical concentration ranges in the bath as far as the mechanical properties of the plates are concerned. Formaldehyde and especially coumarin and trimethyl aconitate are examples of such compounds and are additives which can be used alone in the Watts nickel baths to give semibright, ductile, sulfur-free plate. It appears that such compounds as coumarin and trimethyl aconitate compete with class I brighteners for the same adsorption sites, which may be the reason for their similarity to the class I compounds in noncriticality with respect to high concentrations in the Watts bath [40, 41]. In this respect, these compounds are unique class II compounds and deserve a special subclassification, as pointed out by Levett et al. [41]. These compounds are further discussed under the topics of class II nickel brighteners and semibright nickel plating.

3.3.9 CLASS II NICKEL BRIGHTENERS

The brighteners designated as class II nickel brighteners are the ones used in conjunction with class I brighteners to obtain brilliant leveling nickel plate. The most effective class II brighteners are bath-soluble organic compounds containing unsaturated groups [43, 69, 70] such as the aldehydic HCEO group as in formaldehyde [71] and bromal [72]; the olefinic C=C group as in coumarin [73]; the linkage [74] as in dimethylethynylcar-
binol and butynediol; the C=N group as in pyridine or quinoline and their quaternary salts [75]; and the 07=N group as in ethylene cyanohydrin [76]. The aldehydic group is the least effective in leveling, and the C=N as in pyridine, quinoline, and isoquinoline and the CEC linkage as in acetylenic alcohols and amines are the most effective in leveling and brilliance.

This does not mean that every bath-soluble organic compound containing an unsaturated linkage will be a good class II nickel brightener; for example, acetylene dicarboxylic acid is very harmful in a Watts nickel bath used either alone or in conjunction with class I nickel compounds [77], causing dark, brittle plate with no leveling. Mixtures of unsaturated compounds are often used together with mixtures of class I compounds to obtain maximum bright plating ranges, maximum leveling, or maximum ductility for a given rate of leveling.

There are cations, such as zinc and cadmium ions, which in small concentrations improve the brightness obtained with class I compounds. Saturated amines improve the brightness, but without aliphatic unsaturated linkages, high leveling does not occur with these amines. Saturated, soluble alcohols such as ethyl or propyl alcohol, butanediol, have no effect on the plate. Unsaturated allyl and propargyl alcohol, butenediol, and butynediol, are class II nickel brighteners.

It is interesting in this connection that for the strong leveling class II brightener pyridine, an amino or carboxylic acid group on a carbon atom of 7 the ring is detrimental to its effectiveness as a class II nickel brightener. A sulfonic group on a carbon atom of the pyridine ring converts pyridine from a class II to a class I brightener [58]. On the other hand, a sulfonic group attached to the nitrogen atom of the pyridine ring through an intermediate small alkyl group actually improves the pyridine as a class II brightener even though higher concentrations are needed for optimum leveling results [78].

In general, long alkyl chains, too many alkyl groups, phenolic OH groups, and carboxylic acid groups are detrimental to brightness and leveling.

The efforts to improve organic addition agents, that is, to make possible maximum beneficial effects with minimum harmful effects and noncritical-ity, are based on the study of the structures of organic compounds with various functional groups and are similar in many ways to the effort to obtain optimum sulfa drugs and the like. Such studies on addition agents are always linked to the improvement of production plating for the attainment of maximum brightness with minimum metal plate and minimum rejects, and with maximum corrosion protection and consistent plating quality. It is for these reasons, and the fact that nickel plating rejects are very costly, that processors rely on the services of supply houses [79].
In 1936, a bright nickel alloy plating bath containing cobalt (see Chapter 6) in low concentrations was developed by Weisberg and Stoddard [71] and also by Hinrichsen [81] which did not use a class I brightener and the plate from which did not contain sulfur. It was much more prominent in the U.S. than the original Schlotter bath. The alloy plate contained about 15% cobalt. Vigorous air agitation was used, without which the plate would have been cloudy. The brightness depended on the use of formate buffer in addition to boric acid; also, to maintain the brightness with thicker plate, low concentrations of formaldehyde and ammonium ion were employed by Weisberg and Stoddard. The plate was bright on fully bright substrates such as buffed brass or buffed copper. The bath did not produce leveling plate, and mainly for this reason, did not survive for bright plating. Present-day bright nickel-cobalt baths produce leveling plate [200].

3.3.10 LEVELING

In addition to producing a lustrous surface, the modern nickel baths used for decorative-protective plating have leveling properties which make possible the filling in, that is, the leveling of polishing scratches and microirregularities in the surface of the substrate, and thus reduce or eliminate expensive polishing and buffing operations. The peculiarities of metal plate distribution on microirregularities in the substrate were first observed by Meyer in 1935 [82]. (See Chapter 3.)

Acidic nickel plating baths have a low concentration polarization, that is, the baths have a high concentration of dischargeable ions over microirregularities in the cathode surface, and as a result have good microthrowing power and comparatively poor macrothrowing power. Geometrical leveling from plain nickel baths is relatively unimportant compared to the exceptional microthrow or true leveling which is obtained in nickel baths with the use of certain class II addition agents such as coumarin or trimethyl aconitate in semibright nickel plating, or with the combination of class I and class II addition agents in high-leveling bright nickel plating baths. Leveling, or smoothing out of surface imperfections with the use of addition agents, was mentioned in the patent literature [68, 72], but it was Gardam [83, 92] who suggested the correct basis for the mechanism. He studied the leveling of nickel plate from baths containing addition agents such as zinc, cadmium, and iron, and from this and a study of the brightness produced by aromatic sulfonates, he suggested that as a result of diffusion, micropeaks receive and have deposited on them above average amounts of addition agents which increase the local resistance and thus reduce the local current density on the peaks with respect to the microgrooves.
With the development of excellent leveling baths, various shaped surface imperfections were used for a detailed study of leveling. Du Rose and co-workers [213, 219] studied the strong leveling of a semibright, sulfur-free nickel. Thomas [84] used electroformed replicas for reproducible V-shaped microdepressions of varying depths and with varying angles for his study of leveling. Foulke and Kardos [85] used phonograph record grooves for microprofiles as did Watson and Edwards [86]. Raub [87] used larger V-shaped profiles and cylindrical cavities to study the transition from micro-to macrothrowing power. Beacom and Riley [88] found a greater codeposition rate of radioactive tagged addition agents on peaks and measured the thickness of the diffusion layer over the peaks and recessed areas. Rogers et al. obtained similar results with thiourea [89].

Kardos [90] and Watson and Edwards [86] at about the same time proposed the now accepted theory of leveling based on the influence of the local variation of the effective thickness of the diffusion layer on local polarization. Kardos and Foulke [91, 92] have reviewed the history and theory of leveling. Leveling depends on the relationship of the mass transport of a high concentration of dischargeable ions and the low concentration of the leveling agents, most class H addition agents, into the diffusion layer which has a greater thickness directly over a scratch or microgroove compared to the edge of the scratch or the flat portion. It is also necessary for the pH of the nickel bath to be in the range of about 3 to about 5.5 for the best leveling action to take place, and the only buffer that usually can be used for maximum leveling is boric acid, though small concentrations of other buffers may also be present.

Kruglikov [203], Reinhard [214], Leidheiser [215], Elze [216], Bertorelle [201], and their co-workers have also made important contributions to the study of leveling phenomena [91, 92].

The best results from the standpoint of ductility and consistent quality as well as maximum leveling for semibright, sulfur-free plate are obtained in Watts baths of low chloride content. The best results from the standpoint of highest leveling for the bright nickel baths employing class I together with class II compounds are obtained not only in Watts baths but also in high-chloride and sulfamate baths. Fluoborate baths give ductile plate, but the leveling is, relatively poor for both-serie bright, sulfur-free plating and for fully bright plating. The sulfamate baths for semibright, sulfur-free nickel can give inconsistent results, especially on prolonged use, probably because of the decomposition of sulfamate anion on polarized anodes.

The leveling agents cause the incorporation into the plate of carbonaceous material. Whether it is adsorbed leveler, a dimer, or a polymer has not been clearly established [40, 66]. The percentage incorporated is higher in low-than in high-current-density areas [66]. This is true
for the organic levelers as well as for zinc and cadmium. The leveling agents are consumed at a higher rate than the class I aromatic sulfon compounds. High pH of 4 to 5 favors leveling.

It has been reported [197] that with pulse plating, a bright Watts nickel deposit can be obtained on a bright substrate without the use of additives.

3.3.11 WETTING AGENTS

Certain anionic wetting agents are used in nickel baths to prevent bubbles of hydrogen from adhering to the cathode and causing pits in the deposit. They function by reducing the surface and interfacial tension, and with the correct wetting agent the contact angle between the liberated hydrogen bubbles and the cathode is reduced to zero. The bubbles disengage before they can grow to a size to cause pitting by blocking the plating at the point of contact of the bubbles. Sulfates of normal primary alcohols containing from 8 to 18 carbon atoms [94], in concentrations of 0.1 to 0.5 g/l, were the first successful wetting agents used commercially in bright nickel plating baths. Sodium lauryl sulfate, free from lauryl alcohol, was the most extensively used wetting agent of this class. It is important for ductile dull nickel plating that the wetting agents have no adverse effects on the deposit, and in this respect, these wetting agents are unique. Very few others can be used, and none other in ductile dull nickel plating. Sodium lauryl ethoxy sulfate or sulfonate [95] can be used in semibright and bright nickel baths.

When air agitation is used in the nickel plating to make possible the use of higher current densities, the chain length of the wetting agent should be six to eight carbons, and mildly branched chains of a total of eight carbons can be used in these cases. The shorter chain sulfate or sulfonate wetting agents do not cause overfoaming with the air agitation, and since agitation with clean air is itself active in antipitting, the normally less effective shorter chain surfactants are usually sufficiently effective. Extremely fine bubbles of air, as from air leaks in pumps causing emulsified air, can cause fine pitting. Another value derived from the use of the wetting agents is the diminished dragout of nickel salts because of the fast runoff from points and edges of the articles due to the low surface tension. Activated carbon removes the wetting agents from the bath, especially the longer chain compounds. Bright or semibright nickel baths containing certain unsaturated addition agents which function by depolarization of hydrogen are seldom subject to pitting when clean conditions are maintained and air agitation is used. Formaldehyde, various unsaturated aliphatic sulfonic acids, and monosulfobenzaldehydes are effective in this respect. Nevertheless, even in most of these cases, the use of wetting agents is still desirable.
Traces of nonionic wetting agents, 1 mg/l and less, have been used to suppress "honeycombing" in thick cathode deposits in the electrodrefining of nickel [199].

### 3.4 ADVANCES IN CORROSION PROTECTION

The bright nickel plating baths which were developed starting in 1934 were continually improved. After the end of the World War II, the use of bright nickel-chromium plate expanded very rapidly. For indoor or mild exposures, the corrosion protection afforded by bright nickel-chromium plate was satisfactory, but it became apparent after 1945 that the sulfur-containing bright nickel with the final thin chromium plate was not giving satisfactory corrosion protection to steel- or copper-plated zinc die castings on the exterior of automobiles.

The automobile industry forced the development of composite decorative nickel-chromium plate that would provide greatly improved corrosion protection of the underlying metal against damp, acidic industrial atmospheres, and against the very high concentrations of salt used in large northern cities to de-ice the streets in winter [96]. These improvements for outdoor corrosion protection started with the development of ductile, semibright, sulfur-free nickel plate.

#### 3.4.1 SEMIBRIGHT NICKEL PLATING

In 1945, Du Rose [73] introduced the use of coumarin to obtain a high-leveling, ductile, semibright, sulfur-free nickel plate from Watts baths which became prominent in the plating of automobile bumpers. This plate was easily buffed bright and then chromium plated. The chromium-plated sulfur-free nickel gave excellent corrosion protection results. Later, in order to eliminate the buffing, sulfur-containing bright nickel was applied on top of the semibright sulfur-free nickel in a thickness less than that of the semibright plate [97].

While it was not apparent from static roof exposure tests in industrial atmospheres, the corrosion protection with this chromium-plated double-layered nickel coating was superior to even the good performance of the same total thickness of chromium-plated sulfur-free buffed semibright nickel. This superior performance was manifested in the cities that used salt to de-ice the streets in winter [98]. This double-layered nickel coating was an important step in obtaining greatly improved corrosion protection results with nickel-chromium coatings. The corrosion pits starting in the bright nickel underneath the pores in the top thin chromium plate are diverted laterally on reaching the more noble sulfur-free nickel layer, thus greatly delaying the corrosion pitting penetration to the underlying steel or zinc die-cast substrate (Figure 2).
Static roof exposure tests did not markedly show this sacrificial protection because the acidity of the industrial atmosphere was due mainly to moist sulfur dioxide which attacks sulfur-free nickel about as readily as nickel containing 0.08% sulfur. On the other hand, in the presence of acidic saline solutions, the sulfur-containing nickel is attacked anodically more rapidly than sulfur-free nickel [99]. The neutral salt spray test was practically useless for predicting outdoor exposure results with nickel-chromium and copper-nickel-chromium plate: The development and extensive use of the accelerated corrosion tests, Corrodkote [100] and CASS [101] tests (197-1959) (see Chapter 30), proved to be of immense benefit in indicating that the double-layered nickel plating system could confer greatly improved outdoor corrosion protection to copper-plated zinc die castings as well as to steel articles, especially under acidic saline exposure [104, 105, 224].

Fig. 2 Cross section of double-layered nickel plate on steel, consisting of 253.1m of semibright, sulfur-free- nickel with a 10-mm top layer of sulfur-containing bright nickel after 24 hr CASS test. The final 0.25-Am-thick chromium plate is too thin to discern at 250x original magnification. The cyanide-persulfate etch was used to show the columnar structure of the semibright nickel and the lamellar structure of the bright nickel.

Further improvements in diverting the corrosion pitting laterally were obtained by using a thin layer of nickel (3.2-2.5 Am), containing 0.15% sulfur, between the sulfur-free nickel and the top bright nickel, containing 0.04 to 0.08% sulfur. This triple-layered nickel plate uses a 50:50 ratio of semibright to bright nickel instead of the 70:30 preferred ratio for the double nickel [102].

Finally around 1958-1960, the porosity of the chromium plate itself received increased attention [103, 220, 221]. At first it was thought, based on static industrial atmosphere exposure results, that a thicker crack-free chromium plate with as few pores as possible would give far superior corrosion protection to the underlying metal than the usual thin (0.25-0.5 Am) chromium plate. However, the high stress in the thicker chromium plate very often caused gross cracking in mobile tests on salted streets [104, 105]. It turned out that just the opposite condition to crack-free chromium gave dramatically improved corrosion protection. In 1958, it had been mentioned that a high density of pores or craze cracks would be superior to a low density of pores or cracks in the final chromium plate [103]. However, the only means suggested for obtaining such highly porous decorative chromium was the use of a dull nickel or semibright, sulfur-free nickel as a strike coating on top of the bright nickel plate before the chromium.
The first important development in the commercial use of a highly porous decorative chromium was with a microcracked deposit [105, 2211. The microcraze-cracking resulted from the composition and operating conditions of the chromium plating baths as well as the use of increased thickness of plate (see Chapter 5). Next was the development of microporous chromium plate obtained by depositing the usual thin chromium plate on top of bright nickel plate containing densely codeposited, extremely fine, bath-insoluble, nonmetallic particles [106]. In this indirect way, the entire usual final chromium plate, 0.25 to about 0.75 pm thick, is made completely microporous. Another method for obtaining a highly porous decorative chromium plate has been developed [39] which involves the use of a thin, highly stressed nickel deposited from a high chloride nickel bath on top of the bright nickel plate. This step results in the development of microcracking in the usual thin final chromium plate by virtue of the high tensile stress of the nickel plate and the additional stress of the chromium plate. Another method for increasing the porosity of conventional decorative chromium involves mild impingement of the chromium surface with fine particles [217]. It was also known that chromium plated from trivalent chromium solutions is microcracked [107], but these baths are more difficult to control for decorative plating than hexavalent chromium baths, and moreover, the plate is usually darker.

With the highly porous chromium plate obtained by these various methods, the resulting greatly increased number of exposed tiny anodic areas causes a greatly decreased anodic (corrosion) current density in the nickel and consequently the rate of pitting penetration is markedly decreased. Using the highly porous chromium on top of double nickel plate (60:40 or 50:50 ratio of sulfur-free nickel to bright sulfur-containing nickel) results in important improvements in corrosion protection. Furthermore, with the highly porous final chromium plate, it was found that copper is markedly beneficial [105, 109, 115] as an undercoat, especially to bright nickel and also to double- or triple-layered nickel, in corrosion protection, unlike the case when the top chromium plate is the usual one with its moderate porosity. Clauss and Klein [109] found, however, that copper was not beneficial in outdoor corrosion protection under semibright, sulfur-free nickel with the highly porous type of final chromium plate directly over the sulfur-free nickel. They showed that it was necessary to have bright nickel also present before copper becomes a beneficial undercoat when a final highly porous chromium is used. Copper in the past [109, 110] was not considered to be beneficial in outdoor corrosion protection when used under buffed dull Watts nickel with the usual final chromium plate. It is interesting in this connection that the usual 0.25-gm-thick conventional chromium plate when deposited on buffed or unbuffed plain Watts nickel shows a much higher porosity than on bright nickel [103]. Knapp [111, 116] studied the effect on the corrosion protection of steel of thin electroplates of various metals and alloys sandwiched
between two layers of nickel plate. Chromium gave the best protection. However, this system was never put in commercial practice because of the danger of dragging of chromic acid into the second nickel plating bath.

The use of highly porous chromium plate, microcraze-cracked or microporous, on double- or triple-layered nickel with or without, but especially with, an underlayer of copper, has made possible great improvement in outdoor corrosion protection of steel and zinc die castings compared to the same thickness of single-layered bright nickel or single-layered bright nickel with an undercoat of copper and with the conventional final chromium plate [109, 113, 114, 117, 202, 210].

3.4.2 CODEPOSITION OF PARTICLES

Various kinds of bath-insoluble fine particles dispersed in the nickel baths can be uniformly occluded or codeposited with the nickel plate. If the suspended or dispersed fine particles are nonconducting or practically nonconducting and of a particle size less than about 5 \( \mu \text{m} \), they generally can be uniformly and smoothly codeposited. The fine nonconducting particles tend to acquire a charge in the electrolyte, and those that acquire a weak, negative charge or that are practically neutral codeposit to a smaller extent than those that tend to acquire a positive charge. Fine amorphous silica powders tend to be neutral or acquire a small negative charge in the nickel baths, and codeposit less readily on vertical cathodes than do fine alumina, titania, zirconia, silicon carbide, and barium sulfate particles [106, 118]. The mechanism of codeposition has not received much study.

The codeposition of nonconducting particles with nickel for purposes of abrasion, wear resistance, antifriction, or for dispersion hardening has been studied for many years [119, 120]. Diamond powders have been codeposited with nickel for use in abrasive tools such as drills and abrasive wheels [120]. For dispersion hardening about 2 to 6 vol % of extremely fine alumina particles have been codeposited with nickel [121]. Dispersion-hardened nickel tends to maintain hardness at elevated temperatures. In applications for abrasive or wear-resistance uses, a high volume percent of particle codeposition is required, and this often necessitates conditions other than merely dispersing the powders in the bath and plating on vertical cathodes, because the volume percent codeposited in this way is not as great as on horizontal cathodes. To obtain about 30 vol % or higher requires plating techniques that allow the powders to settle uniformly and regularly on the surface of the horizontal cathode [122]. In this manner, a high volume percent of particles as well as larger particles can be included in the plate.
One unexpected application for codepositing fine bath-insoluble nonconductive particles with nickel plate was for decorative use, and for attainment of highly improved corrosion protection results in industrial and marine atmospheres with nickel-chromium plate. For this purpose particles of about 0.02 to about 5 pm in size of such materials as aluminum silicates, titania, zirconia, glass, amorphous silica, and barium sulfate, [106] are dispersed, usually by air agitation, in semibright and bright nickel plating solutions. Concentrations of about 1 to about 150 of particles can be used, although usually 10 to 100 g/l. The resultant composite nickel plate is very smooth and when deposited in thicknesses greater than about 2 µm the plate has a uniform hazy and satin-like appearance, depending on the brightness of the substrate or underplate, the nature, size, and shape of the particles, their concentration in the bath, and whether they are dispersed in a semibright or bright nickel plating bath.

3.4.3 SATIN NICKEL

Satin nickel finishes are often desired, and traditionally have been obtained by mechanically scratch-brushing a nickel deposit before chromium plating. Besides the brushed or butler satin finish, there are satin-like finishes obtained by blasting the plate with various types of particles. As already mentioned, hazy or satin finishes can be obtained directly from the bath by codepositing fine nonconducting particles dispersed in semibright or bright nickel plating baths and using plate thicknesses greater than about 2µm [106]. This type of satin nickel plate deposited on top of 10 to 15 inn of copper or semibright sulfur-free nickel, or even on top of bright nickel, was found to give outstanding corrosion protection in marine and severe industrial atmospheres [106, 109, 114]. Other methods of obtaining satin and nonglare finishes directly from the nickel bath depend on the use of organic addition agents which produce low gloss instead of bright finishes. Satin finishes have also been obtained by the use of very fine dispersions or emulsions of organic compounds in semibright and bright nickel plating baths [123]. Various low-gloss satin-like nickel-chromium finishes are often used in combination with bright finishes for pleasing decorative effects. An important use is for an antiglare finish on automobile instrument panels.

3.5 HEAVY NICKEL PLATING

Electrodeposited nickel is employed for resistance to process industry corrosion, for combined corrosion and wear resistance, and for salvaging worn or mismachined parts. It is also used for direct electroforming of articles which, because of their intricate shapes or requirements for surface finish, would be difficult or costly to produce by conventional metal-
working procedures. The thicknesses of nickel involved in such applications range from about 75 µm to the extreme realized in an electroformed supersonic wind tunnel section weighing 3635 kg and having a wall thickness ranging from 3.8 to about 10 cm. Eisner [198] introduced a high-speed method of depositing nickel and other metals which may help in heavy nickel plating. This method involves the use of controlled cathode abrasion during electroplating.

3.5.1 BATH TYPES

Choice of bath composition is dictated primarily by the mechanical properties desired in the deposits. Engineers have turned to electrodeposition to solve fabrication or salvage problems because the mechanical properties of electrodeposited metals can often be varied over wider limits than those of the same metals produced by conventional means.

A summary of methods, special precautions for, and applications of heavy nickel plating is available [124]. The various types of nickel baths used for the production of nondecorative deposits are listed in Table 3. Typical properties of deposits from these baths are also given. The Watts and sulfamate baths are by far the most widely used.

3.5.2 Watts Bath

A typical composition for engineering applications is listed in Table 3. The deposits are ductile and relatively soft. Variations in the plating conditions cause variations in the mechanical properties of the deposit in the manner previously described [26]. Applications for such deposits are the production of coatings or electroforms that are to be subsequently drawn or formed, the plating of chemical vessels, pipe, and so on, for protection against corrosion. Annealing for 15 min at 760°C increases the elongation to 55%, which is sufficient for severe forming or drawing operations. Care must be taken not to overanneal, since this causes excessive grain growth and marked loss in ductility. Certain impurities in very small amounts cause embrittlement when heated; as little as 0.02% lead may have a noticeable effect. In addition, annealing should not be attempted with deposits containing sulfur, which is introduced if class I addition agents are used in the bath as stress reducers.
3.5.3 Hard Nickel Baths

A bath recommended by Wesley and Roehl [125, 126] for producing hard nickel deposits has been used for applying nickel on the surfaces of rolls, the salvaging of worn or mismachined parts, and coating machine parts for abrasion resistance. Close control of pH, temperature, and current density is necessary in this bath to maintain the desired hardness values. The tensile strength increases and the ductility decreases with an increase of pH and a decrease in temperature. The deposit has a rather low annealing temperature and will not retain full hardness above 232°C. Disadvantages of this hard nickel bath are a greater tendency to form nodules and trees than the chloride or Watts bath and a high internal stress in the deposits which can cause sporadic cracking.

In almost all cases, it is much better and much simpler to use the class I addition agents, the stress reducers, in Watts or sulfamate baths to obtain the desired hardness without tensile stress. The stress reducers such as saccharin, p-toluene sulfonamide, sodium m-benzene disulfonate, sodium 1,3,5-naphthalene trisulfonate, o-sulfobenzaldehyde (o-formyl benzene sulfonate), which introduce about 0.03% sulfur as sulfide in the plate, are most generally used. In no case does the stress reducer endow the plate from a Watts solution with a compressive stress of the same order of magnitude as the original tensile stress. Carr [127] found that the o-formyl benzene sulfonate produced deposits with a hardness of 440 to 710 Vickers and a compressive stress of 170 to 365 kg/cm2. Such deposits have been used successfully on steel airplane propellers where hard, abrasion-resistant, ductile, and compressively stressed coatings must be employed. Metzger and coworkers [128] reported on the use of disodium m-benzenedi-sulfonate to harden deposits from a Watts bath.

Electrodeposits of nickel containing phosphorus [129-131] offer another means for increasing hardness. This type of deposit has the advantage that suitable heat treatment increases the hardness. Hot hardness, however, is still low. The range of phosphorus codeposited is from 2 to 15% depending on the amount of phosphorous acid in the plating bath.

The addition of oxalate to a nickel bath has been reported to give a hard deposit with a high percentage of carbon [132].
3.5.4 Chloride Baths

Blum and Kasper [21] worked with an all-chloride bath operated at the boiling point. Later, Wesley and Carey [17] made a comprehensive study of the chloride-boric acid electrolyte and the properties of the deposits produced. Deposits are smoother, fine grained, harder, and stronger than those from a Watts bath and more highly stressed. Although it is possible to operate this bath under conditions giving hardnesses over 400 Vickers, such deposits are so highly stressed that they may crack spontaneously. Kendrick [133] found that high-frequency periodic current reversal with relatively large amounts of deplating during each cycle resulted in soft ductile deposits with greatly reduced stress. High conductivity of the all-chloride bath permits operation at lower voltages, saving power costs. High current densities can be employed, anode and cathode efficiencies are high, and deposits have less tendency to form pits, nodules, and trees.

Mention should be made of two other high-chloride electrolytes, the chloride-sulfate and the chloride-acetate baths. Pinner and Kinnaman [18] describe a sulfate-chloride bath which overcomes some of the disadvantages of the all-chloride bath but retains many of the advantages. Aside from decorative plating with suitable organic addition agents, it has found some use in resizing worn parts.

The chloride-acetate bath [134] has low resistivity and produces deposits of moderate hardness and high tensile strength. It has found use in plating stereotypes and electrotypes, building up worn parts, and plating steel billets as a bonding layer before cladding and rolling.

3.5.5 Nickel-Cobalt Baths

Nickel-cobalt alloy deposits [71] have been used for a number of engineering or functional applications. A bath used for the production of nickel electrotypes [135] in the graphic arts industry is given in Table 3. Deposits are hard but have ample ductility to withstand distortion normally encountered in press operations.

**TABLE 3. NICKEL BATHS**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Applications</th>
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<tr>
<td>20% nickel</td>
<td>High cobalt, nickel plating on bronze magnetic tapes used in calculating machines, automatic ticket machines, and other electronic devices. For these uses, the preferred composition of the deposit is 20% nickel,</td>
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</table>
80% cobalt. The bath is a mixture of nickel and cobalt sulfates and chlorides maintained at a pH of about 3 and a temperature of 61°C. To obtain the desired magnetic properties and uniformity, the superimposition of alternating current on a steady direct current has been employed. A high internal stress has also been found to favor proper magnetic properties [226].

Nickel-cobalt alloy plate from sulfamate baths has received considerable study [136]. These alloys retain their strength and hardness on heating which is important for electroforms that have to stand heating up to 620°C.

3.5.6 Nickel-Iron Baths.

Nickel-iron plate and its magnetic and decorative properties have been studied extensively [103, 137, 208, 230].

3.5.7 Nickel-Fluoborate Baths.

Nickel-fluoborate plating baths have some unique qualities which make them applicable for a number of uses, despite the higher initial cost of the electrolyte [138, 139]. Control of the fluoborate bath is very simple; it usually involves only a specific gravity reading and a pH determination. The bath is buffered more highly than the conventional sulfate or chloride baths. As a result, changes in pH during operation are not as rapid. Nickel fluoborate has high solubility, allowing the use of nickel concentrations far above those possible in chloride-sulfate solutions. This characteristic, along with high conductivity and excellent anode corrosion over wide variations in conditions, permits high current densities to be employed at reasonable voltages. Other favorable characteristics are freedom from sludge formation and higher tolerance to metallic impurities. The deposits are light in color, ductile, and smooth and do not tend to tree or show nodule formation at higher current density areas. Their internal stress is even lower than that of deposits from the Watts bath. Nickel-fluoborate baths are used for facing stereotypes [140]. Other applications are for the production of electrotypes, electroform Mg, barrel plating, and the drawing of nickel-plated copper wire.

Titanium anode baskets cannot be used, and the solution is also very corrosive to lead and high-silicon cast iron. Silica-containing diatomaceous earth filter aids cannot be used, but paper pulp is satisfactory.
3.5.8 Nickel-Sulfamate Baths

Sulfamic acid, the basis of nickel sulfamate plating solutions, has been available commercially since the late 1930s. Cambi and Piontelli [141] suggested the use of nickel sulfamate baths in 1938. A broad patent on sulfamate plating solutions was issued to Cupery [142] in 1943. Commercial use of this type of bath did not start until 1949, however, when it was first introduced by Barrett [143] and employed for producing electrotypes [143-145].

In 1954, Diggin [146] reported on the operating characteristics of sulfamate-chloride baths and presented detailed data on the properties of the deposits. Stress values can be lowered by reducing the chloride concentration or by the use of a stress-reducing agent. The sodium salt of naphthalene trisulfonic acid (7.5 g/l) reduces the stress to 210 kg/cm² compressive, increases hardness to 520 Vickers, and tensile strength to 11,000 kg/cm². Organic stress reducers should not be employed where the deposits are to be subsequently heated to over 300°C.

Barrett [147] in 1954 proposed the use of a chloride-free sulfamate bath. This bath gives deposits with low stress and good ductility. Actually it is desirable and most often necessary to have about 3.5 g/l of chloride ion in the bath to promote proper anode corrosion and attendant pH stability [148] unless SD electrolytic nickel anodes [124, 136, 148] are used. Nickel bromide, unlike the chloride, does not affect the mechanical properties of the nickel plate adversely [136, 148, 160]. This difference does not appear to be very important when only about 10 g/l of nickel chloride is used in the sulfamate baths.

Because nickel sulfamate baths are usually employed to produce deposits for engineering purposes, the control of mechanical properties, particularly stress, ductility, and hardness, is important. Low stress, the lowest of any commonly used nickel electrolyte, can be obtained from baths which have been thoroughly treated to remove inorganic and organic impurities. Nickel sulfamate is much more soluble than the sulfate, and the use of a concentrated nickel sulfamate solution (600 g/l) makes possible very high rates of deposition with the possibility of obtaining consistently low internal stress if continuous conditioning [149] is used. These advantages are particularly valuable in electroforming simple shapes and in electrotyping.

Sulfamic acid is not as stable as sulfuric acid, and the sulfamate baths require more careful control than Watts baths. Low pH, below 3.0, and temperatures above 60°C cause marked hydrolysis to ammonium sulfate [149, 159]. The concentrated bath [149] can stand slightly higher temperatures. Highly polarized anodes or the use of insoluble anodes in sulfamate baths cause the formation of azidosulfonate [150, 151] which introduces sulfide into the nickel plate and can change a low-tensile-stressed columnar-structured deposit to a bright laminar deposit.
with compressive stress [149, 150, 209]. Hammond [148] has comprehensively reviewed the nickel sulfamate baths and the properties of the plate including the effect of cobalt additions.

Deposits from nickel sulfamate solutions, either with or without stress-reducing agents, are extensively used for electroforming complicated shapes, salvage of worn or mismatched parts, production of phonograph record stampers, manufacture of electrotypes, facing of stereotypes, production of screens, cladding of pipe and chemical vessels, and duplication of geometric surface standards, as well as the plating of typewriter parts in barrel plating equipment.

3.5.9 CORROSION AND WEAR RESISTANCE

Thick nickel coatings are used on process equipment to resist corrosion or combined corrosion, wear, and fatigue. Nickel-lined steel pipe is available commercially and is in service in corrosive oil wells and in the chemical industry. An old application is the coating of huge, highly polished, cast iron drums used in manufacturing photographic film. The degree of polish required in this service is so high that it cannot be attained with wrought metals because they contain nonmetallic inclusions which cause tiny pits on buffing. The coatings now used on these drums are deposited from a high-chloride Watts bath under conditions giving nickel of moderate hardness. Nickel-lined food-processing kettles, nickel-coated paper mill rolls, and nickel-coated filter presses for viscose rayon solutions are outstanding examples of heavy nickel plating on large units.

In applications where steel tends to fail by corrosion fatigue, a nickel coating has a great beneficial effect [152]; for example, the life of sucker rods in corrosive oil wells is lengthened many times by application of 150 pm of nickel [153] from the Watts bath. Nickel coatings seem to be particularly effective in preventing "fretting corrosion" [152]. Nickel plating, like chromium plating, can reduce the fatigue strength of plated steel components subject to alternating stressing or vibration [154]. A compressive stress in the nickel favors a minimum loss of fatigue strength [222].

Hard nickel is generally specified for applications involving wear. The performance of nickel from the other baths, however, is better than might be expected, because this metal work-hardens rapidly under sliding action. Thus the life of hardened steel gasoline pump gears, which failed by seizure and dragging, was multiplied more than fivefold by application of 5 to 7.5 gm of nickel. For the most severe conditions of contact with steel under high pressure, it is preferable to use a composite coating consisting of nickel plated with a few micrometers of chromium.
3.5.10 RESIZING

The long-standing British practice of building up worn or in ismachined parts by heavy nickel plating [155] is in use in this country on a modest scale, particularly in connection with the maintenance of trucks, buses, and airplanes. There is nothing unusual about the nickel plating operation itself, the bath being selected to give deposits of the desired mechanical properties. Preparation of the basis metal to guarantee perfect adhesion, setting up the anodes, and stopping off or shielding the work to secure good metal distribution can be exacting [156].

There are numerous advantages in using nickel for salvage: It can be deposited rapidly, uniformly, and economically; the metal can be ground and, in addition, machined by conventional methods; it is corrosion resistant and tough, and it withstands shocks. Where heavy deposits with a hard surface are required, it is good practice to make up the major portion of the desired thickness with nickel and then finish with several micrometers of chromium.

3.5.11 ELECTROFORMING

Numerous publications [1, 157, 158, 205] reveal an impressive accumulation of literature on electroforming which recounts the commercial production of a long list of articles ranging in size from hypodermic needles to a 4-ton, precision-plated, wind tunnel nozzle. Electroforming has inherent advantages over other processes of fabrication for parts which (1) require a very high surface finish, especially on internal surface contours, (2) require high precision in certain dimensions, (3) incorporate intricate details, and (4) are needed in quantities too small for die-casting runs.

Nickel is the favored metal because it provides greater strength, toughness, hardness, and corrosion resistance. Residual stress in nickel deposits, tensile or compressive, may cause warping of the product. However, stress can be easily controlled with modern baths and methods of operation. Sometimes it has been the practice to apply a layer of nickel to the surface of the mold in starting electroforming, then build up to the desired thickness with copper. The nickel layer thus is in a position to supply wear and corrosion resistance plus some stiffening of the object.

Sulfarnate baths are increasingly used for electroforms because their deposits have low tensile stress. The \TVatts baths require the use of a stressreducer for low internal stress, and because of the sulfur content of such deposits, it is necessary to avoid temperatures above about 310°C for such electroforms. About this temperature and higher, the sulfide-containing nickel suffers severe embrittlement. In general, for electroforming operations,
the stress reducers should be used at the lowest concentration to accomplish minimum stress.

Electrotypes are the oldest kind of electroformed article. Electrotyping is a process for producing duplicate printing plates to eliminate the need to reuse the expensive original, usually a composite of photoengravings and type. In modern methods a plastic mold, usually vinyl, is made from the original and made conductive with a reduced silver film and then plated 150 to 200 A/m2 thick which is the required nickel shell thickness. A low-stress bath is necessary to start the plating on the silver film without preliminary copper plating. Nickel sulfamate baths are generally used on both lead and plastic molds. After an initial plate of about 7.5 mm is deposited at medium current densities on the vinyl mold, the rate of plating can be increased to 20 to 30 A/dm2 to produce an all-nickel electrotype shell in 30 to 40 min. Small concentrations of nickel fluoborate can be added to the sulfamate to prevent burning at the edge of the mold. In stereotypes, a soft low-melting lead-based metal is used for printing and is protected against wear by nickel electroplate about 13 mm thick, usually from the sulfamate bath.

Another old and widely used application of electroforming, also illustrating its ability to reproduce faithfully the details of the mold surface, is the making of high-fidelity phonograph record matrices and stampers. Recordings are first cut on thin aluminum disks coated with an acetate lacquer and then coated with a film of chemically reduced silver. An initial layer of nickel a few micrometers thick is deposited at low current density of about 1 A/dm2 to prevent burning when the higher current density is applied to obtain a nickel thickness of about 0.8 mm. Cathode rotation is provided for high-speed plating. After separation from the "acetate" the electroform serves as the Metal Master. It is cleaned and given a passive thin chromate film, rinsed, and plated with nickel. This new electroform, called a Mother, is mechanically separated from the Master. The Mother serves as the mandrel on which the pressing stampers are formed. A majority of the industry electroform the Masters, Mothers, and stampers in solid nickel to obtain the required properties for extended use. The stampers are sometimes plated with a final thin layer of chromium to extend their useful life and to prevent adhesion of some plastic materials used in manufacturing records.

A large new application for electroformed nickel is the cylindrical screens that are used for textile printing. These screens are about 125 /Am thick, 12.5 to 30 cm in diameter, and 2.5 to 6 m long. They are used in tandem with each roll applying a pattern of a single color to the fabric.
Important applications of nickel electroforming include Pitot-static tubes for air-speed indicators, precision tubing of rectangular cross section, and radar fittings, waveguides, computing cams, large searchlight reflectors, constant mesh screens, and Venturi tubes used in the jet propulsion program [158, 165]. Electroforming plastic dies and casting dies has an advantage owing to the high cost of hobbing them out of solid metal [158]. Electroformed molds are used for nylon gears, ratchets, cams, and plastic toys and dolls [158].

Carlin [156] describes methods of ensuring adhesion in thick nickel deposits and electroforms if current interruptions occur during plating. Methods of maintenance of the purity of the nickel solution are also given.

### 3.5.12 MACHINING

Soft and hard nickel electrodeposits can be readily machined if suggested speed, feeds, and tool rakes are adopted [124].

### 3.5.13 HEAT TREATMENT

The general practice in England [155] is to subject heavy nickel deposits to a low-temperature treatment to improve adhesion, expel hydrogen, and, in some cases, reduce stress. The time and temperature have not been standardized, but they vary from 0.5 to 3 hr at 150 to 290°C.

### 3.6 SPECIAL PURPOSE BATHS

A number of applications for nickel plate require baths of special composition. Bath formulas and preferred operating conditions are shown in Table 2.

#### 3.6.1 ELECTROTYPING BATHS

In addition to the baths discussed in the previous section, solution A of Table 2 is typical of those recommended in the past for plating over wax and lead molds [166]. The ammonium salt increases conductivity and provides buffer action at the high pH. Boric acid is not included because it leads to undesirable stress and to cracking of the plate at the low-temperature—high-pH conditions necessary for covering or spreading over the surface of a treated wax mold. Air agitation is commonly employed to permit operation at the upper end of the current density range. Modern practice for electrotypes and stereotypes is to apply nickel from standard warm fluoborate or especially sulfamate baths on sheets of vinyl plastic, lead-, or aluminum-backed plastic instead of on waxes [157].

#### 3.6.2 THE DOUBLE-SALT BATH
Solution B, one of the oldest nickel plating baths, finds little application in this country. It can be employed only at room temperatures (20-30°C) and low current densities. It was used for deposition of thin coatings on, for example, brass, costume jewelry, and novelties. A brightener like gum tragacanth, gum arable, or a cadmium salt was often used.

3.6.3 BARREL PLATING BATHS

Barrel nickel plating is carried out with large numbers of small parts which are too difficult to rack. Solution C, being somewhat more concentrated than B, has the wider range necessary for the barrel plating of small parts in bulk. The brighteners used with bath B, especially a cadmium salt, are also encountered here. These room temperature solutions still find some use. Modern proprietary warm bright nickel baths based on the Watts solution, usually with higher nickel chloride content and using some of the same brighteners used in rack plating but in different proportions, are now available for barrel plating to yield a superior product at higher rates of plating [167]. The modern baths are required to give bright deposits over a very broad current density range down to the very lowest. Usually a very low foaming surfactant, similar to the ones used in the air-agitated baths, is added to decrease dragout.

Table 2 Special purpose Nickel Baths

3.6.4 THE HIGH-SULFATE BATH

Solution D is of a type developed by Thompson [168] for plating nickel directly upon zinc alloys. The high content of sodium sulfate suppresses ionization of the nickel sulfate and thus tends to prevent the deposition of granular nickel by chemical displacement on the zinc surface. Live entry ("hot contact") is usually used. Brighteners other than small concentrations of cadmium ions are not suitable in this bath because of the high concentration of ammonium ions, and in general, thicknesses less than about 15 pm are used with this cold bath. The covering and throwing powers, though superior to a Watts bath, are not comparable to the cyanide copper bath, and the latter is practically universally used as the first plate on top of zinc die castings. Solution D is useful when copper is not desired for plating on aluminum and magnesium alloys which have been coated with zinc by an immersion process.

3.6.5 THE BLACK NICKEL BATH
Bath E is for deposition of a decorative black finish which contains not only nickel but also large amounts of zinc and sulfur [169]. A modification of this bath, which contains chlorides in place of sulfate, is said to be easier to control [170]. Black nickel is a thin decorative finish which reproduces the underlying surface, lustrous black on smooth surfaces, and dull black on mat surfaces. It is used to achieve color effects and should not be considered corrosion resistant. A nickel undercoat is used to protect the basis metal.

3.6.6 ALKALINE NICKEL BATHS

Nickel can be deposited from alkaline baths, and baths of this type have been developed mainly for direct plating of zinc die castings with the view of eliminating the need for cyanide copper as the first plate and also for obtaining generally better throwing power [171]. These baths in general give rather brittle plate. The bond to zinc is good but not always the best. It is mainly for these reasons that these baths are seldom used. However, an early bath consisting of ammoniacal pyrophosphate and citrate complexes of nickel with some added bisulfite, and known as the Zialite bath [171], has been in small-scale use for many years. It is used to plate directly and protect intricate zinc base castings such as spray guns, because of its very good covering power. The pH of the bath is usually kept at about 8 to 9 and temperature at about 35°C. The plate is lustrous semibright and usually is not chromium plated. Later [172] improvements and faster plating have been claimed by using warmer baths, potassium instead of sodium salts, and some changes in ratio of the components.

3.7 MAINTENANCE AND CONTROL OF NICKEL BATHS

Maintenance and control should start with the installation of the tank and its auxiliary equipment. Satisfactory, thoroughly tested tank linings and internal heating elements are available. Heating of the solution by means of an external heat exchanger is much preferred. As materials for internal heating elements, lead, impervious carbon, and glass coils are commonly employed. Although lead was at one time used almost exclusively, it has been replaced by either impervious carbon or glass in order to avoid the possibility of metallic contamination. Since lead is soluble in high-chloride nickel baths, lead coils should not be used where the nickel chloride content is higher than 60 g/l. They should also not be used in baths containing organic acids that form soluble lead salts such as acetic and formic acids, or in baths with high concentrations of sulfonic acids. They cannot be used in sulfamate, fluoborate, all-chloride, or high-chloride baths.
Impervious carbon heating elements are widely used in such baths, and, since they have good heat transfer properties, they may be employed in any type of nickel plating solution. The one disadvantage of such heating elements is their fragility. Special precaution is required to place them in the tank so that danger of physical damage is minimized. Glass heating coils avoid both metallic contamination and stray electrical currents, but have the disadvantage of a relatively poor coefficient of heat transfer.

Since insulation defects may be the direct cause of poor adhesion and may result in current loss or poor plate distribution, tanks should be mounted on positive insulators such as glass or glazed ceramics. All piping connections for water, steam, and air exhaust should be equipped with permanent insulating joints in order to avoid electrical grounds and short circuits. The ground lights described by Borchert and Kinnaman [218] are useful control devices. All anode and cathode bars, racks, and contact points should be kept reasonably free from encrusted salts for good electrical contact. Contamination of the bath with copper must be avoided. Wrapping the anode bars with polyethylene sheeting is a step in that direction [173].

Proper cleaning and preparation of the work are important parts of maintenance and control of nickel plating baths. This is discussed in Chapter 23.

### 3.7.1 EFFECT OF CONTAMINANTS

In the modern acidic nickel plating baths, small percentages of metallic contaminants such as copper, lead, zinc, or tin exert profound effects on the appearance and properties of the nickel deposit, especially in the low-current-density plating range. The harmful effects of these impurities are additive.

Copper in concentrations over about 5 mg/l is detrimental to adhesion to steel, or leads to poor adhesion when current is interrupted or decreased to very low current density during the nickel plating. This is also true for similar concentrations of lead. Copper in these and higher concentrations causes dark, low-current-density plate especially evident in bright nickel plating. Lead in concentrations higher than 5 mg/l causes dark, fine-grained, brittle, poorly adherent deposits [176, 207]. Stannous tin in low concentrations causes dark, low-current-density plate; it can be removed by oxidation to the insoluble stannic form, and thus this impurity can be confused with an organic impurity in the rare case where a tin anode gets mixed in with nickel. Zinc impurity in bright nickel baths, while not as critical as copper, lead, and tin, can cause whitish, and with higher concentrations, dark plate in the low-current-density areas, and even cause shiny black streaks in the plate [58]. In general, the bright nickel baths can tolerate about 20 to at least 100 mg/l of zinc, depending on the configuration
of the work. Iron(III) impurity tends to precipitate readily at pH values of about 3.5 and higher, and can cause speckling on settling surfaces, unlike the case of iron(II) which codeposits compatibly with nickel. Good filtration minimizes this iron(III) problem.

Hexavalent chromium in concentrations of 3 to 5 mg/l introduced from spray from chromium plating baths or dragin from faulty rack coatings causes skip plating in low-current-density areas, and in higher concentrations, streaked, peeled plate [176]. Small concentrations of sodium bisulfite reduce the hexavalent chromium to the very much less harmful trivalent form. Trivalent chromium and aluminum in appreciable quantities lower the limiting cathode current density and tend to precipitate out at pH values above about 3.5 and cause roughness especially on settling areas of a cathode. Nitrate ion is reduced to ammonium ion at the cathode and, like oxidizing agents, decreases the cathode efficiency and in appreciable concentrations causes skip plating in the low-current-density areas. Nitrate is not nearly as critical as hexavalent chromium. Phosphate ion lowers the limiting current density through formation of nickel phosphate in the cathode film and the precipitated phosphate particles also cause roughness.

Many organic compounds in small concentrations, as well as large excesses of many class II brighteners, can cause brittle plate and dark low-current-density plate. Grease, oil, improper surfactants, rubber accelerators, and so on, can cause brittle, cloudy plate.

3.7.2 REMOVAL OF INORGANIC CONTAMINANTS

In plants processing steel, iron is the usual contaminant and with constant good filtration, iron usually presents few problems. High-pH treatments (5.2-5.5) in an auxiliary tank with moist nickel carbonate dispersed with good agitation of the bath are used to remove excessive concentrations of iron, as well as aluminum, trivalent chromium, or phosphate ions. The addition of about 0.5 to 1 m1/l of 30% hydrogen peroxide with the high-pH treatment removes all the iron as ferric hydroxide, provided at least 2 hr of agitation is used and the temperature of the bath is kept at around 60 to 65°C. Also, carbon dioxide evolved from the use of nickel carbonate is removed by the agitation and heating.

In plants processing copper, brass, or zinc die castings, the contaminants copper and zinc are best removed by low-current-density purification, preferably continuously [175, 207]. Zinc, copper, and lead may all be removed at the same time by electrolyzing at about 0.2 A/dm2. The faster the agitation, the higher is the current density that can be used to remove these metallic impurities.
3.7.3 REMOVAL OF ORGANIC CONTAMINANTS

Organic contaminants may be introduced by improperly chosen tank linings, rack coatings, filter hose, patching rubber, by airborne contamination from thick dust, lint, or oil spray or drippings, from loose welding scale on workpieces, from inferior cleaning methods, and by breakdown at the anode or cathode of certain class II addition agents.

If the bath is excessively contaminated with organic material, the best method of removal is by adsorption on activated carbon in the auxiliary tank, after correcting as far as possible the sources of the organic contamination. Addition of hydrogen peroxide as previously described, and agitation of the bath for several hours with 1 to 3 g/l of the activated carbon, at 60 to 65°C, as well as raising the pH to about 5.2 with nickel carbonate, will help the purification. After settling with filter aid and testing a sample of the treated solution in the laboratory for the condition of the plate, the solution if approved is filtered back into the plating tank.

The use of small amounts of activated carbon in the filters, such as 2 to 4 g/100 l of solution and adding similar amounts to the filter once or twice a week is an excellent method of avoiding or minimizing costly batch treatments of plain, semibright, or bright nickel plating baths. A check must be made at regular intervals to be sure that the wetting agent or other brighteners are not excessively adsorbed. The baths operated with air agitation using clean air blowers and not compressed air can be kept in constant excellent operating condition by this method of using small amounts of carbon in the filter and changing the carbon when a total of about 16 g/100 l has been added to the filter. The air-agitated baths operating with low-foaming wetting agents and with addition agents that are not readily adsorbed and do not form harmful breakdown products are especially adaptable to this type of operation since the carbon does not adsorb excessive amounts of any of the addition agents, and is therefore especially effective for the small amounts of organic contaminants that tend to get into the bath. In practice, many baths have run for years without the necessity of a batch purification.

3.7.4 DETERMINATION OF MAIN BATH CONSTITUENTS

Control of pH. pH is generally measured electrometrically, and throughout this chapter all pH values are electrometric unless stated otherwise.

Knowledge of the allowable range of pH for the particular bath, and of its rate of change, should govern the frequency with which pH determinations and corrections are made. For the Watts or bright nickel plating baths, the pH will ordinarily be found to increase
during use; it is lowered by the addition of sulfuric or hydrochloric acid or both. If the pH drops, anodes are polarizing due to low anode area or poor contacts.

Determination of Surface Tension. Surface tension is related to concentration of wetting agent and its determination provides a means of control [177]. (See Chapter 22).

Analytical Methods. For sampling the bath and the analytical procedures to be used for the principal constituents in the bath the reader is referred to Chapter 22, textbooks, and plating handbooks.

Methods for estimating metallic impurities have been developed or standardized by Serfass et al. [178]. Atomic absorption spectrophotometry is the modern method.

Methods of analysis of proprietary brighteners and addition agents are furnished by their vendors.

3.8 ANODES

With the introduction in 1916 and subsequent widespread use of the Watts bath, the old 90 to 94% or the 95 to 97% nickel anode (balance iron), used in the cold, low-speed, pH 5.5 nickel bath, gave way to the chill-cast 99% nickel anode. Next came the rolled 99% nickel anode depolarized with small amounts of nickel oxide. This anode corrodes smoothly, forming a light brown film that washes off as it is formed. Since small amounts of loose nickel are formed on corrosion in all solutions based on the Watts formula, anode bags are generally necessary to prevent formation of nodular deposits as a result of the physical inclusion of these particles. This 99% nickel rolled anode is used in baths of pH above 4.

After the rolled depolarized anode came the cast carbon-nickel anode, and still later, the rolled carbon-nickel anode. Both of these contain more than 99% nickel and have the feature of forming their own "bag" on corrosion. This "bag" consists of a rather tenaciously adhering but porous carbon-silica film that holds back loose anode particles provided they do not form in excessive amounts. The high-purity carbon-type anodes are used only when the pH of the bath is 4.5 or lower. Such anodes are sometimes used without any cloth bags in baths that are not air agitated.

The corrosion behavior of an anode depends on the pH and the chloride content of the bath. The uniformity of corrosion (sometimes called anode activity) should not be confused with anode efficiency. Only a small chloride content, 15 to 22 g/1 nickel chloride, is necessary to make the latter 100% for all types of nickel anodes under the usual conditions.
where the anode area is at least equal to the cathode area. The selection of the best type of nickel anode for a given process is based not only on the purity of the nickel, costs, special shapes, and type of plating solution, but also on the anode current densities to be encountered.

With the introduction of perforated and wire mesh titanium anode baskets [179], the use of primary nickel has become the predominant nickel anode material. Small squares of electrolytic nickel, usually about 2.6 x 2.6 cm or small squares or buttons of sulfur-depolarized electrolytic nickel (designated SD nickel or S nickel° [179, 180]), or Mond nickel pellets are the forms used. Electrolytic nickel is the least expensive and purest form of anode nickel and about 90% of all the nickel anodes now used in the U.S. are these electrolytic squares, the SD type amounting to about 50% of the total. The SD electrolytic nickel, like regular electrolytic nickel, has very low (about 0.01%) iron and copper impurities, but contains about 0.02% sulfur dispersed through its structure, which makes the nickel uniformly reactive, and for this reason is the least critical nickel anode material with respect to pH, anode current density, and very low chloride concentration. Regular electrolytic nickel contains no depolarizer and is the least active nickel anode material. The SD nickel can be used in chloride-free and high-pH baths of sulfate and sulfa' mate types. There is no metallic sludge with SD nickel, but the nickel sulfide formed, while not voluminous, nevertheless can be carried out into the bath if the anode bags are not kept above the solution level, which should be the general practice anyway. The best bags for regular electrolytic nickel are not necessarily the best bags for SD nickel, for which a tighter weave is preferred. Double bagging is especially preferred for titanium baskets over 1 m long, the outside bag being made of approved plastic fibers and of a more open weave. Cotton bags, when used without an auxiliary outer plastic bag, must in general be changed about every six to eight weeks of service due to deterioration which may lead to breaks in the bag. Great care should be exercised in changing bags to keep anode sludge from falling into the tank. It is for these reasons that plastic bags which do not rot are tested to find combinations that are as good in holding back the sludge as the best cotton bags. If bags plug from iron precipitation or saturated solution, polarized anodes might result. This is another reason for periodic (six—eight week) bag inspection. When placing bags on titanium baskets, extreme care should be taken not to cut the bags on any sharp corners or edges of the basket, as the bags are to fit snugly on the baskets, unlike the case for bar anodes where several centimeters must be allowed in the length of the bag to provide space for anode sludge.

The use of anode baskets makes possible a constant area with anode additions at weekly or other regular intervals, and eliminates problems with stubs and scrap.
While titanium baskets are excellent for Watts, high-chloride, and sulfamate nickel baths, certain precautions must be observed. Titanium baskets containing nickel anodes are corrosion resistant as anode baskets in these solutions because they readily anodize at low anodic current densities; in fluoride or fluoborate baths they do not anodize, but corrode instead. If a basket is only partly filled or a gap develops between the walls of the basket and the nickel anodes, there is a danger that the potential at the titanium surface may rise to the point where oxygen or chlorine will evolve. Since the potential of SD electrolytic nickel is much lower at a given anode current density than that of regular electrolytic nickel, it is possible to use at least 50% more current before an appreciable liberation of chlorine occurs using the same area of nickel anodes.

There are some cases for engineering uses where only an insoluble anode can be used; then an all-sulfate bath must be used. Lead is satisfactory unless the nickel deposit will be subjected to a high temperature, because even a trace of lead causes high-temperature embrittlement. Insoluble anodes of carbon or platinized titanium can be used. Where slow corrosion of the anode can be tolerated, pure nickel is satisfactory. Where auxiliary anodes for recessed areas are used and do not take more than about 3 to 5% of the total current, the use of nickel rod or platinized titanium in chloride-containing nickel baths does not cause excessive breakdown of brighteners. Some brighteners can tolerate much more anodic Polarization than others.

3.9 PREPARATION OF BASIS METAL

In preparation for applying a plated finish to an article, polishing is often used to smooth the surface before more refined finishing procedures (See Chapter 23). Subsequent buffing is usually used on such metals as copper, brass, zinc die castings, and aluminum alloys before plating. Because of high cost, steel is seldom buffed before nickel plating. Where a buffed surface is desired, a common practice has been to apply a copper plate before buffing. More recently, the use of high-leveling bright nickel baths, or a combination leveling semibright bath and a bright nickel bath, or a high-leveling, bright, ductile acid copper plating bath [117] eliminates or reduces appreciably the amount of buffing required to produce a lustrous finish.

3.9.1 POLISHING AND BUFFING

The nature and surface condition of the basis metal can have a profound effect on the performance of the nickel plate. Proper preparation of articles to be plated with nickel starts with the manufacture of the basis metal. Many investigators have shown that rolling
seams, slag inclusions, blowholes, sand inclusions, and the like affect the protective value of nickel plate [181]. Moreover, the manner in which the metal is processed, either before or after being formed into articles of manufacture, has been proved to affect the porosity of the nickel deposit. Pinner [182] showed the effects of polishing steel with differently sized grits. In general, his results show that rough grinding was detrimental to the protective value of nickel plate, and, in addition, that smoothing out and rounding off the tops of scratches, as, for example, with a well-lubricated, final polishing wheel, was important from the standpoint of enhancing the protective value of nickel. A final sisal wheel accomplishes the same result, especially of eliminating slivers.

3.9.2 CLEANING AND PICKLING

The purpose of cleaning before plating is to remove all the interfering substances from the surface to be plated. Adhesion, smoothness, and corrosion resistance of nickel plate depend on a proper cleaning cycle (see Chapter 23). Diffusion of one metal into the other (alloying) is not necessary for adhesion and may be detrimental when the alloy layer or any part of it is weaker or more brittle than the individual metals. Harmful substances which cause poor adhesion are oxides, graphite, oils, grease, and immersion coatings of copper or lead from contaminated acid dips or from the presence of chromates, even in small concentrations, in the rinse water or in the plating baths. If cathodic cleaners are used that are contaminated with dissolved zinc, copper, or lead and thus plate out a nonadherent film, or when cathodic cleaners are used in the cleaning or activating sequence for longer than 1 min without an anodic activation, or when bipolar or intermediate electrode effects occur in the plating steps, poor adhesion will result.

With few exceptions, the parts to be plated are given an acid treatment subsequent to the cleaning operation, the purpose being to remove oxides and tarnish films that would prevent adhesion, and also to dissolve the outermost layer of polished metal. Commercial hydrochloric acid in varying concentrations is the most commonly used acid. A high concentration, up to 50% (vol), is used on steel; a medium concentration of about 10% (vol) on copper and brass; and a low concentration, 1 to 5%, on zinc and zinc die castings. Sulfuric acid is also employed, especially to neutralize the alkaline film present on copper undercoatings deposited from a cyanide bath. Brass and copper parts are sometimes cleaned in sodium cyanide solutions, preferably containing some caustic soda to prevent rapid decomposition.
For steel parts such as bumpers the use of an anodic acid etch is favored as a preparation for excellent adhesion. Such baths are composed mainly of concentrated sulfuric acid and may contain addition agents such as glycerin. In operation, the previously cleaned parts are made anodic at current densities of about 20 A/dm². Pinner [182] has shown that the anodic acid etch is quite effective in removing a large proportion of the metal slivers that may be on the polished steel surface. The removal of these loosely held steel particles has been shown to improve the smoothness of the deposit and its corrosion-resistant properties. Anodic etching should not be prolonged to avoid exposing basis metal imperfections.

The basis metal is frequently copper plated before nickel plating. Such a procedure is practically universally used on zinc and zinc alloys; see Chapter 26. Copper is deposited of sufficient thickness to form an alloy layer with the zinc and provide additional copper which remains unalloyed under the nickel.

As suggested by Schkitter [183] and confirmed by Macnaughtan and Hothersall [183], copper from a cyanide bath covers imperfections in the steel surface better than does nickel plate, and thereby reduces porosity. A cyanide copper strike before the nickel plate has been shown to be very helpful in this connection in passing CASS tests. The copper is a better base [200]. In the case of zinc die castings with surface flaws, the alkali left in the surface defects prevents the weakly acidic nickel baths from plating into these stopped-up pores. If bright leveling acid copper is used on top of alkaline cyanide copper plate, the strong acidity of the bath can dissolve the alkaline salts in the surface flaws and put a conductive coating into them by immersion plating, thus enabling the subsequent filling in of the flaws by the excellent microthrowing power of the bright acid copper and nickel baths [117]. If the zinc alloy die casting has large blind holes, the acid copper baths usually cannot be used because of the strong attack of the zinc in the blind holes not covered by the alkaline copper plate.

For plating on aluminum, magnesium, and their alloys, the cleaned parts are most often coated with adherent zinc films by chemical displacement. Copper is then usually plated, followed by nickel as in the case of zinc alloys (see Chapters 24, 25). Improved corrosion protection results have been obtained by Jongkind using an immersion bronze film instead of zinc, from a stannate solution followed by a bronze strike plate [184]. The zincate process has been modified by using a zinc alloy immersion film from the zincate solution [185]. The electroplating of aluminum alloys has been reviewed by Vanden Berg [185]. The anodic treatment of aluminum in phosphoric acid solution [186] which is applicable to only a few aluminum alloys in addition to 1100 and 3003 makes possible good adhesion and improved corrosion protection results for these alloys compared to the zincate process. The
thin anodized layer is partially removed on entry into the nickel plating bath. (See Chapter 24.)

Magnesium and its alloys may be prepared for plating by using a pyrophosphate-type zinc immersion process described by DeLong [187]. (See Chapter 25.)

3.10 TESTS OF DEPOSITS AND SPECIFICATIONS

The permanence of a lustrous finish and the protection afforded a basis metal depend on both the basis metal surface and the subsequent plates. The concern in measuring quality of coating is reflected in the extensive research on accelerated corrosion tests. The American Electroplaters’ Society Research Project 15 resulted in the Corrodkote test and the copper-modified acetic acid-salt spray (CASS) test. The details of these are covered in Chapter 30. These tests have provided the means to help select the best combinations of nickel and chromium, and copper, nickel, and chromium plate for the best outdoor corrosion protection performance. A new electrochemical method (EC test) has been developed by Saur and Basco[108, 188] for rapid estimation of corrosion protection performance valuable for quality control and research work.

3.10.1 CHEMICAL RESISTANCE AND CRACKING TENDENCY

Without a top chromium plate, bright nickel will protect steel better than pure nickel in outdoor exposure. Nickel-cobalt or nickel-iron alloy, dull or bright plate, will protect steel better than bright nickel [58]. The protection is based not on weight loss but on the much lesser tendency to pitting attack. Duplex nickel plate consisting of sulfur-free nickel followed by an equal or somewhat thinner plate of sulfur-containing nickel, 0.03 to 0.2% sulfide sulfur, is very much better than the sulfur-containing nickel itself. With a final 0.25 /cm chromium plate, pure nickel is superior to bright nickel mainly because the porosity pattern of the thin chromium plate is much denser on buffed or unbuffed sulfur-free nickel than on sulfur-containing nickel [58, 103], and also because the latter is a more active nickel.

Bright nickel, which is not as ductile as sulfur-free nickel, is severely hydrogen embrittled by the final chromium plating, and for plated articles which must undergo some deformation in use, especially outdoors, a substantial thickness of ductile semibright nickel plate, ductile copper plate, or both must be used underneath the bright nickel plate [109]. These are also the best combinations of plate for obtaining the best outdoor corrosion protection, especially if the final chromium plate is microporous or microcracked.

3.10.2 ADHESION
The bond to the basis metal is another factor in the performance of plated coatings. Methods of measurement are described in Chapter 30. The most commonly used shop method is the grinding wheel test, or rough file, or sharp bending if possible. These shop methods do not lend themselves very well to specifications.

Nickel deposits for industrial purposes often depend for their value largely on tensile properties and adhesion. Tensile properties are usually gauged by means of a Vickers or Knoop hardness test, adhesion by the modified 011ard tests [189], in which a specially prepared test piece is subjected to a tensile test. See Chapters 2 and 30.

3.10.3 THICKNESS SPECIFICATIONS

The protection afforded by nickel-chromium and copper-nickel-chromium plate depends not only on the type and thickness of plate and the nature of the basis metal and gross porosity, but also, of course, to a primary extent on the corrosiveness of the atmosphere. These factors have led to adoption, by ASTM and the American Electroplaters’ Society, of specifications covering these properties. Such specifications, ASTM designation B456-71, are available [190] for nickel coatings on zinc and zinc alloys, and on copper and copper alloys. The standard requirements for the different grades of coatings are summarized in Table 3. The British specifications 1224:1970 are quite similar. Standard test methods for measuring nickel thickness are described in references ASTM-AES specifications [191]. These specifications permit the use of the nondestructive magnetic test for nickel coatings applied on nonmagnetic surfaces [192]. The magnetic test has been modified to permit its use also with a nonmagnetic coating, such as copper, between the nickel and a magnetic basis metal [193]. Specifications on other tests include eddy-current method [194], coulometric method [195], and microscopic examination of a cross section [196]. (See Chapter 30).

Industry, especially most of the automotive industry, has followed ASTM-AES specifications with only minor variations. Novelty goods and the like, and unfortunately, sometimes even plumbing goods (brass), are frequently plated to lower specifications or none at all.
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