



# Capsule Report

## Nickel Plating: Industry Practices Control Technology and Environmental Management



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National Risk Management Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Cincinnati, Ohio 45268

## **Notice**

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## Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Hugh W. McKinnon, Director  
National Risk Management Research Laboratory

## **Preface**

This capsule report provides an overview of the nickel plating emission and waste release issues within the nickel plating industry. Emphasis will be placed on pollution prevention and control technology options. It is the objective of this report to assist the metal finishing community and specifically, those involved with nickel plating operations, with the management of environmental challenges that result from wastes that are potentially generated by nickel plating. Both the electrodeposition and electroless deposition processes for nickel plating have been profiled to examine resultant waste streams and potential releases.

Nickel plating practitioners are challenged with making a high-quality product that meets the needs of the customer while being competitive within the market. Furthermore, nickel plating practitioners must deal with environmental, regulatory, and technical requirements to protect human health and the environment. This report serves as an advisory to nickel plating practitioners by providing technical information to reduce environmental impacts and lower the liabilities associated with environmental releases.

## Abstract

This capsule report, entitled “Nickel Plating: Industry Practices, Control Technologies, and Environmental Management,” was prepared under the direction of EPA’s Office of Research and Development (ORD) to assist the metal finishing community with the management of nickel plating environmental issues. Information provided by this capsule report provides the rationale for developing the document, identifies the intended user audience, and presents the framework for evaluating nickel plating management practices from case studies that incorporate cost-effective solutions to solving persistent nickel plating problems. The capsule report provides a current analysis of the nickel plating industry from a technical, economic, and regulatory perspective.

This capsule report is organized into six chapters including recommendations.

- Chapter 1 provides an introduction and scope of the issue.
- Chapter 2 presents a profile of the nickel plating industry, including an overview of both the nickel electro-deposition process and electroless nickel deposition process. Nickel plating is accomplished by using a variety of chemical reagents in a rectified-direct current (electroplating) or via a chemical reducing agent with no rectified current (electroless plating). Decorative and other engineered coatings define the type of additives and formulations required by the plating practitioner. These formulations and additives are included in this overview.
- Chapter 3 concentrates on the potential environmental releases from conventional operations within the nickel plating industry. While some of these practices vary among authorized regulatory offices, most apply to the nickel plating industry within the United States. Air emissions, wastewater releases, and toxic and hazardous waste management issues are discussed in the context of worker safety and environmental impacts.
- Chapter 4 addresses economic, technological, and regulatory factors.
- Chapter 5 applies pollution prevention and control technology options to environmental release issues.
- Chapter 6 presents conclusions and recommendations, which include:
  - Economically achievable pollution prevention and control technology options;
  - Environmental compliance consistency;
  - Continued research and development needs for reducing waste generation through process changes, material substitution, water use reduction, metals recovery/recycle and bath life extension;
  - Government-industry partnerships involving trade associations and professional organizations to consider solutions to environmental problems;
  - Long-term research and development planning by the industry to identify what is needed years from now to enable companies to remain sustainable and competitive within a changing global economy.

### Major Recommendations

This capsule report includes five major recommendations. The first recommendation is for facilities to continue the conduct of environmental audits and pollution prevention opportunity assessments. These tools have been very successful in assisting nickel-plating practitioners to identify where P2 and environmental compliance can be accomplished. These tools help to establish baselines to provide for a systematic approach for environmental decision-making. The second recommendation is to embrace environmental management techniques and approaches that encourage a more comprehensive life-cycle assessment; pollution prevention; environmental management systems that incorporate ISO 14000; and environmental cost accounting, such as activity based costing. The third recommendation is to improve production and reduce environmental impacts through enhanced technology transfer by government, industry, academia, and trade associations. Several nickel-plating practitioner needs can be met with technical and management information transfer through case studies, reports, workshops, journal articles, meetings, and newsletters. The fourth recommendation builds on the first three recommendations and

calls for a continuation and enhancement of the existing EPA-Industry partnerships for out-year planning by promoting more competition in the global market while reducing environmental impacts and improving productivity. The fifth recommendation is for government and industry to develop more efficient plating solutions that utilize lower concentrations of nickel and produce lower levels of air emissions and other releases. These five recommendations encourage the nickel-plating industry to use existing environmental management tools and technologies, improve upon their environmental management and technology base, seek competitive cost-effective environmental solutions using compliance through pollution prevention approaches, and conduct joint government-industry research and development that targets specific industry environmental issues.

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# 1. Introduction

## 1.1 Objective

The purpose of this capsule report is to inform the metal finishing community, stakeholders and decision makers, including both industry and regulatory communities, about the management of nickel plating environmental issues by providing technical information and practical examples of cost-effective, environmentally acceptable practices. The capsule report's review of the nickel plating industry provides an understanding of nickel plating uses, processes and chemistry used by metal finishers. Metal finishers have the opportunity to compare and contrast their own operation and maintenance, source reduction, control technologies and equipment with those presented in this capsule report. Assessments of demonstrated performance for innovative practices along with the regulatory and economic drivers impacting the nickel plating industry are evaluated.

## 1.2 Scope

The updated *National Metal Finishing Environmental R&D Plan* (EPA 600/R-00/035) dated March 2000, identified nickel

plating emissions as one of the upcoming environmental issues requiring additional research and development within the metal finishing community. The U.S. Environmental Protection Agency (EPA), working with stakeholders from the private and public sectors, determined that producing this capsule report will assist the metal finishing community by identifying and evaluating releases from nickel plating operations (both electrodeposited and electroless). The scope of this capsule report includes a profile of the nickel plating industry; pollution prevention and control technology options; and economic, technological and regulatory influences within the nickel plating industry. This capsule report includes a description of the nickel plating industry, current nickel plating management practices, and alternative approaches for waste reduction and control technologies. In addition, research opportunities are described which have the potential to meet the regulatory and economic demands for environmentally sound technology.

## 2. Nickel Plating Industry Profile

### 2.1 Industry Overview

The nickel plating industry is part of the larger metal finishing community in the United States. It consists of job shops (independently owned plating businesses) and captive shops (metal finishing operations contained in larger manufacturing facilities). There are over 3,000 U.S. job shops that average fewer than 50 employees each with annual sales of, approximately, \$5 million. Captive shops that support larger manufacturing facilities can vary in size depending on their role within the company. The metal finishing industry is regulated for environmental protection and occupational health and safety due to the nature of the processes and materials required to satisfy industrial and public consumer demand. Nearly all manufactured products require some type of surface finishing. Consumers demand products that have aesthetic appeal, will not deteriorate, and have durability. The nickel plating industry provides a product that improves appearance, slows or prevents corrosion, and increases strength and resistance to wear for manufactured parts and products.<sup>1</sup>

Most of the nickel plating industry is located in or near major metropolitan areas and may generate air emissions, water discharges, and solid wastes that add to overall pollution concerns. Pollution abatement costs and expenditures for the metal finishing industry comprise nearly 20% of its budget. Industry representatives are working together with government, trade associations, and professional organizations to encourage technological advances that lead to more efficient, cleaner production while reducing waste generation and control costs.<sup>1,2</sup>

Nickel plating is most commonly applied through the utilization of aqueous chemical reagents by means of electroplating or via chemical reducing agent that is referred to as electroless plating. Typical constituents of nickel electroplating solutions include nickel sulfate (or nickel sulfamate), nickel chloride, and boric acid, along with inorganic or organic additives that modify the crystal structure of the deposit. While a variety of formulations for nickel plating exists, the Watts, Woods, and Sulfamate processes comprise the majority of the formulations used by the metal finishing industry. Figure 2.1 depicts a typical metal finishing process.<sup>2,3</sup>

The types of additives used in nickel plating formulations tend to be categorized by product specificity: decorative or engineered coatings. Decorative nickel plating solutions

contain brightening additives that refine the grain structure of the deposit and additives that modify the surface defects of base parts. The latter additives are called leveling agents. Engineered nickel plating formulations also tend to contain additives for reducing stress, modifying hardness, or modifying the ductility of the deposit.<sup>4</sup>

Additives may modify the nucleation and growth of crystals, as they are formed on the cathode (part). They also correct surface imperfections partially insulating regions that are plating at faster rates. Additives account for the variation in desired surface appearances ranging from dull to satin-like, semi-bright, or full mirror bright. In many cases, the finish requires no further polishing or buffing.<sup>5</sup>

### ***Decorative Nickel Plating***

When nickel is plated for aesthetic reasons, it is termed “decorative” nickel plating. Decorative nickel finishes may range from 2.5 to 50 microns of one or more layers of electroplated nickel. In almost all decorative nickel plating applications the nickel deposit is followed by the application of a thin (0.1–0.5 microns) layer of chromium to enhance the longterm appearance and abrasion resistance of the finish. Decorative nickel plating is applied by electroplating versus electroless plating technique. There are some decorative nickel plating processes that yield a metal deposit that is bright black or pearlescent in appearance. These finishes are commonly used on components that match the black color of surrounding surfaces or on parts that must be non-reflective, such as antennae and camera parts. Typical decorative nickel plating applications include consumer products, such as toaster housings, automotive trim, writing instruments, door hardware, shelving, lighting fixtures, and appliance trim, such as handles and knobs.<sup>1</sup>

### ***Engineered Nickel Plating***

When the appearance of nickel is secondary to other properties, such as low stress, high corrosion resistance, modified magnetic property or increased wear resistance, the deposited nickel is termed “engineered” nickel plating. Engineered nickel plating is typically produced using either electroplating or electroless plating methods, depending on the desired property of the deposit. Typical engineered nickel plating applications include computer connectors, oil drilling components, valve components for highly corrosive liquids, specialized cutting saws, disks in computer hard drives, printing rolls, filtration screens, and mold production for plastic injection molding. Nickel plating can also be used to

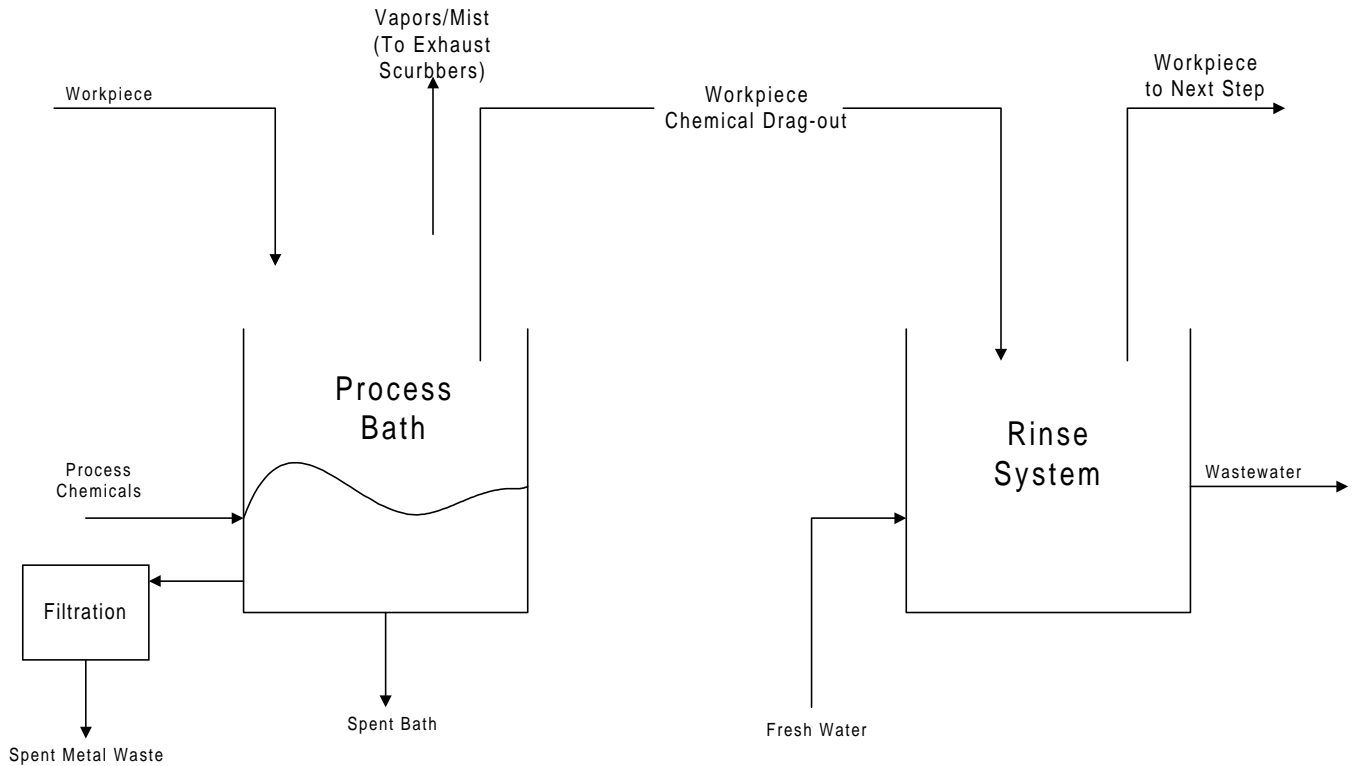


Figure 2.1. Metal finishing process flow diagram.

salvage improperly machined parts that would be costly to scrap. Engineered nickel deposits are often used as an underlayer for other metals. For example, gold, silver, palladium, palladium-nickel, platinum, or rhodium plating is applied over an underlayer of nickel that is electrodeposited for the enhancement of corrosion resistance, prevention of base metal diffusion into the precious metal, enhanced appearance of the deposited precious metal on the exterior surface, ductility of the component, or reduced stress (porosity) of the component.<sup>6</sup>

Another form of engineered nickel electrodeposition is electroforming. Electroforming is the deposition of a relatively heavy thickness of metal over a disposable or re-usable mandrel. The mandrel is separated from the nickel deposit, thus, leaving the product. Economics often prohibit the manufacture of electroformed products by other fabrication methods. Such electroformed products include seamless belts, compact disk (CD) stampers, mesh products for batteries, filtration screens, printing screens, porous electrodes, and molds for the production of a wide variety of products, including interior plastic panels of automobiles, automobile dashboards, reflector tail-lights and optical lenses.<sup>6</sup>

### **Electroless Nickel Plating**

Nickel coatings are also applied by electroless techniques. Electroless plating was discovered in 1944 as a chemical coating process that operates without electricity. The initial

nickel deposit is itself catalytic to the chemical reduction process, with the deposition of nickel continuing until the operator terminates the process. The terms “autocatalytic” or “self-catalyzing” often refer to electroless nickel plating. This process is applicable for conditions where uniform thickness is critical; a nonconductor is being plated to prevent electromagnetic interference; the material being coated has low porosity and deposition in recesses is required.<sup>7</sup> Electroless plating provides hardness, wear resistance and corrosion resistance while maintaining solderability, a diffusion barrier and the manipulation of magnetic properties. The manipulation of magnetic properties is especially important in computer hard drive manufacturing, since electroless nickel can be plated with no magnetism or with partial (controlled) magnetism. Similarly, the control of magnetism plays a critical role in the re-manufacturing of developer rolls which are a component of most recycle grade printing cartridges in laser printers and copiers. Electroless plating utilizes reducing agents to supply the electrons that convert dissolved nickel ions back to nickel metal. The type of reducing agent determines the type of nickel alloy deposited by the process. For example, the use of sodium hypophosphite (the most commonly used reducing agent for electroless nickel plating) will produce a nickel alloy containing approximately 2 to 15% phosphorus. If dimethyl amine borane is used as the reducing agent, the nickel deposited is an alloy of nickel and boron, containing approximately 0.6 to 5% boron. Other electroless plating

process reducing agents for nickel include borohydride compounds and hydrazine.<sup>1,7</sup>

Advantages of electroless nickel (EN) over electroplated nickel include higher corrosion resistance, a very uniform thickness over the most complicated shapes, high as-plated hardness, very high hardness after a heat treatment procedure, high solderability and bondability, and control over magnetic properties. Disadvantages of EN, compared with electrodeposited nickel plating, include much higher cost (5 to 6 times as expensive to apply), a slower deposition rate (0.25 to 0.5 microns an hour versus 10 to 400 microns an hour, depending on formulation and agitation levels) and a shorter bath life (months versus years). EN requires a higher bath temperature (95°C versus 21°C to 65°C) which may produce more brittle deposits. EN also requires better chemical control. As a rule, EN should not be considered a substitute for electrodeposited nickel plating; rather, should be used where the unique deposit characteristics or process capabilities are an advantage in functional and engineering applications.<sup>7</sup>

### **Other Nickel Plating Techniques**

Nickel coatings can also be produced by techniques other than electroplating or electroless plating including chemical vapor deposition (CVD), physical vapor deposition (PVD), high velocity oxygen fuels spraying (HVOF) and by plasma spray methods, along with other vacuum technologies.<sup>7</sup>

## **2.2 Nickel Electrodeposition Processes**

Electrodeposition or electroplating of nickel usually takes place in a tank containing water and at least one salt of the metal to be deposited. This metal salt (nickel) is dissolved in the water producing ions. Nickel ions are positively charged; whereby, each atom of metal loses two electrons, as the salt is dissolved into the water. While nickel solution is typically emerald green, the deposited nickel will be silver or gray on the electroplated object. The nickel ions are free to move about in the solution. The positive charge attracts the nickel ions to the negatively charged cathode or the part to be plated. The excess electrons on the negatively charged part return to the outer orbit of the nickel ions producing neutrally charged nickel metal atoms at the surface of the part to be plated. This is the basic process of electroplating. Typically, the electroplating solution also contains hydrogen ions, as the pH of the solution approaches 4. These hydrogen ions, also, are reduced to hydrogen gas, thus, reducing the efficiency of the process from 100 to, approximately, 90 - 95%.<sup>1</sup>

The pH of the plating solution is an important control parameter, since it can affect the appearance, efficiency, and physical properties of the deposit. In general, lower pH values produce more ductile deposits, while reducing the efficiency of the process. Each process has an optimum operating pH range. There are a number of nickel electrodeposition processes in use today. The following sections describe some of the more common processes and solutions.

### **Watts Nickel Electroplating Process**

The basic constituents for a Watts nickel plating solution include: nickel sulfate (26 to 35 oz/gal, or 195 to 262 g/L) as the primary source of nickel ions, nickel chloride (6 to 12 oz/gal or 45 to 90 g/L) as a secondary source of nickel ions and for improved anode corrosion, boric acid (5 to 6.5 oz/gal or 37.5 to 49 g/L) to stabilize the pH of the solution and water. Boric acid also enhances the “whiteness” of deposit and enhances the performance of the leveling agent. Nickel sulfate and nickel chloride are nonvolatile, highly conductive and soluble in water.<sup>1</sup>

Addition agents are added for hardness, leveling, anti-pitting, and/or brightness. Solutions for decorative plating differ with the types of addition agents employed to produce surfaces that are bright, semi-bright, or satin. Addition agents for brightening may be organic or inorganic. Trace amounts of cadmium, for example, may be added to the Watts formulation for producing a deposit of semi-bright to bright appearance (without leveling). Addition agents for leveling or anti-pitting are organic chemical compounds.<sup>1</sup>

In Watts decorative nickel plating processes, there are two distinct classes of brighteners. Class I brighteners are distinguished by the presence of an unsaturated carbon bond and a sulfon group. Class I brighteners are mirror bright when initially introduced and gradually become semi-bright as the deposit thickens on the object. Examples of Class I brighteners are benzene disulfonic acid, benzene trisulfonic acid, naphthalene trisulfonic acid and benzene sulfonamides. These brighteners infuse sulfur into the deposit. The added sulfur causes the deposit to be less noble or more active than pure nickel deposits or nickel brightened without sulfur. The downside of adding these brighteners are a reduced resistance to corrosion and embrittlement. However, when combined in a two or more layer system, the less noble nickel can provide galvanic corrosion protection to a more noble layer of nickel (usually a semi-bright deposit containing no sulfur); thereby dramatically increasing the overall corrosion resistance of the nickel layer. Such two layer nickel deposits are referred to in the industry as “duplex” nickel plating. Such multiple layers are applied to parts used on exterior automotive and marine applications, where high resistance to salt corrosion is necessary.<sup>1</sup>

Class II brighteners are sulfur free, cationic organics with unsaturated carbon bonds in either long chain (aliphatic) or ring (aromatic) structures. These brighteners add a small amount of carbon into the deposit and have a milder effect (semi-bright) on the nickel deposit when used alone. Examples of Class II brighteners are formaldehyde, coumarin, ethylene cyanohydrin and butynediol. High concentrations of Class II brighteners can yield highly stressed deposits. Therefore, it is important to balance the concentrations for low internal stressed, fully bright, ductile deposits. Class II brighteners also act as leveling agents to provide relatively smooth surfaces. This results in a product that requires less end polishing and buffing.<sup>1</sup>

Leveling agents function in a similar manner to brighteners, but are much more aggressive to ensure surface perfection



without peaks and valleys. The leveling agents (organic compounds) are incorporated at a higher rate during the peak of surface imperfections (moderately higher current density areas); thereby, insulating the peaks slightly and redirecting the current into the valleys. The valleys then receive a greater amount of current than the peaks and the overall deposit tends to be level.<sup>1</sup>

The broadest range of operating conditions for the Watts nickel plating solution is a temperature range of 21 °C to 65 °C, a pH range between 1.5 and 4.5, a current density range from 300 to 700 A/dm<sup>2</sup> and air and/or mechanical agitation. For specific applications, these conditions are controlled to within more narrow windows of operation. Typically, the Watts nickel plating solution is about 95% cathode current efficient. The remaining 5% of the cathode current generally produces hydrogen gas bubbles and causes the pH of the solution to rise as the solution is spent. Some Watts bright nickel solutions are available in “high speed” versions that contain high concentrations of nickel salts, higher operating temperatures and greater agitation.<sup>1</sup>

The Watts nickel plating solution may be operated without addition agents, in which case a “dull,” highly ductile deposit is produced. Such a deposit can be used in both decorative and engineered applications. High concentrations of any organic additives in a Watts or sulfamate nickel plating solution cause a dramatic increase in tensile or compressive (depending on the additive) stress in the nickel deposit.<sup>1</sup>

### Sulfamate Nickel Plating Process

Electrodeposition of nickel for applications in the electronic industry require more ductility and a lower level of porosity than what is typically obtained from a Watts formulation. The sulfamate nickel process is used to obtain such properties. The sulfamate solution increases the process cost, as nickel sulfamate is significantly more expensive than the sulfate salt, but the sulfamate process offers lower internal stress, higher purity, higher ductility, and a lower level of porosity.<sup>1</sup>

The sulfamate nickel plating process utilizes nickel sulfamate, boric acid and in many applications, a small amount of either nickel chloride, nickel bromide or magnesium chloride to enhance anode corrosion and promote conductivity. These halogen compounds increase tensile stress which is then controlled by the addition of a small amount of stress-reducing compound. An example of a common stress reducing compound is saccharin.<sup>1</sup> The primary function of chloride, in both the Watts and sulfate nickel formulation, is to improve anode corrosion, especially in solutions using non-sulfurized anode materials. Magnesium chloride may be used as an alternate source of nickel chloride for nickel sulfamate plating solutions. The magnesium chloride has a lesser tendency of increasing tensile stress in the nickel deposit.<sup>1</sup> Control of stress in nickel plating is extremely important in electroforming operations, as high tensile or compressive stresses tend to deform the electroformed part resulting in poor replication of the mandrel. Ideally, the nickel should have zero stress, which can be obtained using proper operational controls or a combination of operational controls and the use of stress modifying agents.<sup>1</sup>

Another common additive to sulfamate nickel plating solutions is a wetting agent to reduce the pitting tendency. Wetting agents lower the surface tension of the plating solution to a range of 30 to 40 dynes/cm, reducing the tendency of hydrogen gas bubbles to remain on the surface of the part. These bubbles, eventually, will burst and produce a pit on the plated part. Wetting agents are typically organic soaps.<sup>1</sup> Nickel sulfamate is non-volatile, highly conductive and soluble in water. It is more soluble than nickel sulfate and breaks down at the anode to form a beneficial, stress-reducing compound. On the other hand, when using such solutions without chlorides there is a tendency to create anode polarization that will lead to unstable pH and result in a decrease of nickel concentration in the solution.<sup>1</sup> Boric acid is an inexpensive pH buffer and tends to stabilize the pH in the cathode film of all nickel plating solutions. Boric acid has a limited solubility of about 7 oz/gal (52 g/L) at 65 °C. To avoid roughness from boric acid crystals, the crystals should not be added directly to the solution. Additions should be made by hanging an anode bag containing the crystals in the solution until they are dissolved.<sup>1</sup>

### General Operational Information for Nickel Plating

Table 2.1 lists constituent and operating conditions of typical nickel plating solutions.

#### Anodes/Anode Baskets

Anodes, bagging, and anode baskets are important parts of the nickel plating process. In a well-operated nickel plating process, anodes replace the nickel ions at about the same rate as nickel ions are converted back to metal at the cathode. There is a variety of anode materials available for nickel plating. For high pH applications, nickel oxide or carbon

Constituent and Conditions	Plating Solutions	
	Watts	Sulfamate
Nickel sulfate, NiSO <sub>4</sub> * 7H <sub>2</sub> O	300 g/L (40 oz/gal)	—
Nickel chloride, NiCl <sub>2</sub> * 6H <sub>2</sub> O	60 g/L (8 oz/gal)	—
Nickel sulfamate, Ni(NH <sub>2</sub> SO <sub>3</sub> ) <sub>2</sub>	—	400 g/L (60 oz/gal)
Boric Acid, H <sub>3</sub> BO <sub>3</sub>	7.5 g/L (5 oz/gal)	30 g/L (4 oz/gal)
pH	3.0–4.0	4.5
Temperature	20°C to 60°C	30°C to 60°C
Current density, A/m <sup>2</sup> (A/ft <sup>2</sup> )	430 (40)	430 (40)

depolarized anodes function well. In Watts bright nickel applications, sulfurized anode materials are most commonly used. In most applications, bagging is either recommended or required to prevent particle roughness. The purpose of the bag is to filter residues that are created as the nickel metal dissolves. Such residues consist of metallic compounds and non-metallic impurities. Anode bags should be durable, fit tightly, be correctly sized, and be made of appropriate woven cotton, cotton flannel, Dynel® or Dacron® material. Double bagging in specialized applications is also employed. Bags should be periodically inspected, emptied of residuals and washed clean before reuse.<sup>1</sup>

Anode baskets are used to provide a higher economy and to maintain a constant anode current density, since a full basket will always have the same current density for a given rectifier setting. Baskets should be kept full to prevent etching of the titanium and be placed in a manner for the tops of the baskets to be above the solution level to prevent residues from inside the bags from entering the plating solution. This allows for easy inspection and material replacement. Titanium baskets are preferred except in rarely used fluoborate-based nickel plating solutions.<sup>1</sup>

**Solution Agitation**

Agitation (mixing) of the plating solution is necessary to maintain optimum placement of the nickel deposit, prevent anode/cathode polarization effects and improve coverage. Inadequate levels of agitation can result in dull, burnt, pitted, and streaky deposits. The Watts solution may be agitated using air or mechanical means, such as recirculating pump, moving cathode rod, or eductor systems. Air agitation is most commonly used in decorative bright nickel plating. For those processes requiring air agitation, 2 to 3 cfm/ft<sup>2</sup> of tank surface area is recommended. However, many installations have successfully switched to the use of eductors to avoid the air emissions that air agitation tends to produce. The sulfamate solution is most commonly agitated via mechanical means.<sup>1</sup>

**Filtration**

Filtration of bright nickel plating solutions is important for obtaining a deposit that is free from roughness and has an optimum brightness appearance. Continuous filtration at 2 to 3 turnovers per hour is desirable to maintain the optimal deposit appearance. The filter pore size should be between 10 to 15 microns. Sufficient filtration surface area (media) should be installed to allow for adequate design operation of the filter. Typical design specification for cartridge filters is one 12" cartridge filter per 50 gallons of solution.<sup>1</sup>

**Nickel Plating Problems**

Plating problems caused by pitting, poor adhesion, brittle deposits, and rough deposits can result in rejects. Rejects due to defects in plating can be costly, since rejected parts must be either replaced or stripped and re-plated; effectively, generating two or more times the waste beyond normal operation. While there are many factors contributing to poor performance, Table 2.2 lists the more typical ones.<sup>1</sup>

Inorganic contaminants can affect the nickel plating solution causing undesirable appearances (dark deposits in low

Problem	Potential Cause
Pitting	pH too low, inadequate agitation, current density too high, low wetting agent content, organic contamination, copper contamination, poor surface preparation
Poor Adhesion	Poor cleaning/rinsing, hexavalent chromium, contaminated pickling acid.
Brittle Deposits	pH too high, organic contamination, high sodium content, high chloride content.
Rough Deposits	Calcium contamination, torn anode bag, poor filtration.

current density areas), poor adhesion and roughness. Purification processes, such as carbon treatment and low current density dummmying (plating at very low current density onto scrap steel sheets) are used to remove common metallic and inorganic contaminants, such as copper and zinc.

**Barrel Nickel Plating**

Since nickel plating solutions typically exhibit poor throwing power in comparison to other metal plating solutions, the process and plating solution formulation requires adjustments for barrel plating. Typically, barrel nickel plating solutions use the Watts formulation with higher concentrations of nickel sulfate and nickel chloride.<sup>1</sup>

**Electroforming**

Nickel electroforming is generally performed by the sulfamate process due to economical advantages, high plating speeds, and low internal stress. The Watts nickel plating solution is used for electroforming of rotary printing screens. The typical properties of electroformed nickel are shown in Table 2.3.<sup>1</sup>

Property	Watts	Sulfamate
Tensile Strength (MN/m <sup>2</sup> )	345–4485	415–620
Tensile Strength (psig x 10 <sup>3</sup> )	50–70	60–90
Elongation (%)	15–25	10–25
Hardness (VHN <sub>100</sub> )	130–200	170–230
Internal Stress (MN/m <sup>2</sup> )	125–185 tens.	0–55 tens.
Internal Stress (psig x 10 <sup>3</sup> )	18–27	0–8
Note: 1 Mega Newton/m <sup>2</sup> (MN/m <sup>2</sup> ) = 1 N/mm <sup>2</sup> = 1 Mpa = 145 Pounds/in <sup>2</sup> (psi)		



## Other Nickel Plating Solutions

There are numerous nickel plating solution formulations, including all-chloride and fluoborate-based solutions, which may be employed in high-speed plating. In addition, there are black nickel process solutions used in decorative applications, including two formulations that bear special mention called "strike" solutions. A nickel strike solution is typically a very thin (usually, less than 2.5 microns) deposit that is designed to activate (activation is the term used for any process that removes oxides from the surface of metals) and, simultaneously, deposit a thin film of relatively pure nickel that readily accepts the final deposit(s) without loss of adhesion. Nickel strike solutions are commonly employed in processing metal alloys that yield poor adhesion due to the presence of a chemically resistant oxide film that quickly re-forms upon exposure to air. Examples of such metal alloys include most stainless steel alloys, Monel®, Kovar®, Invar® and other nickel-iron alloys. Nickel strikes are also employed when processing hardened steel and tool steel alloys. Two formulations of nickel strikes commonly found in the nickel plating industry are the Wood's process solution and the Sulfamate strike.<sup>1</sup>

### Wood's Nickel Strike

The Wood's formulation employs a solution that has only three ingredients: water, nickel chloride (225 g/L) and hydrochloric acid (5 to 8% volume). Typically employed current densities range from 1000–3000 A/dm<sup>2</sup>. The solution is intentionally formulated to produce a large volume of hydrogen gas. The hydrogen gas chemically reduces oxides present on the metal surface while depositing a thin film of nickel.<sup>1</sup> The Wood's nickel strike may contain as much as 8% by volume hydrochloric acid, producing fumes and mists which must be removed from the exhaust by a scrubber. The solution is very corrosive and tends to corrode metal components that are near the tank; often corroding the building itself.<sup>1</sup>

### Sulfamate Nickel Strike

This solution also contains only three ingredients: water, sulfamic acid (150 g/L) and nickel sulfamate (320 g/L). The sulfamate process solution is favored over the Wood's nickel formulation since it eliminates hydrochloric acid, which generates fumes that pose worker health issues during make-up and control of the process, along with the corrosion problems. The sulfamate process does produce solution mist that should be scrubbed from the exhaust.<sup>1</sup>

## 2.3 Electroless Nickel Deposition Process

Electroless plating occurs without applying electric current, utilizing an oxidation-reduction chemical reaction instead (see Figure 2.2 for comparison with electrodeposition). The electrons are supplied by a chemical reducing agent (sodium hypophosphite, amine boranes, or hydrazine) dissolved in the plating solution. The deposited nickel acts as a catalyst for the continuation of the chemical reaction until the plating process is terminated by an operator.<sup>7</sup>

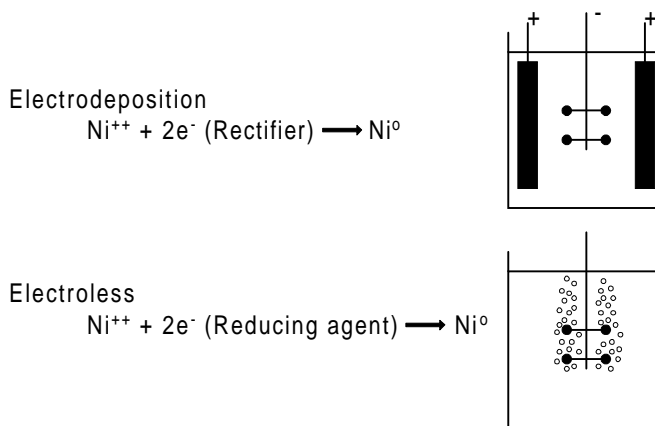


Figure 2.2. Comparing electroplated to electroless nickel.

## Sodium Hypophosphite Reducing Agent

The hypophosphite ion is known to be catalytically oxidized on the object's surface to release hydride ions which are available for reduction of nickel ions at the surface. The products of this reaction are the nickel-phosphorus deposit, phosphite ions, hydrogen ions and hydrogen gas. The phosphorus is co-deposited with nickel to the extent of 1% to 15% by weight.<sup>7</sup>

## Sodium Borohydride/Amineborane Reducing Agents

Sodium borohydride and amineborane are two other reducing agents used in electroless nickel plating. If either borohydride or an amineborane is used as a reducing agent in place of hypophosphite, boron is co-deposited with nickel in the range of 0.2 to 6% by weight.<sup>1</sup>

## Alkaline versus Acid EN Formulations

The two types of EN solutions currently in use are acid and alkaline solutions. These solutions are described in the following paragraphs and Table 2.4.

### Acid EN-Phos Solutions

Acid solutions with pH ranging from 4 to 5.5, are the most commonly used EN plating solutions. Acid solution can be utilized to deliver a broad range of nickel phosphorus alloys ranging from low-phosphorus alloys (typically 2 to 6% P) to medium-phosphorus alloys (typically 6 to 9% P) to high-phosphorus alloys (9 to 15% P). The high-phosphorus alloys are typically utilized in applications where the deposit must be non-magnetic or highly corrosion resistant. Low- and mid-range alloys are more readily heat treated to yield exceptional hardness and wear resistance that approaches that of chromium (Vickers Hardness Number 800 compared to 1000 for chromium).<sup>8</sup>

Typical ingredients of acidic EN solutions are nickel sulfate, sodium hypophosphite, complexing agents, buffers and stabilizing agents. The pH range for EN acid solutions should be carefully controlled since the deposition rates below a

Table 2.4 Typical Electroless Nickel Solution Constituents and Operating Parameters <sup>8</sup>					
Electroless Bath	Temperature	pH	Deposition Rate	Metal Salts	Reducing Agents
Acid Nickel	77–93°C (170–200°F)	4.4–5.2 (for medium to high P) 6.0–6.5 (for low P)	12.7–25.4 micrometers/hr (0.25–0.7 mils/hr)	Nickel sulfate Nickel chloride	Sodium hypophosphite Sodium borohydride Dimethylamine borane (DMAB)
Alkaline Nickel	26–95°C (79–205°F)	8.5–14	10–12.7 micrometers/hr (0.25–0.5 mils/hr)	Nickel sulfate Nickel chloride	Sodium borohydride Sodium hypophosphite DMAB Hydrazine

pH of 4 are too slow, and above 5.5 can cause the formation of insoluble nickel compounds which can lead to spontaneous decomposition of the solution. This occurrence can be extremely dangerous with large amounts of heat and gas generated in a burst of energy, causing hot process solution to be ejected from the tank. Precipitated nickel compounds can also cause rough deposits.<sup>8</sup>

In an acidic EN plating process, the phosphorus content decreases with an increasing pH. The phosphorus content may also be affected by the temperature of the EN solution, the concentration of the sodium hypophosphite and other EN solution additives. The major change in phosphorus, typically, comes from an increase or decrease in the pH or chelate/additive(s) concentration and this change can affect deposit properties. A decrease in pH will cause an increase in phosphorus content resulting in changes in properties that may decrease ferro-magnetism and decrease tensile strength while, simultaneously, increasing wear resistance and corrosion resistance. Manipulation of the pH to change the phosphorus content in the deposit is typically not done. Rather, solutions are formulated to deliver the desired alloy composition when operated within carefully controlled pH windows.<sup>8</sup>

### Alkaline EN-Phos Solutions

EN alkaline solutions yield nickel deposits with 3% to 7% phosphorus. Alkaline EN solutions typically operate within the pH range of 8 to 10. The pH is maintained by the addition of ammonium hydroxide (NH<sub>4</sub>OH). However, there are a number of alkaline EN solutions that do not use ammonium hydroxide to control the pH.<sup>8</sup>

In the alkaline EN plating process the nickel deposition rate and phosphorus content is not significantly affected by the operating pH of the solution. Instead, the type and concentration of chelate and additives present in the solution determine the alloy composition when the process is operated within a narrow pH range. A visual inspection of the EN alkaline solution will indicate a need for adding ammonium hydroxide when the solution changes color from

blue to green. The phosphorus content of the alloy is controlled by the concentration of the reducing agent.<sup>8</sup>

### Operating Temperatures of EN Solutions

One of the most important factors affecting the nickel deposition rate for EN hypophosphite solutions is temperature. Alkaline EN processes are typically used for obtaining conductive nickel films over nonconductors such as plastics, since the process can be operated at relatively low temperatures versus acidic EN processes. The alkaline process can be operated at temperatures as low as 86°F (30°C) or as high as 185°F (85°C). The acidic process typically operates in the temperature range of 180 to 190°F (82 to 88°C) in order to take advantage of higher deposition rates. Low temperature alkaline EN plating solutions may contain ammonium citrate, a nickel complexing agent, to prevent precipitation of nickel hydroxide at the lower operating temperature.<sup>7</sup>

There is a concern that the solution may decompose with the formation of nickel-phosphorus particles, as the temperature of the EN acid solution increases. It is preferable to use indirect heating of the EN acid solution. Hot water or steam in heat exchangers or jacketed tanks are the most common indirect heating techniques. For smaller tanks (5 to 100 gallon), electric immersion heaters are frequently used. A low nickel deposition rate and a decreased EN acid solution life can occur when the EN acid solution is held at the operating temperature. Low EN acid solution loading can cause a high usage of the reducing agent. A minimum EN acid solution loading of 0.6 dm<sup>2</sup>/L (0.25ft<sup>2</sup>/gal) is recommended.<sup>7</sup>

### EN Deposition Rates

The nickel deposition rate for EN hypophosphite solutions are most effective when controlling the pH, temperature, and the concentrations of nickel and hypophosphite. This requires the operator to keep the concentrations, pH, and temperature at optimum levels with periodic analysis and monitoring of the solution.<sup>7</sup>

The nickel deposition rate from EN acid solutions can be substantially increased by the presence of organic additives, such as hydroxyacetate, succinate, acetate, propionate, malate and lactate. The functions of these organic additives are to increase the nickel deposition rate, stabilize the pH, and form complex Ni<sup>++</sup> ions. For EN alkaline solutions, the nickel deposition rate can be increased, the pH stabilized and the ion complexes formed with organic additives such as citrate and pyrophosphate. This is particularly important for EN alkaline solutions that require replenishing for several nickel turnovers due to an increase in the phosphite ion concentration. The precipitation of nickel salts and/or the introduction of other unwanted particles from the chemicals or atmosphere may provide the necessary conditions for catalytic deposition. This condition causes nickel fallout, and these highly active surfaces will spontaneously decompose resulting in deposit roughness. Filtration (continuous or periodic) of the EN solution is required to remove these suspended solids. The filtration requires a 1 to 5 micron filter and a pump displacement that can produce 5 solution turnovers in a one-hour period.<sup>7</sup>

Binary alloys of nickel and phosphorus or nickel and boron comprise the best known electroless deposits. The number of metals that can be deposited by electroless means is rather limited. The incorporation of additional metal elements into the electroless deposits can be an important means of enlarging the range of chemical, mechanical, magnetic and other properties attainable.<sup>7</sup>

Ternary (three elements) and quaternary (4 elements) alloys of nickel deposited from electroless solutions offer some unique properties and applications. Notably, Ni-Co-P deposits of varying compositions can be produced from similar alkaline ammoniacal solutions. Ni-Co-P alloys can be utilized to enhance the corrosion protection of an EN system in similar fashion to "Duplex Nickel" electroplating. The outer layer of Ni-Co-P is galvanically more active and provides cathodic protection of the layer underneath which, typically, is a Ni-P alloy. In essence, the underlayer Ni-P becomes the cathode in the galvanic cell formed between the two layers of alloys, while the Ni-Co-P alloy becomes the anode.<sup>7</sup> Ni-W-P alloys can be employed in applications where the coating is subjected to high temperatures, as the melting temperature of the alloy is much higher than Ni-P.<sup>7</sup>

Ni-Mo-P and Ni-Mo-B alloys can be utilized to control magnetic properties. For example Mallory found that Ni-Mo-P alloys typically are no harder in the plated condition when compared to Ni-P alloys, but are harder after heat treatment. Ni-Mo-B alloys were about 10% harder in Vickers hardness readings than similar alloys without molybdenum and also were harder after heat treatment than binary nickel-molybdenum alloys.<sup>7</sup> Even a small amount (1%) of copper can improve ductility, brightness, and corrosion resistance. The deposits are virtually non-magnetic, even at elevated temperatures, and may be utilized on computer memory disks, as a corrosion resistant, non-magnetic under-coat for the outer magnetic deposit.<sup>7</sup>

Ni-P-Cu-Sb is a quaternary alloy, used for superior resistance in marine environments (salt resistance). Ni-P-B is a compromise between the best features of each binary alloy process. The deposit is harder and more wear resistant than Ni-P, and more corrosion resistant than Ni-B. Ni-Fe-B alloys can be used in applications requiring specific levels of ferro-magnetism. Ni-Pd alloys can be utilized in electronic applications where a uniform thickness over a very complex shape is necessary and electroplating the alloy can not yield the desired uniformity.<sup>7</sup>

### ***EN Containing Particulate Matter***

More recently, the incorporation of PTFE (Teflon®) into electroless nickel deposits has become available. Most applications employ coating thicknesses of approximately 0.25 to 0.5 mil, with a preferred underlayer of pure electroless nickel for added corrosion resistance. Typical electroless nickel-PTFE composite coatings incorporate PTFE in the range of 25% by volume, with focus on deposits having 18 to 25 volume percent. Contrary to the inclusion of wear resistant particles (e.g., silicon carbide and diamond), electroless nickel-PTFE composite coatings appear to be limited to particles of 1µm or smaller.<sup>7</sup>

The mechanics of composite electroless plating are different from prevailing practices for conventional electroless plating. Finely divided, solid particulate material is added to and dispersed throughout the electroless plating solution. The dispersed particles are not filtered out. The dispersion of the particulate matter results in a new surface area loading in the range of 100,000 cm<sup>2</sup>/L, which is 800 times greater than the plating load generally acceptable in electroless nickel plating.<sup>7</sup>

Uniformly dispersing micron or sub-micron particles provides enhanced wear, abrasion resistance and/or lubricity of the surfaces of base substrates. The adoption of such a coating can yield ways of conserving both energy and natural resources. The use of a composite electroless coating also offers the benefit of reduced solution handling and waste treatment problems, as well as reduced reliance on strategic materials (e.g., chromium) for wear applications.<sup>7</sup>

Particles are suspended and prevented from coagulating by means of "Particulate Matter Stabilizers" (PMS); patent numbers: 4,997,686 and 5,145,517. These materials (combinations of wetting agents) impart a zeta potential to the particles and prevent plating on the particles by maintaining solution stability. Not all particles require these PMS materials.<sup>7</sup> While a wide variety of particulate matter can be co-deposited with EN, at present, commercial composite electroless plating activities have been limited to natural and synthetic (polycrystalline) diamond, silicon carbide, aluminum oxide, fluoropolymers (PTFE) and fluorinated carbon.<sup>7</sup> The above information regarding EN containing particulate matter can be obtained by referencing the AESF Electroless Deposition Course materials, AESF, 12644 Research Parkway, Orlando, Florida.<sup>7</sup>



## **Addition Agents for EN Processes**

Additions of trace quantities of certain catalytic agents (“poisons”), in a narrow concentration range, will stabilize EN solutions against general solution decomposition. Most EN solutions use stabilizers such as lead acetate, lead sulfide, thiosulfate, thiourea, molybdcic acid, and thiocyanate in low concentrations of a minimum/maximum number of 1 mg/L for lead acetate and a minimum/maximum range of 1 mg/L to 10 mg/L for molybdcic acid. As with the use of all stabilizers and additives, only demineralized or preferably deionized water should be used for make-up and replenishment of EN solutions. Water containing impurities can only shorten the life of the EN solution and may also affect the appearance of the nickel deposition. It is best to rinse parts in counterflowing deionized water to reduce impurities before implementing any EN solution process.<sup>7</sup>

## **Surface Treatment Prior to EN Plating**

Provided that there is a chemically clean surface, metals that are spontaneously deposited with nickel, when immersed in an EN solution, are nickel, cobalt, iron, aluminum (usually processed through a zincate treatment prior to plating to enhance adhesion), zinc, titanium, beryllium, and palladium. Plastics, ceramics, and silver require catalytic activation and copper and copper alloys may require galvanic initiation, or a thin nickel electrodeposit (strike). Metals such as lead, cadmium, antimony, and bismuth are normally incapable of direct EN deposition since they are catalytic poisons. These metals can be EN deposited by first applying a copper or nickel electrodeposit.<sup>7</sup>

Some typical activation procedures for surface treatment of metals include the application of momentary cathodic current, the application of palladium film, and the immersion of the part in reducer solution such as dimethylamineborane (DMAB).<sup>7</sup> Copper and silver can be plated directly in EN-boron processes.

For nonconductors, typical activation procedures require immersion in a colloidal palladium suspension, followed by immersion in an “accelerating solution” that is comprised mostly of hydrochloric acid. This is known as the “two-step” process for activating plastics. A single-step process consists of immersing suitably cleaned and etched plastic in a single solution containing tin/palladium complexes and colloids stabilized by excess stannous chloride in a hydrochloric acid solution.<sup>7</sup>

## **Production and Maintenance of EN Solutions**

EN plating solution formulations can be found in the literature. Some companies produce their own solution from basic ingredients, but most companies utilize commercially available solutions. Commercial EN solutions are produced by blending concentrates supplied by the company selling the formulation. The concentrates typically contain nickel salt, complexing agents and stabilizers, hypophosphite, and a pH adjuster.

Work load dictates the frequency of chemical replenishment, but some degradation occurs even if the solution is not utilized. For this reason, tanks should only be as large as the load, minimally, requires. A “turnover” occurs when the maintenance addition of nickel salt is equal to the original concentration. For example, if the solution is initially made up with 28 g/L of nickel sulfate, as the nickel alloy is being used in the EN process, a “turnover” occurs when the total amount of nickel sulfate added to the process over time is 28 g/L. After a number of turnovers, the contaminants (primarily the orthophosphite byproduct of the chemical reaction) are so concentrated that the solution no longer delivers an adequate deposition rate and the solution is taken out of service and replaced. The number of turnovers obtained from an EN process before the solution is no longer usable depends upon careful control of contaminants, solution loading, chemical concentrations, temperatures, and filtration.<sup>7</sup>

Equipment is available for the selective removal of contaminants such as ortho-phosphite from the EN process. This equipment is based upon “electrodialysis” principles. In installations where this technology has been used, the EN solution has lasted more than a year without degradation of the process. Also, a commercially available formulation (Everon TM) that selectively precipitates the orthophosphite from the EN solution, yields 60 to 150 turnovers before the solution requires replacement. Installations that do not use either of these life prolonging technologies can experience between 4 and 14 turnovers before the EN solution is no longer suitable for production use.<sup>7</sup>

## **Treatment of Spent EN Solutions**

The spent solution must be treated to reduce the nickel concentration to an acceptable level before it can be discharged. Electroless nickel plating solutions employ chelating agents to keep nickel ion activity at a controlled concentration. Once the plating solution becomes “spent,” it must be treated to reduce the dissolved nickel below regulated limits.

Treatment methods include autocatalytic decomposition which employs the following:

1. The room temperature solution is loaded with a high surface area substrate. Steel wool is a cheap, readily available, high surface area substrate.
2. The solution temperature is slowly raised and the level of gassing is monitored. As gassing subsides, the temperature is further increased until the boiling point is approached. No further increase in temperature beyond the boiling point is feasible.
3. Additional reducing agent is added in small amounts until further additions result in no further gassing. At this point, the dissolved nickel concentration has been reduced to a concentration of about 5 to 50 ppm.
4. The remaining dissolved nickel is precipitated using starch xanthate, DTC (pH>11), sodium hydrosulfite, or sodium borohydride. Bench testing in the laboratory

is typically used to discover the most effective of these agents for the solution.<sup>7</sup>

Electroless nickel bearing wastes can also be treated utilizing displacement of the nickel with calcium added as the oxide. The treatment is rather time consuming, but is effective on a variety of wastes. Either lime (calcium hydroxide) or sodium hydroxide can be used to raise the pH to 12, prior to treatment with calcium oxide. Numerous other treatment schemes can be found in the literature.<sup>7</sup>

### **EN Plating Equipment**

The plating tanks are usually fabricated of polypropylene or passivated stainless steel to resist reaction with nitric acid which is used to strip off nickel that is typically deposited onto the tank surfaces over time. Disposable plastic liners (15 to 30 mil polyvinyl chloride) can be used in tanks which add additional chemical resistance and ease of waste disposal, as less nitric acid is required to remove unwanted nickel deposits on the tank walls. Parts with blind holes must be fixtured to allow the escape of hydrogen gas that would otherwise be trapped on the surface during the plating reaction. Plastic or plastic-coated racks will help to reduce the waste of nickel. Small parts may be plated in a rotating plastic basket. Another plating set-up includes suspending the part to be plated with a wire or hook. Whatever method is used for providing the fixture or set-up, good solution agitation and work piece movement are recommended and the plating solution chemicals should be kept at near optimum operational conditions.<sup>7</sup>

### **Surface Preparation**

Metal parts are prepared for EN plating in very much the same manner as for all electroplating, and it is perhaps more critical that the part be clean. Cleaning usually involves the part being soaked in a hot alkaline cleaner. After a rinse, the part is subjected to electroclean-anodic or periodic reverse, and rinsed again. The next step typically is immersion in a dilute acid solution (sulfuric acid, 10% by volume is commonly employed) before the part is double or triple rinsed. This cleaning process should render the part ready for EN plating. Aluminum parts are typically processed through soak clean, rinse, electroclean, rinse, zincate dip, rinse, acid dip (nitric), rinse, zincate dip, and rinse prior to EN plating. Proper pretreatment cycle for each type of metal to be plated is critical for proper adhesion.<sup>9</sup>

### **Modifying EN Hardness**

While EN plating provides a harder deposit than electrodeposited nickel, the hardness of nickel-phosphorus deposits can be further increased from a Vickers hardness of about 500 kp/mm<sup>2</sup> to about 800 to 1000 kp/mm<sup>2</sup> with the application of a heat treatment. The heat treatment requires the part be heated to 400°C for an hour. Lower treatment temperatures and longer times can be used as well, but the ultimate hardness obtained is lower than 800 kp/mm<sup>2</sup>. The resulting hardness is comparable to that of electroplated hard chromium. It is the crystallization of the nickel and the formation of a nickel phosphide (Ni<sub>3</sub>P) precipitate in the coating by the heat treatment that produces dispersion hardening. In general, heat treatment of a non-magnetic, high-phosphorous EN deposit will re-introduce magnetism into the deposit.<sup>7,10</sup>

Nickel-boron EN deposits are harder than nickel-phosphorus EN coatings in both the plated condition (650 to 700 VHN compared to 500 to 600 VHN) and after heat treatment (1000 to 1200 VHN compared to 800 to 1000 VHN). However, the EN-boron alloy deposited is notably more porous and does not offer the same combination of corrosion resistance and hardness as the EN-phosphorus alloys.<sup>7</sup>

EN-Boron (NiB) plating can be accomplished with reducing agents to produce plated parts requiring a greater hardness, wear resistance, wire bondability and solderability. Such parts are used for automotive and jet engine applications. Other NiB applications are for printed circuits, electrical contacts, and electronic components. Electroless NiB plating is a good example of the use of EN plating to take advantage of one or more of the unique characteristics: exceptional deposit thickness, deposit uniformity, low porosity, solderability (if the boron content is below 1%), ability to deposit directly on copper, silver and nonconductors, and particular chemical, mechanical, or magnetic properties of the deposit.<sup>6,7</sup>

EN-B processes are also available in alkaline and acidic formulations. The alkaline process typically utilizes sodium borohydride as the reducing agent, at a pH ranging from 12 to 14 and at a temperature of 90 to 95°C (195 to 205°F). The boron in the deposited alloy typically is in the 5 to 6% range. The acidic-neutral EN-B process typically utilizes dimethyl amine borane (DMAB) as the reducing agent. These processes operate at pH levels of 4.8 to 7.5 and at temperatures of 150 to 170°F (65 to 77°C). The deposit boron content ranges from 0.1 to 4%.<sup>7</sup>

### 3. Potential Environmental Releases from Production

#### 3.1 Wastewater

Industrial wastewater is generated in all phases of electrodeposition and electroless nickel plating processes. The pretreatment of the part or product to be treated requires the use of solvent baths, alkaline cleaning baths, vapor degreasing, pickling baths, and a variety of spray rinses and rinse baths. The process requires cooling water, boilers, steam condensates, rinse water, and wash water. There are spent plating bath solutions and cleaning solutions that are contaminated with reducing agents, nickel compounds, acids, alkalines, complexing agents, buffers, stabilizers, rate promoters, organic additives, and other chemicals depending on the process (see Table 3.1). Wastewaters are commonly treated with NaOH to neutralize and precipitate residual nickel.<sup>3</sup>

The primary source of wastewater is from rinsing operations. Most of the waste contaminants result from drag-out from plating baths where plating solution remains in blind holes, seams or other crevices that remain on the part. This solution becomes the primary source of rinse water contamination. Therefore, when examining primary locations to decrease drag-out, an attempt to quantify the drag-out rate should be made. If a process utilizing a nickel plating tank has a single flowing rinse immediately after the plating operation, a theoretical equation that assumes ideal mixing can be used to estimate the drag-out rate. This calculation is as follows:<sup>3</sup>

Waste	Waste Stream	Process	Potential Hazards
Alkali (hydroxide)	Wastewater	Cleaning, etching	Corrosivity
Acid (nitric, sulfuric, hydrochloric, hydrofluoric)	Wastewater	Cleaning, pickling, etching, bright dipping	Corrosivity
Surfactants	Wastewater	Cleaning	Aquatic Toxicity
Oil and Grease	Wastewater	Cleaning	Aquatic Toxicity
Nickel oxide, nickel hydroxide, and traces of cadmium, zinc, nickel, copper, other metals	Plating bath, drag out, rinse water, spent filters, sludge	Plating	Toxicity
Perchloroethylene, trichloroethylene, other solvents	Spent solvent (liquid or sludge), air emissions	Cleaning	Toxicity
Cyanide	Spent plating bath, drag out, rinse water, other wastewater	Plating, tumbling, stripping, heat treating, desmutting	Toxicity
Chromium	Plating bath, drag out, rinse water, sludge, other wastewater, mist	Plating, chromating, etching	Toxicity
Water	Rinse water, drag out, process bath, air emission (evaporation), cooling water, boiler blowdown	Various	

$$V_2 = (V_{rtw} * C_{rtw})/C_{pb}$$

where,

$V_2$	=	volume drag-out
$V_{rtw}$	=	volume flow rate in the rinse
$C_{rtw}$	=	concentration of contaminant in the rinse
$C_{pb}$	=	concentration of the contaminant in the process tank

In cases where mixing is far from ideal or a single rinse is not in use, drag-out must be estimated using other methods. One such method is to convert the first rinse to a non-flowing rinse and monitoring the buildup of nickel over time; then, back-calculating the volume of nickel solution required to achieve such a buildup of nickel in the stagnant rinse.<sup>3</sup>

A survey of 318 plating shops in the United States revealed that an average of 160,000 L/day of water is discharged from a typical plating shop. With an estimated 3,500 job shops in the U.S. consuming 160,000 L/day, the total water discharged by job shops alone would be over 145 billion liters per year. With an average water and sewer cost of \$0.01/L, this represents about \$1.45 billion per year for the electroplating industry. Therefore, reducing water usage and reducing wastewater is a major environmental and financial issue.<sup>11</sup>

### 3.2 Air Emissions

Air emissions from nickel plating operations are generated in the form of mists during the process due to the evolution of hydrogen and oxygen gas and acidic fumes from highly acidic processes such as the Wood's nickel strike. Hydrogen gas bubbles are formed in the process tanks on the surface of the submerged part or on anodes and/or cathodes. These gas bubbles rise through the plating solution and "burst" upon reaching the surface escaping into the air forming a mist. There are a number of factors that determine the rate of gassing, including the temperature of the solution, the current densities in the plating tank, the solution composition, solution pH, the surface area of the parts being processed, and the surface tension of the plating solution. Air sparging can also result in emissions from the bursting of air bubbles at the surface of the plating tank liquid. Usually, nickel plating baths (other than strikes) have high cathode efficiencies, so the generation of mist in nickel plating is minimal. Other air emissions, such as volatile organic compounds (VOCs), may be generated in preparing the part for plating from degreasing, solvent cleaning, and open containers of solvents. There also may be emissions from exhaust ventilation, spills or leaks, and, especially, from stripping of rejects. The most commonly used stripping solutions are either nitric acid or sulfuric acid (used with direct current). Cyanide-based nickel stripping solutions may also be used. These solutions have a high temperature and are without current. Air emissions from cyanide-based stripping solutions may include ammonia from decomposition of cyanide.<sup>12</sup>

In addition to the atmospheric releases, nickel plating operations also pose a hazard to workers from inhalation of fugitive emissions. Emission factors for nickel electroplating from the process tank are 0.63 grains/A-hr without a wet scrubber or  $6.7 \times 10^{-6}$  grains/dscf. Worker exposure results from the release of airborne aerosols containing soluble nickel compounds, hydrochloric acid if a Wood's nickel strike is utilized or sulfamic acid if a sulfamic acid strike is utilized. Exposure can be reduced by adequate ventilation in the work place and/or the use of respirators.<sup>12</sup>

Air emissions to the atmosphere from nickel plating processes are becoming increasingly regulated in California and may become regulated in a number of other states. The nickel plating industry is faced with many legislative regulations, and federal, state, regional, and local environmental guidelines. The emission limits vary from jurisdiction to jurisdiction, and it is the responsibility of the plating shop owner to determine which emission standards are applicable. Consequently, many platers are unaware of their compliance responsibilities. Government inspectors from the various jurisdictions will help sort out the applicable air emission regulatory requirements. Fortunately for nickel platers, air emissions from nickel plating shops appear to be a minor environmental concern to many regulatory agencies.<sup>12</sup>

Nickel, as an air emission, has gained a lot of attention in recent years. California has declared all nickel compounds to be toxic air contaminants and considered carcinogenic. Therefore, in California, all water soluble nickel compounds are listed as inhalable carcinogens and will be regulated accordingly. There is controversy regarding the decision to declare nickel and nickel compounds as carcinogenic. This topic will be discussed in greater detail in the next section regarding regulatory issues.<sup>12</sup>

### 3.3 Toxic and Hazardous Wastes

Most toxic and hazardous wastes are generated during the cleaning part of the process. More specifically, surfactants are used to remove oil and grease from spent EN solution, nickel plating solution is contaminated beyond beneficial reuse, and sludge that contains metals is formed as a result of wastewater treatment. Absorbents, filters, filter cakes, still bottoms, contaminated solvent, carbon, wipe rags, aisle grates, and abrasives are generated solid wastes that are potentially hazardous. Under the Resource Conservation and Recovery Act (RCRA) (Code of Federal Regulations [CFR], 40 CFR 261.21-261.24), the two types of hazardous wastes are listed and characteristic waste. Although nickel plating wastes are not included as listed RCRA wastes, (except for F006 waste generated from wastewater treatment systems), some may be characteristic hazardous wastes.<sup>13</sup>

Wastes that exhibit toxic characteristics defined by the presence of metal ions and other organic compounds, which are eventually placed in a landfill, would likely leach hazardous concentrations of these toxic constituents into the environment. These constituents are subject to the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP extracts the toxic constituents from a waste in a



manner that simulates the leaching action which occurs within a landfill. The TCLP is EPA's regulatory leachate test. Wastes must pass the leachate test before disposal in a Class D landfill. Wastes that fail the TCLP must be handled and discarded in a hazardous waste landfill to restrict leaching into groundwater or surrounding soils. Generally, tank residues from the nickel plating processes have to be transported off-site for treatment and disposal because they are typically defined as characteristic hazardous wastes.<sup>13</sup>

### 3.4 Worker and Environmental Impacts

There are many soluble nickel compounds that pose adverse human health and environmental impacts in the nickel plating industry. Such compounds include nickel chloride, nickel nitrate (produced in stripping of nickel in nitric acid), nickel sulfamate, nickel carbonate (used in pH adjustment), and nickel sulfate. Nickel chloride (CAS No. 7718-54-9) is an odorless, monoclinic, green crystalline compound. Nickel chloride ( $\text{Cl}_2\text{Ni} \cdot 6\text{H}_2\text{O}$ ) is soluble in water, alcohol, and ammonium hydroxide, and insoluble in ammonia. The anhydrous compound is not used in the electroplating industry. Nickel nitrate (CAS No. 13138-45-9) is an odorless, green, deliquescent powder or crystalline substance, commonly found in the hexahydrate form. Nickel nitrate ( $\text{Ni}_2\text{O}_6 \cdot \text{Ni} \cdot 6\text{H}_2\text{O}$ ) is soluble in water, alcohol, and ammonium hydroxide. Nickel sulfamate,  $\text{H}_4\text{N}_2\text{NiO}_6\text{S}_2$ , (CAS 13770-89-3) is an odorless, green crystalline compound, that is most often purchased by a plater in dissolved (in water) form. Nickel carbonate,  $\text{CNiO}_3$ , (CAS 3333-67-3) is an odorless, pale green dusty powder that is only moderately soluble in water but is commonly added to acidic nickel plating solutions to raise the pH. Nickel sulfate (CAS No. 7786-81-4) is an odorless, crystalline substance that commonly occurs in the form of hexahydrate or heptahydrate crystals. The anhydrous material is a yellow to green color, hexahydrate appears as blue to pale-green, and the heptahydrate is green. Nickel sulfate ( $\text{NiSO}_4$ ) is soluble in water in any form. The hexa- and heptahydrate forms are also soluble in alcohol, while anhydrous  $\text{NiSO}_4$  is insoluble in alcohol, acetone, and ether.<sup>14</sup>

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for soluble nickel compounds is 1 milligram per cubic meter ( $\text{mg}/\text{m}^3$ ) of air as an 8-hour, time-weighted average (TWA) concentration. This PEL is referenced in 29 CFR 1910.1000, Table Z-1. The exposure to soluble nickel compounds can occur through inhalation, ingestion, and eye or skin contact. Although nickel compounds are not absorbed in sufficient concentration through the skin to cause systemic toxicity, they are capable of inducing contact dermatitis in sensitized individuals. Nickel is also, relatively, non-toxic by ingestion. Positive findings in many epidemiology studies attest to the potential human carcinogenicity of nickel compounds. The American

Conference of Governmental Industrial Hygienists (ACGIH) has assigned nickel a low threshold limit value (TLV) because nickel compounds have been identified as suspected carcinogens. Although there is a current debate about the possibility of all nickel compounds being carcinogenic, the general consensus in the industry is that there is no elevated cancer risk when airborne levels are below the OSHA PEL. EPA considers only nickel refinery dust, nickel subsulfide, and nickel carbonyl to be carcinogenic. The California Air Resources Board (CARB) in 1990 listed all nickel compounds as toxic air contaminants under the state's "hot spots" law. Therefore, soluble nickel is considered to be carcinogenic. In animals, nickel is toxic to the kidneys, cardiovascular, respiratory, and reproductive systems. In humans, soluble nickel compounds can affect the cardiovascular system, kidneys, and central nervous system.<sup>15</sup>

Prevention and control methods for worker exposure include process enclosure, local exhaust ventilation, general dilution ventilation, elimination of air agitation system (often replaced with eductor systems), and personal protective equipment. Plating company owners whose employees are exposed to soluble nickel compounds are required to implement medical surveillance procedures. These procedures include medical screening, replacement medical evaluation, periodic medical evaluation, biological monitoring and termination medical evaluation. Special precautions should be taken for personal hygiene, workplace monitoring and measurement, storage of soluble nickel compounds, and leaks or spills.

EPA requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management can change over time. At the time of this writing, soluble nickel compounds were not subject to EPA emergency planning requirements under Title III of SARA in 42 United States Code (USC) 11022.<sup>14</sup>

The reportable quantity for soluble nickel compounds is 100 pounds. If an amount equal to or greater than 100 pounds of soluble nickel is released within a 24-hour period in a manner that exposes persons outside of the facility, owners are required to immediately notify the National Response Center (800-424-8802) in accordance with 40 CFR 302.6. In the event of any release (spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing) into the environment, owners must notify the proper federal, state and local authorities, as required in 40 CFR 355.40.<sup>14</sup> Nickel and nickel compounds are on the Community-Right-To-Know List and are subject to Toxic Release Inventory reporting to EPA. Nickel and its compounds are also on the TSCA Inventory list.<sup>14</sup>



## 4. Economic, Technological, and Regulatory Factors that Influence the Resolution of Nickel-related Environmental Problems

### 4.1 Economic Factors

There are a number of economic factors to consider regarding nickel plating, pollution prevention, and control technology for the nickel plating industry. These factors may differ from one facility to another but, in general, include the level of government intervention, the size of the individual companies, and the opportunities for reducing raw material costs.

Government intervention usually occurs as regulations and policies are enacted which govern the way industry manufactures goods. Such factors include environmental rules and regulations, labor policies and regulations, transportation laws, local energy policies, and local community resource systems, such as water and sewage. Often, consideration of these factors determines the final profit of the firm. According to Department of Commerce estimates, over a fifth of a metal finishing company budget is for pollution abatement and compliance requirements.<sup>2</sup>

The nickel plating industry in the United States is comprised primarily of small businesses who strive to be competitive. Nickel plating shops are not highly capitalized and cannot afford to make major changes in processes unless the capital payback is short-term. Investment in capital-intensive projects for environmental compliance can compete with those for improving profits. It is, therefore, necessary to assure that profitability is compatible with environmental improvement projects in both the short- and longterm. One area for consideration is capital improvement projects that reduce costs for pollution abatement and waste treatment through recycling, resource recovery, and pollution prevention.

The loss of raw materials associated with process operations can result in five distinct cost items that need to be considered in an economic evaluation targeted for reducing environmental impacts:<sup>2</sup>

- Replacement of raw material
- Removal of product from the waste stream before release
- Disposal of unwanted materials from the waste stream

- Replacement of water
- Processing the wastewater

These same cost items are applicable to waste reduction, recycle, and reuse opportunities. By eliminating the discharge of process wastewaters by closing the loop, metal finishers can eliminate the administrative costs and risks of non-compliance, while reducing production costs and enhancing public relations. Striving for efficiency and quality will reduce the reject rate and related costs. It is reported that electroplaters lose about 5% of production because of rejects due primarily to improper process control.<sup>2</sup>

### 4.2 Federal, State, and Local Regulatory Factors

The metal finishing industry is regulated under several federal environmental laws:

- The Clean Water Act (CWA)
- The Clean Air Act (CAA)
- Resource Conservation and Recovery Act (RCRA)
- Toxic Substances Control Act (TSCA)
- Superfund Amendments and Reauthorization Act (SARA)
- Emergency Planning and Community Right-to Know Act (EPCRA)
- Comprehensive Emergency Response, Compensation, and Liability Act (CERCLA or Superfund)<sup>16</sup>

In addition, the metal finishing industry must comply with federal, state, and local regulations for occupational safety and health, and transportation. Regulatory factors impact technology choices and economic decisions that can provide solutions to reducing wastes.

#### **Water Discharges**

Wastewaters from nickel plating operations are generally discharged to the sewer provided that the effluent meets the established categorical discharge limits (40 CFR part 433.13 regulates nickel at 3.98 mg/L daily maximum and

2.38 mg/L monthly average). EPA has established national “effluent guidelines” for the metal finishing industry.<sup>17</sup>

EPA regulations require permits of operators who discharge directly to surface waters. This also includes water quality-based limitations for all pollutants at concentration levels that cause, have a reasonable potential to cause, or contribute to an excursion above any state water quality standard. Nickel plating operations that discharge directly to a public sanitary sewer system do not require a National Pollutant Discharge Elimination System (NPDES) permit but are often required to obtain a surcharge permit from the local publically owned treatment works (POTW).<sup>17</sup>

Most plating operations are regulated under the Clean Water Act pretreatment program. Under the pretreatment program, limitations are imposed on industrial users of a POTW through a permit or agreement issued by the POTW. The pretreatment regulations are found in Title 40 of the CFR, Part 403. Nickel wastewaters are commonly treated with sodium hydroxide, magnesium hydroxide, lime, or combinations of these alkaline compounds to neutralize and precipitate residual nickel concentrations to meet the compliance limits. These wastewaters typically come from acid pickling, stripping, cleaning and rinsing processes. Other liquid wastes contain spent plating bath solutions (RCRA F007, F008, F009) and sludges that contain metals (RCRA F006). These wastes are commonly shipped off-site for treatment, recycle, or disposal. A reduction of wastewater through process changes, recycle, and/or on-site treatment and reuse, is a target for the nickel industry.

Pretreatment requirements are enforceable by EPA, state, and local pretreatment POTW authority.<sup>13</sup>

### **Air Discharges**

Air emissions from nickel plating operations, typically, include VOCs in the few cases where solvent degreasing is performed or open containers of solvents are used. Other sources are acid/alkali mists, particulates and vapors emitted from process and plating baths, exhaust ventilation, spills, and leaks.

Emissions to the atmosphere from stacks and other ventilating systems are becoming increasingly regulated on a local basis (California). It appears doubtful that air emissions from nickel plating shops pose any significant environmental impacts; however, controversy exists concerning health risks and nickel emission impacts.<sup>12</sup> These health impacts are currently under review.

Control of nickel emissions from nickel plating tanks may include a mist eliminator or a scrubber. The cost of controls to meet any air emission compliance requirements for nickel tanks could impact competitiveness. The controversy first raised in California, is the designation of soluble nickel as a carcinogen. The California Air Resources Board (CARB) in 1990 listed all nickel compounds as toxic air contaminants under the state’s “hot spots” law. Currently, no other state or the federal EPA has declared soluble nickel to be a carcinogen. The National Association of Metal Finishers

(NAMF) and the Metal Finishers Association of Southern California (MFASC) have partnered with EPA and Health Canada to perform a new risk assessment on soluble nickel salts. The MFASC is hopeful that the designation of soluble nickel compounds as a carcinogen will be reviewed in California.<sup>15</sup>

### **Solid Wastes**

The major concerns governing nickel plating solid waste are related to industrial wastewater treatment sludges that contain nickel, along with other heavy metals resulting from electroplating operations (such as, copper, chromium, iron, and lead).<sup>18</sup> As previously mentioned, not all RCRA wastes are listed wastes. Some are characteristic wastes by definition in the RCRA Code, with the responsibility for identifying the hazard being imposed upon the generator. These wastes are accumulated in drums or specially designed tank or roll-off boxes to be collected at appropriate time intervals by recyclers and/or public or private disposal operations. Characteristic waste must meet regulatory leachate tests (TCLP, SPLP) before final disposal in a landfill. If the solid waste fails the TCLP, the waste is restricted from disposal in a municipal waste landfill. Many platers prefer having others collect and dispose of their solid and hazardous wastes.<sup>18</sup>

While most nickel-containing wastes are not RCRA listed wastes, they are included on the “California List” of metal-containing wastes that were prohibited from land disposal at specified concentrations by the 1984 RCRA Amendments. It is, therefore, necessary to treat aqueous nickel wastes by chemical precipitation to convert the toxic constituents into an insoluble form. There are a few metal plating shops that are located near a centralized waste treatment facility for metals recovery and treatment.<sup>18</sup>

Metal finishing facilities that generate small quantities of RCRA hazardous waste can reduce or eliminate many regulatory requirements, waste handling expenses and other liabilities by implementing low-cost waste reduction alternatives. While the federal regulations institute baseline requirements, compliance also requires adherence to additional state requirements. In some instances, state requirements can be more stringent than federal laws.

Wastes from most facilities in the nickel plating industry are regulated under the CAA, CWA, and RCRA. TSCA, SARA, EPCRA, and CERCLA are much less likely to affect the nickel plating industry if the facility is in compliance with the CAA, CWA, and RCRA. It is important to recognize the applicability of these federal environmental regulations for wastes being generated at a specific facility and understand the options and alternatives for compliance. Most federal environmental regulations are managed through state regulatory agencies, with states implementing pollution prevention (P2) regulatory integration programs. State P2 programs are evolving from technical assistance to integration of P2 into state environmental activities, such as enforcement, inspection, and rule-making. The next section of this report addresses P2 options.<sup>18</sup>

## 5. Integrating Best Management Practices and Control Technologies

Environmental solutions for the nickel plating industry include the reduction and control of wastes generated by the industry. This waste reduction and control approach integrates the concepts of pollution prevention and waste management control technologies. The Pollution Prevention Act of 1990 reinforces EPA's "Environmental Management Options Hierarchy" which assigns the highest priority to preventing pollution through source reduction, reuse, and/or closed-loop recycling. Pollution prevention focuses on product and process changes that reduce the volume and toxicity of production wastes and the reduction of end-product wastes during the product lifecycle. When waste cannot be reduced by pollution prevention methods, the preferred alternatives are recovery/reuse/recycle of the process materials during the lifecycle of the product. Where prevention and/or recycling are not feasible, waste treatment followed by authorized disposal is required to achieve environmental compliance. "End-of-pipe" approaches were the earlier methods for achieving environmental compliance, controlling releases and environmental clean-up. These approaches not only can be expensive, they often transferred pollution from one media to another. Today's trend is to integrate the best practices and technologies available to meet the goals of industry and regulatory agencies.

This report presents pollution prevention and end-of-pipe control technology options in addressing the environmental issues affecting the nickel plating industry. This practical approach allows the nickel plating community to determine the best options for managing pollution. The nickel plating industry uses numerous chemical processes. There are technical, cost, and regulatory limitations to consider on a process-by-process and facility-by-facility basis. While it is important to recognize the differences and similarities of waste management approaches, the desired outcome for the individual nickel plater is to be competitive and compliant while producing high quality products. In most cases, there will be waste disposal concerns for the producer and consumer. Therefore, all waste management options should be considered in addressing the environmental issues of the nickel plating industry.

### 5.1 Recovery, Recycle and Extended Bath Life

The most common P2 option for nickel plating being implemented today is reusing the drag-out rinsewater. This involves using the tank water where the parts have been rinsed (before the parts are rinsed in a flowing-water rinse),

to replace the process tank water lost through evaporation. This reuse of drag-out rinsewater reduces chemical loss. Other waste rinsewater P2 alternatives include:

- Operate equipment to reduce drag-out;
- Increase solution temperature;
- Lower the concentration of plating bath constituents;
- Use an air knife to reduce, drag-out from the process;
- Reduce speed of product withdrawal to allow for drainage time;
- Use surfactants to lower solution surface tension;
- Position part properly on rack for maximum drainage;
- Use multiple rinse tanks in countercurrent series;
- Use fog nozzles and sprays for rinsing simple work pieces;
- When still-rinsing, recycle rinsewater upstream (reuse the water elsewhere upstream in the process line);
- Use automatic flow instrumentation to control flow rate;
- Reuse rinsewater when possible;
- Increase rinsing efficiency by agitating rinse bath.<sup>3,18,19</sup>

P2 alternatives for work cleaning wastes are:

- Reduce cleaning frequency when possible;
- Design process and equipment to minimize surface area of exposed process liquid;
- Record cleaning costs as a separate item;
- Convert from a batch process to a continuous process;
- Maximize dedication of process equipment;
- Avoid unnecessary clean-ups;
- Operate equipment to inhibit fouling;
- Minimize residue buildup during operation;
- Minimize the amount of cleaning solution used;
- Recycle cleaning solution by filtering solids from used solution;

- Substitute cleaning system with a proprietary process (“Bio-Clean”) that bio-degrades the oil, generating almost no oily waste.<sup>3,5</sup>

P2 alternatives for waste treatment include:

- Install a sludge dewatering system;
- Improve operating practices;
- Install a metal recovery system;
- Segregate waste streams to facilitate treatment and recovery of metals;
- Use the most efficient precipitating agents;
- Return spent process solutions such as strippers and EN plating solutions to the manufacturer for recycling.<sup>3,5</sup>

There are a variety of technologies that are used within the nickel plating industry to separate plating chemicals from rinsewaters, or to concentrate the chemicals for ease of recycle/reuse. The six most commonly used technologies are:

1. Electrowinning
2. Atmospheric Evaporation
3. Vacuum Evaporation
4. Ion Exchange
5. Reverse Osmosis
6. Electrodialysis

Electrowinning involves placing two electrodes (insoluble anode and cathode) in a solution containing ions, where there occurs a movement of ions toward the charged electrodes. Dissolved metals in the electrolyte are reduced and deposited on the cathode. The deposited metal is removed by mechanical or chemical means and either reused as anode material or sent off-site for processing or disposal. Electrowinning is used to recover valuable common metals for recovery/reuse or to reduce the amount of inexpensive metals for treatment and disposal. This technology is most often applied for gross metal recovery from concentrated solutions. The combination of ion exchange and electrowinning has a much higher potential metal recovery efficiency than electrowinning from a drag-out rinse. Nickel recovery using ion exchange is possible, but it requires de-acidification of the regenerant and close control of pH; thus, it is not commonly performed.<sup>3,5,20</sup> Electrowinning is inexpensive to operate and not labor-intensive. Energy costs comprise only a small part of the total operating costs. The system utilizes an inert anode that is very costly to replace, if damaged. The relative low cost of nickel in today’s market compared to the cost of recovery should be considered in evaluating this technology for recovery of nickel.<sup>3,5,20</sup>

Atmospheric evaporation is used to concentrate liquid plating wastes prior to treatment/storage/disposal. This technology reduces the amount of waste and consequently lowers costs for transportation, treatment, storage and disposal. Atmospheric evaporation is the most widely used method for chemical recovery in the plating industry. An evaporator is a device that evaporates water to the atmosphere and incorporates a pump for moving the solution, blower to move the air, heat source, mixing chamber for mixing the solution and air and mist eliminator to remove any entrained liquid from the exhaust air stream. The capital and operating costs can be relatively low in some installations in arid climates.<sup>3,5,20</sup>

Vacuum evaporation systems are relatively complex and more expensive than the simpler atmospheric evaporation systems. The vacuum evaporator is a distilling device that vaporizes water at low temperature when placed under a vacuum. Vacuum evaporators can be employed for recovering nickel plating solutions, if foaming problems are resolved. At least one supplier of vacuum evaporators has resolved the foaming problem using thin film evaporative methods. Vacuum evaporators consume high quantities of energy, making the technology less competitive on an operational cost basis.<sup>3,5,20</sup>

Ion exchange is a chemical reaction recovery technology that is especially applicable to dilute rinsewaters. It involves exchange of the ions from a plating solution with similarly charged ion attached to an immobile solid particle, such as an ion exchange resin. The resins are typically contained in vessels (columns), and the exchange occurs when the solution is passed through these columns. A simple diagram illustrating the use of the ion exchange method is presented in Figure 5.1.<sup>3,5,20,21</sup>

Ion exchange is not practical for process solutions that are more concentrated than the ion exchange regenerate; therefore, this technology does not work well for concentrated drag-out solutions. The capital and operating costs can be relatively high for the benefits received from nickel chemicals.<sup>21</sup>

Reverse osmosis (RO) is a membrane separation technique applicable to dilute streams. RO is used primarily to separate water from a feed stream containing inorganic ions. The purity of the recovered water is relatively high and the water is generally suitable for recycling. Osmosis occurs when a semi-permeable membrane separates two solutions of different dissolved-solids concentration. Pure water (permeate) will flow through the membrane into the concentrated solution, while rejected ions (brine) are retained behind the membrane. RO occurs when pressure is applied to the more concentrated solution to reverse the normal osmotic flow, with the pure water forced through the semi-permeable membrane into a less concentrated solution. The purified stream that passes through the membrane is called permeate; the concentrated stream retained by the membrane is called concentrate. Chemical recovery by RO is usually not practical for highly concentrated, oxidative solutions, due to fouling. A RO system is relatively inexpensive to construct and operate for the benefits



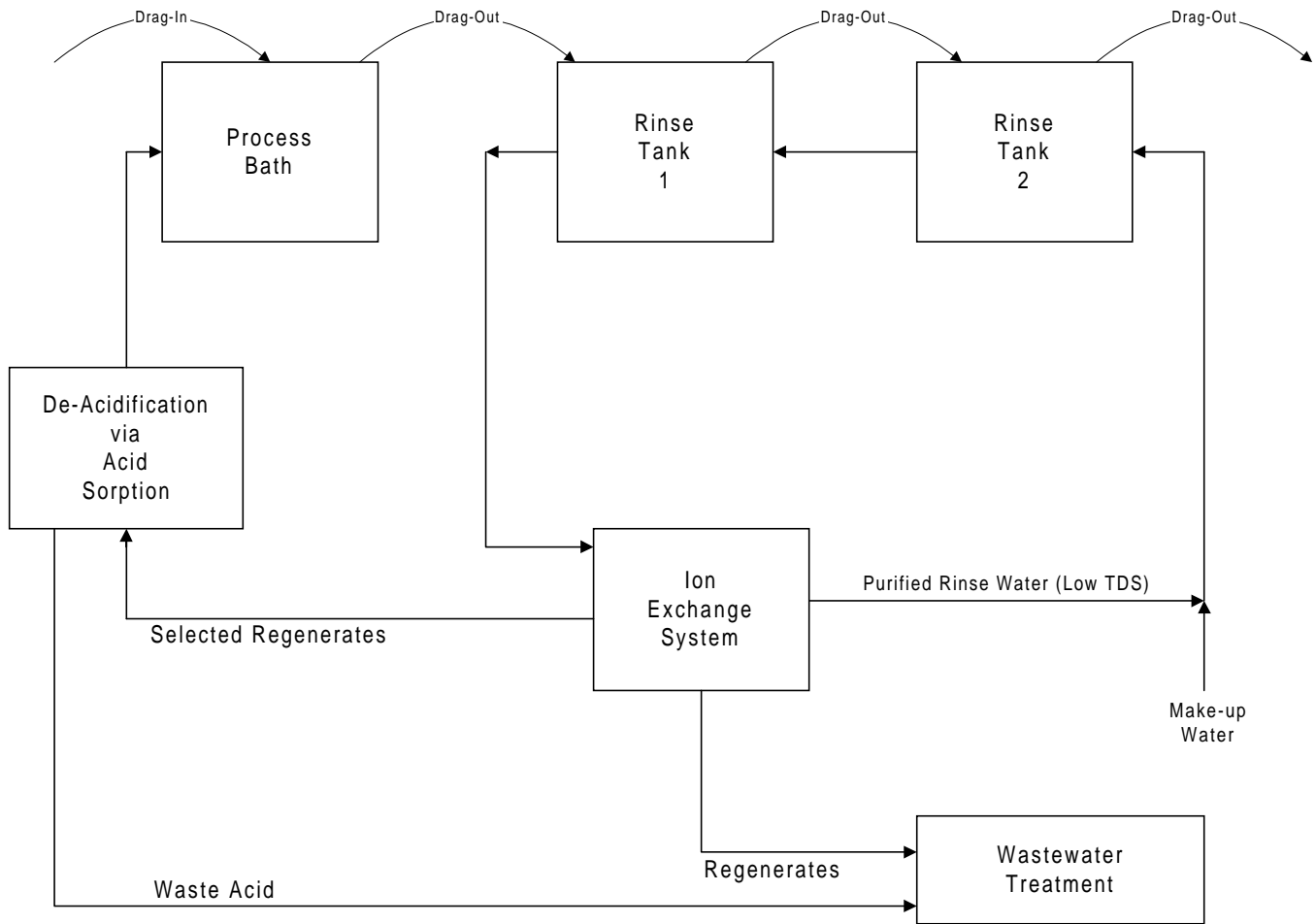


Figure 5.1. Ion exchange flow diagram.

received from nickel recovery. Using a spiral wound cellulose acetate membrane, a number of successful RO systems are in operation for bright nickel, nickel sulfamate, and Watts nickel plating baths. A typical RO application is shown in Figure 5.2.<sup>3,16,20</sup>

After minimizing water use by rinsewater reduction or reuse and metal recycling, the focus for P2 is on extended bath life. An appropriate method to conserve water and conserve chemicals while maintaining bath life is a closed-loop plating bath recycling system. Figure 5.3 shows how a closed-loop plating bath recycling system can be arranged to extend bath life.<sup>3,16,20</sup>

Another method to extend nickel plating baths is to remove contaminants, such as grease, oil, organic impurities from proprietary additives, and unwanted metals from the nickel baths. The most common treatment technologies used are electrolytic treatment (dummying), batch metal precipitation, and batch adsorption. Electrolytic treatment is particularly effective for the removal of copper, zinc, and excess organic

impurities. Metal precipitation at high pH is used for the removal of impurities, such as aluminum and iron. Carbon adsorption is an effective method for removing specific organic contaminants from nickel plating baths. Plating bath contamination occurs most commonly when parts fall into the tank and from bare areas (areas not designed to be plated, such as the inside of tubing) exposed to the solution during the plating process. Therefore, it is important to assure that the parts are properly attached to the racks while in process.<sup>3,20</sup>

Water used for evaporation loss can be a major source of contaminants. Therefore, de-ionized water should be used for solution make-up. Continuous or batch filtration through activated carbon is recommended to eliminate decomposition products and minor levels of oils and greases that may be dragged into the baths. These purification methods can be combined for greater contamination removal. Removing contaminants to extend bath life can reduce costs by reducing process chemicals, energy usage, quantities of wastes for treatment/disposal and the potential

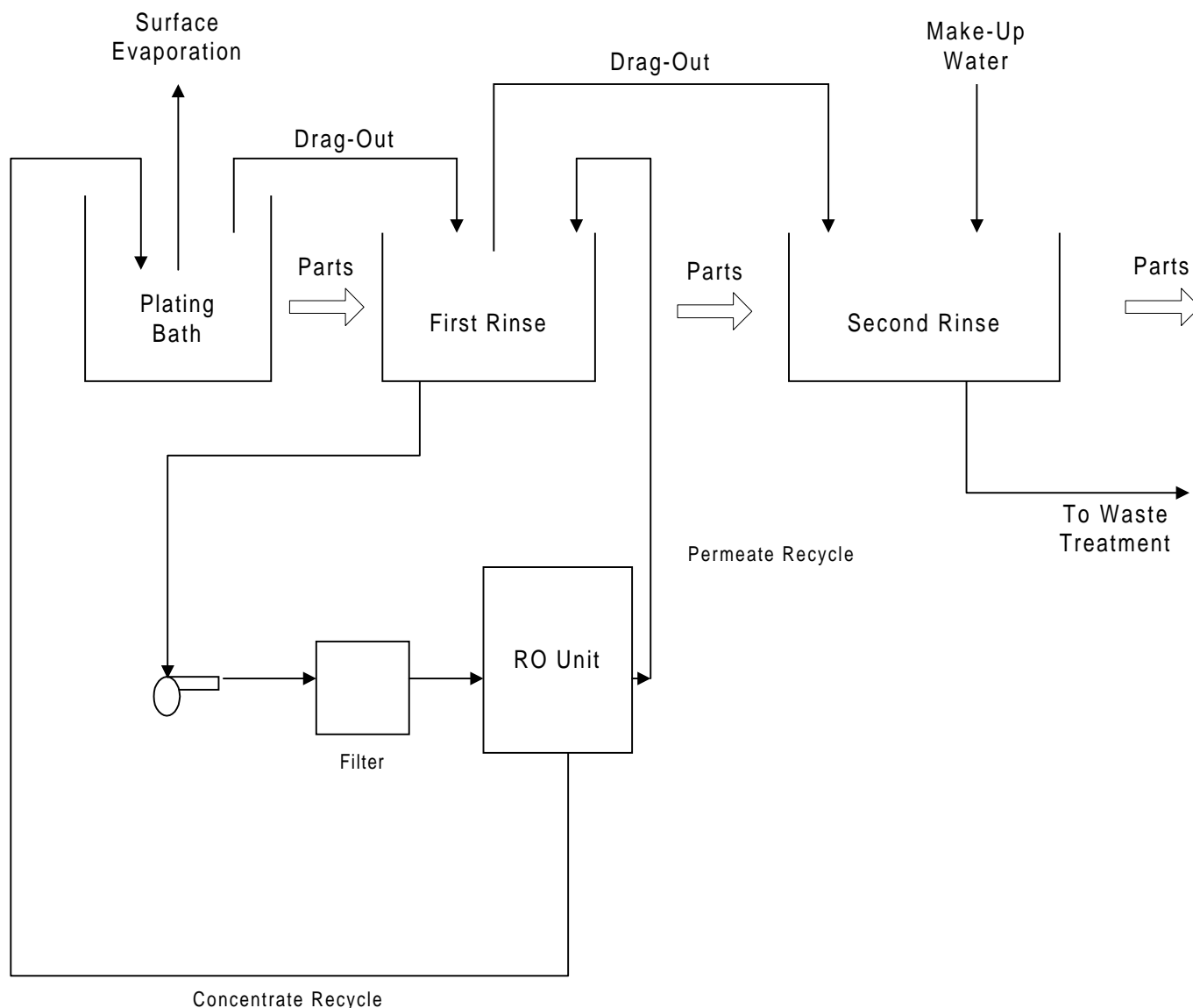


Figure 5.2. Typical reverse osmosis system.

for noncompliance. Plating bath solution maintenance has become a greater priority to plating shops for extending bath life and improving the operating efficiency and effectiveness of a plating solution.<sup>3,20</sup>

## 5.2 Surface Preparation of Substrate

Surface finishing involves direct atom-to-atom bonding between a basis material (such as steel, aluminum, brass, or plastics) and a metal or organic surface top coating that provides the desired material performance and/or appearance properties. Multi-step surface preparation processes remove oils, particulate materials, old coatings, corrosion products, residual cutting fluids, brazing residuals, smut, pickling acid residuals, cleaner residuals, etc. The

surface preparation process removes contaminants, preserves the cleaned surface, and/or modifies the surface for the next coating. It is common for surfaces to undergo more than 10 finishing steps that include degreasing and cleaning (for oil removal and descaling), etching, desmutting, pickling, plating, and rinsing. These baths ultimately are exhausted due to depletion of chemical reagents or buildup of impurities and are a major waste stream.<sup>9</sup>

The volume of hazardous/toxic waste streams produced from metal surface finishing operations is significant. Most of these result from blowdown of the ventilation air scrubber and from tank dumping. Therefore, reducing the number of tanks (surface area) needed for production could significantly

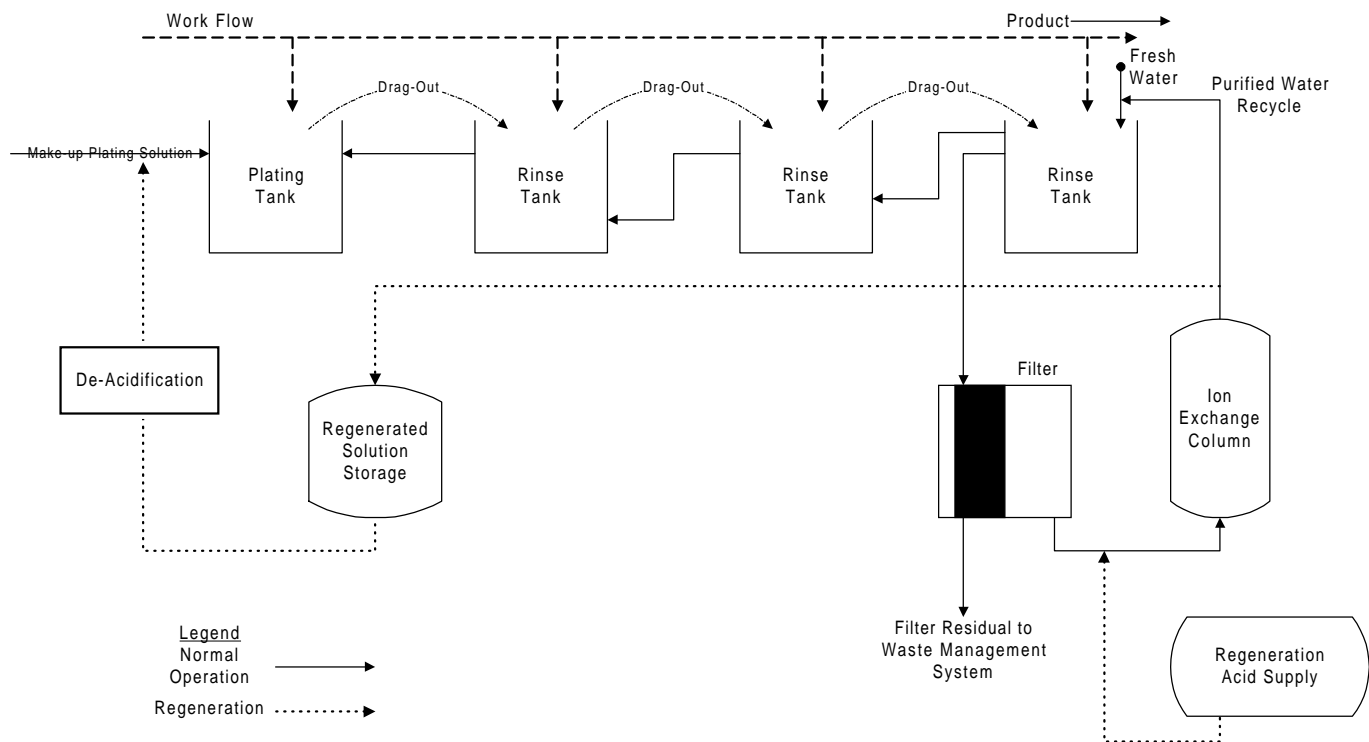


Figure 5.3. Closed loop process flow diagram for bath life extension.

reduce the amount of these wastes. Decreasing gas evolution from the baths (e.g., the hydrogen gas formed during acid pickling) also reduces wastes since bath gassing causes mist formation. Lower operational temperatures also reduce discharges by reducing impurities carried into the process with make-up water.<sup>9</sup>

The elimination of surface processing steps is favored by manufacturers to reduce processing costs, waste production, and energy consumption. With this objective in mind, International Chemical Products, Inc. (ICP, Huntsville, Alabama), has introduced Picklex® as a no-waste surface-finishing agent designed to provide a nearly one-step metal surface preparation operation for metal finishing operations. In a study sponsored by EPA, Picklex® provided metal surface cleaning, pickling, conversion coating, and priming using a process simply consisting of degreasing, one dip-step, one rinse, and final processing. Due to the large number of surface-finishing operations, the potential for sizable waste and cost reductions by using Picklex® is significant. Therefore, EPA's National Risk Management Research Laboratory (NRMRL) performed an assessment of the efficacy of Picklex® in major polluting surface-finishing operations.<sup>22</sup>

Surface coatings on treated test panels were evaluated by common techniques including: tape adhesion, salt fog corrosion resistance, hardness, burnishing, bending, impact adhesion, and microscopic examination. Most of these

evaluation procedures were standard tests performed in accordance with ASTM practices. The test conditions, test data, and detailed process descriptions are available in the referenced report entitled, "Use of Picklex® as a Cost Effective Metal Treatment."<sup>22</sup>

### Conventional Treatments versus Picklex®

Table 5.1 compares the test results for conventional to Picklex® coatings on contaminated (oxidized) and non-contaminated substrates. Although none of the processes was optimized for maximum properties, the results indicate that, in most cases, Picklex®-pretreated and/or conversion coated panels, performed as well as or slightly better than conventionally pretreated panels. However, Picklex® may not be applicable to all systems. For example, it may not be acceptable as a pretreatment for electroless nickel-coated materials when bending of the parts occurs due to lack of adhesion of the plate. Picklex® was not tested on the nickel plating process. Individual testing of substrates should be conducted prior to use. Picklex® appears to be a viable alternative to conventional pretreatments for aluminum substrates. Unlike conventional processes, steel and aluminum can be treated with Picklex®, simultaneously.

Picklex® appears to offer an advantage over the conventional process with respect to top coat adhesion because it

<b>Table 5.1 . Comparison of Coating Performance of Conventionally Produced Panels to Picklex®-Produced Panels</b>						
Coating	Tape Adhesion	Bend	Burnishing	Impact Adhesion	Hardness	Corrosion Resistance
Powder Top coat on Aluminum	Equivalent <sup>(a)</sup> , good on contaminated and noncontaminated-surfaces	Equivalent <sup>(a)</sup> , passed, no peeling/flaking	NA <sup>(b)</sup>	Equivalent <sup>(a)</sup>	NA <sup>(b)</sup>	Equivalent <sup>(a)</sup>
Powder Top Coat on Steel	Equivalent <sup>(a)</sup> , good on contaminated and noncontaminated-surfaces	Equivalent <sup>(a)</sup> , passed, no peeling/flaking	NA <sup>(b)</sup>	Conventional slightly better than Picklex®	NA <sup>(b)</sup>	Equivalent <sup>(a)</sup>
Hard Chromium	Equivalent <sup>(a)</sup> , good on contaminated and noncontaminated-surfaces	Equivalent <sup>(a)</sup> , passed, no peeling/flaking	Equivalent <sup>(a)</sup> , passed	Equivalent <sup>(a)</sup>	Equivalent <sup>(a)</sup> , good on contaminated and noncontaminated	Conventional slightly better
Electrolytic Zinc on Steel	Contaminated, conventional failed	Equivalent <sup>(a)</sup> , passed, no peeling/flaking	Picklex® failed lifting, passed blisters and peeling	Picklex® much better on contaminated, equivalent on noncontaminated	NA <sup>(b)</sup>	Equivalent <sup>(a)</sup> , marginal
ENi on Steel	Contaminated, Picklex® failed	Equivalent <sup>(a)</sup> , passed, no peeling/flaking	Both passed blisters and peeling; only contaminated, conventional passed lifting	Equivalent <sup>(a)</sup> , good	Equivalent <sup>(a)</sup> , good	Equivalent <sup>(a)</sup> , marginal
Alodine®	NA <sup>(b)</sup>	NA <sup>(b)</sup>	NA <sup>(b)</sup>	NA <sup>(b)</sup>	NA <sup>(b)</sup>	Equivalent <sup>(a)</sup> , both need CrCC for excellent performance

<sup>(a)</sup> Conventional and Picklex®-pretreated panels provided the same coating performance.  
<sup>(b)</sup> NA = Not applicable

provided equivalent mechanical strength with fewer steps along with reducing waste production.<sup>22</sup>

EPA test results suggest that Picklex® can provide an effective, one-step metal surface preparation operation for many metal finishing operations. Hence, based on these limited screening test results, Picklex® appears to effectively avoid the production and use of certain hazardous/toxic chemicals in surface finishing operations, such as pickling acids, metal salt phosphatizing solutions, hot alkaline baths and gas mists from electro-cleaning. It appears not to exhaust readily, even when processing heavily corroded surfaces.<sup>22</sup>

### 5.3 Process Changes

Changes can be made in the production process through improved operation and maintenance procedures, material substitutions, or changes in equipment that will reduce waste generation. Operating the plating line more efficiently can reduce waste generation and is usually inexpensive to implement. Instituting standard operating procedures and optimizing the use of raw materials can increase overall

efficiency. An evaluation of all current operating practices will provide an opportunity to identify waste generating activities. In many cases, simple operational changes can reduce waste generation. Areas to target for waste reduction may be identified by following the raw material flow from receiving, through process, and as finished products leave the facility through shipping and/or releases.<sup>23</sup>

A strict maintenance program that stresses corrective and preventative maintenance can reduce waste generation caused by equipment failure. Assuring that all employees are properly trained for operating and maintaining equipment, process materials and managing waste materials is key to increasing efficiency. Well-written, practical guidance manuals coupled with hands-on training and interaction between employees and supervisors are necessary for communicating this ongoing process.<sup>23</sup>

Material substitution is a more difficult means for reducing waste generation because it may require product reformulation with a less hazardous or non-hazardous material, that may adversely impact quality. In the United



States there is increasing pressure to make products that contain less hazardous materials. This pressure is coming from both regulatory agencies with more stringent regulations on hazardous substances and wastes and from consumers looking for safer, more environmentally friendly products. Due to the proprietary nature of product formulations, specific examples are limited. Examples include using water-based cleaning systems instead of solvent, and replacing chlorinated solvents with non-chlorinated solvents. Adding more holes to a product or designing product shape for better drainage or easier shipping may also reduce waste and costs. Redesigning a fixture to allow better escape of gases generated on the plating surface may reduce the waste of plating chemicals.<sup>23</sup>

Modifying process equipment can be a very cost-effective method for reducing waste generation within the nickel plating industry. A number of technologies and equipment have already been discussed in this section for recovery of chemicals, recycling, and extended bath life. The incorporation of such equipment will reduce waste and improve operational efficiency. Improving parts draining before and after cleaning and improving reactor design are two examples of process modification.<sup>23</sup>

#### **5.4 Waste Reduction through Process Simulation**

Process simulation is a general methodology for designing or modifying processes to reduce their environmental signature. In traditional manufacturing process design, attention is focused primarily on minimizing cost while the environmental impact of a process is often overlooked, resulting in large quantities of generated waste materials. By using process simulation techniques and models, it is possible to modify a process to reduce the generation of wastes and their environmental impact while reducing cost resulting in a more “sustainable” process. Most decorative nickel electroplating processes are similar in design and operation. Technologies such as ion exchange, reverse osmosis, and electrowinning are similar in design and operation. A model of these technologies with the typical electroplating process can be simulated to determine the optimum technology to use for a specific operation. This is true for determining operating modifications within a specific nickel plating operation without actually expending capital in a trial and error approach. Software products are available for other industries, such as the chemical and pharmaceutical industries to identify inputs and wastes throughout the operation. The nickel plating industry should consider the development of a computer-based tool to facilitate user input of desired qualities and determine environmental considerations along with process optimization. The advantage of process simulation for nickel platers is being able to consider optimization and waste reduction options by using a model prior to any capital expenditure for modification.

#### **5.5 Life Cycle and Sustainability Considerations**

Environmental decision making is benefitted through life cycle and sustainability considerations for a holistic approach to envision environmental impacts beyond the facility gates. While the major focus of environmental impacts occurs within the manufacturing stage for nickel platers, life-cycle assessment (LCA) utilizes a comprehensive approach by analyzing the entire product life cycle. This approach is comprised of four stages: 1) raw materials acquisition; 2) manufacturing; 3) use/reuse/maintenance; and, 4) recycle/waste management. LCA is a systematic method for identifying, evaluating, and minimizing the environmental consequences of resource usage and environmental releases associated with a product, process, or package. LCA evaluates the mass, energy inputs, and product outputs for an industrial system in an effort to identify their possible environmental significance. The life-cycle impact assessment goes beyond the unit operation to encompass a cradle-to-grave perspective. The purpose of using LCA is to avoid shifting pollution from one media to another or from one life cycle stage to another.<sup>18</sup>

LCA can benefit companies that want to strategically evaluate their position on environmental impacts in reference to the rest of the industry. The life cycle concept can be employed for any product, process or design activity. LCA can be used as a screening tool to help the user determine if impacts occur outside the facility when an improvement is made to the product or process inside the facility. There are several methods, computer programs and models for addressing environmental impacts using LCA principles. These “tools” encourage more informed environmental decision making and can be applied for cost-benefit analysis.

#### **5.6 Integrated Pollution Prevention/Control Technology Case Studies**

Pollution prevention success case studies are increasing with the nickel industry’s increased environmental awareness and pursuit of improved operational efficiency. Four case studies are presented as examples of incorporating sound cost effective pollution prevention techniques into nickel plating operations.

##### **Case Study 1<sup>24</sup>**

Poly Coatings of Sarasota, Florida, is a family business with 12 employees that specializes in electroless nickel, Poly-Ond, and electrodeposited (sulfamate) nickel plating. Poly-Ond is a teflon-impregnated electroless nickel plating solution used in plastic molds for dry lubricity. The company plates a variety of items for many industries, including firing devices for missiles and airbags, molds for injection and blow molding, wear components for sealing devices and other small, high-value components. The company has several established specialized areas of high-quality electroless nickel plating applied in thicknesses ranging from 0.000050 to 0.005 of an inch. The bath chemistry that Poly Coatings has used for more than a decade is Nitec 75, a high-speed, mid-phosphorus product manufactured by Heatbath Corporation of Springfield, Massachusetts.

The company's success in pollution prevention is a result of carefully choosing high quality raw materials and operating the facility at peak efficiency. Mr. Bernie Zapatha, owner and president of the company, supports environmental excellence by reducing odors and waste, and treating waste with effective control technologies. Two fume scrubbers eliminate odors and particulate releases. Rinsewaters do not leave the facility. The plating system is 100% closed loop; therefore, the only wastes leaving the facility are solids which are disposed of in 55-gallon drums. The objective of waste reduction and careful waste management was to be exempt from RCRA permitting. The facility owner used to plate with other metals, however, decided to focus exclusively on nickel plating by installing high-quality systems for Poly-Ond, electroless nickel, and sulfamate nickel. The elimination of chromates, flourides and cyanides made the task of meeting compliance much easier. Choosing vendors who provide high-quality materials and making good housekeeping a priority eliminated many of the operational problems common to nickel plating. Maximum quality is maintained along the plating line. As an example of operational quality, the company seldom plates in the same tanks (manufactured from sheets of polypropylene and free of interior welds) two days in a row. At the end of each workday, workers filter and pump the chemicals into an adjacent tank and clean the tank that has been used for that day. The following morning, a 50% nitric acid solution is used to passivate the tanks and heaters and dissolve the contaminants. The nitric acid is removed in about five hours, with the tank, again, ready for service. This company has provided experienced, well-trained, quality conscious employees who support the concept environmental stewardship.

#### **Case Study 2<sup>25</sup>**

Thomas Industries, located in Hopkinsville, Kentucky, recycles 12,000 gallons of rinsewater per shift while recovering nickel and brass from its plating operation. The company's goals are to exceed all environmental, health and safety regulations in order to support its reputation as a high-quality producer of a complete line of lighting products. These products include chandeliers, wall sconces, flush mounts, and fluorescent, recessed and outdoor lighting. Of special concern for Thomas Industries in operating its plating facility was managing heavy metals in the process stream. The company chose Pollution Application Systems of Hillsborough, North Carolina, to provide the necessary equipment for recycling chemicals and rinsewaters. The water reduction occurs through exponential dilution (extra counterflow rinses), reducing water use up to 90%, while improving the overall rinsing process. Once water needs are reduced, plating baths are recovered using standard atmospheric evaporation. Due to the low level of water needed for the operation, the amount of evaporation is decreased, reducing plating bath contamination. Energy requirements for converting water to steam are reduced due to lower water use. After conventional solids removal, electro-coagulation technology allows for the removal of an additional 90% of the heavy metals.

Due to the high recovery of nickel and brass, the volume of solid waste (after dewatering) has been reduced by 90%.

Dewatering is performed using a plate-and-frame filter press. The company is preparing for the next step to recover and recycle rinsewater from its parts washer and paint pretreatment line. This systematic approach to P2 and pollution control will reduce the facility's waste burden to a very manageable level requiring periodic disposal of reduced amounts of alkaline cleaners, spent acids and filtration backwash from the brass and nickel process tanks. The equipment installed on the plating machine required three weeks to install and another month of adjustment to achieve its present performance.

#### **Case Study 3<sup>26</sup>**

C.J. Saporito Corporation (CJS), located in Cicero, Illinois, offers a variety of metal finishing processes for electronic, aircraft, and commercial applications. Electroless nickel finishes are an integral part of the business CJS has built achieving a reputation for quality and reliability. Training is an important component of the CJS management approach that expands the theoretical and practical knowledge base in electroless nickel plating within the company's operation. CJS currently offers semi-bright and bright mid-phosphorus and teflon co-deposited electroless nickel finishes. Production is carried out in tanks ranging from 180 to 500 gallons, designed to process a wide variety of configurations and load sizes. CJS experienced the traditional waste generation of electroless nickel plating which led to the investigation of a new electroless nickel technology that offers extended bath life and process stability by allowing for the precipitation and removal of the undesirable orthophosphite byproduct.

Using a 180 gallon tank, CJS began the regenerative electroless nickel process plating a variety of base metals in both rack and barrel modes. CJS obtained 10 to 12 metal turnovers (MTO) of bath life from the regenerative electroless nickel solution, as compared to 6 to 8 MTO from the traditional electroless nickel solution. The bath performance exceeded current specifications. After proving the fundamental capability of the process. CJS scaled up the process by adding a 500-gallon tank; with positive results. CJS installed the equipment and put 680 gallons of the regenerative electroless process into production. The contents (200 gallons) from the 500-gallon tank were combined with the entire 180-gallon tank and analyzed after adding 93 g/liter orthophosphite. This concentration was used to determine the quantity of precipitating agent needed. The treatment of the regenerative electroless nickel solution yielded successful results. The process removed 68.1% of orthophosphite with minimal retention of nickel and hypophosphite on the filter cake. Recovery of the nickel and hypophosphite can be achieved by circulating deionized water through the cake. This wash solution can either be used to replace evaporative losses or added to the treated solution prior to adjustment. If necessary, further washing of the filter cake can be carried out to lower the nickel content sufficiently to meet federal, state, and/or local regulatory requirements for a non-hazardous waste. The electroless nickel plating operation at CJS has increased production time and become more efficient and profitable through the

implementation of the regenerative electroless nickel process.

#### **Case Study 4<sup>27</sup>**

Fin-Clair Corporation plates nearly 40 million seat belt assemblies each year at its facility in Knoxville, Tennessee. Fin-Clair tested four bright nickel plating process solutions (PPS) and index-based plating baths to provide good leveling and extremely bright deposits at various deposit thicknesses. The process included a total reclaim of the baths with rinses flowing back into the tank. There is no evaporation or ion exchange used, and the process has no drag-out. Recognizing that PPS-based brightener systems commonly have problems with buildup of degradation products, and each system suffered from buildup of inorganic products such as chloride, the company expected inconsistent plating. Fin-Clair preferred the brightness and ductility of the PPS bath but realized that PPS solution and performance deteriorates with use and causes a buildup that results in a loss of ductility and an overall reduction in brightness and leveling.

In an effort to correct the PPS solution problem, the Fin-Clair switched to a non-PPS, non-index system that was low in chloride, the Enthone-OMI Ultra-Lite 2000 bright nickel plating system. The new system was installed in the duplex nickel/chromium hoist line in the company's St. Louis, Missouri, facility and resulted in better performance without the previous PPS solution problems. The new system was, consequently installed for both lines in the Knoxville facility. The two main reasons for the conversion were the deposit's low stress and excellent ductility. The process is designed for an air-agitated rack plating operation. The low stress and excellent receptivity make it ideal for plating complex-shaped parts, such as seat belt assemblies and wheelchair parts.

The duplex bright nickel line has four semi-bright nickel stations, three bright nickel stations, and one trivalent chromium tank. Rinses before and after the nickel and chromium plating tanks are deionized water, generated from wastewater treatment. Other generated rinses are fresh water and exit sprays used on most of the rinses to reduce drag-out. After the final deionized water rinse, parts are dried using a forced-air dryer.

Fin-Clair is enjoying low maintenance of the plating bath and excellent performance. The only item added beyond the maintenance and carrier is the wetting agent which lowers the surface tension and provides limited detergent action in the nickel solution for pit-free deposits. Since there was no buildup with the non-PPS, non-indexing nickel system (the original reason to switch solutions), Fin-Clair could "close the loop" and enjoy reuse of rinsewater after treatment through a vacuum distillation unit designed and built by the company. The nickel concentrate is pumped from the bottom of the unit and filtered through heavy carbon before being added, as needed, to the plating tank. The last time Fin-Clair used landfill disposal was in 1985.

## **5.7 Wastewater Pretreatment Options**

Typical pretreatment technology options for nickel plating wastewater streams are chemical precipitation and activated carbon adsorption. Section 2.1 of the Standard Handbook of Hazardous Waste Treatment and Disposal indicates that implementation of industrial pretreatment standards by EPA and various states could very well affect hazardous waste generation.<sup>13</sup>

### **5.7.1 Chemical Precipitation**

In many cases, metal-bearing wastes contain several constituents at high concentrations. Treatment of spent plating, cleaning, and pickling baths by precipitation often requires special design and operating conditions. More cost-effective treatment may be achieved if wastes are segregated. This is particularly true with wastes that contain cyanide and hexavalent chromium. Segregation of cyanide and hexavalent chromium will allow pretreatment of smaller waste streams requiring smaller tanks and chemical feed equipment, as well as reduced chemical usage for pH adjustment. Jar testing is recommended to compare alternative precipitation processes. Therefore, custom design is the best treatment procedure for the process waste stream.<sup>13</sup>

Either lime, magnesium hydroxide, caustic, or a blend of these alkaline compounds can be used as the source of hydroxide ions for precipitation of metal hydroxides. Advantages and disadvantages of each of these reagents should be considered in the selection of a system for a particular application. For example, caustic is more expensive than lime, but the cost of chemical feed systems for lime slurry can be substantially more expensive than for caustic. Lime and magnesium hydroxide tend to reduce sludge leachability and break metal complexes that may be present in the wastewater stream.<sup>13</sup>

Among the more common complexing agents encountered in metal-bearing wastes are ammonia, cyanide, and ethylenediaminetetraacetic acid (EDTA). There are a number of treatment procedures for complexed metal-bearing wastes by chemical precipitation and reduction. Most of these complexed wastes contain copper, nickel, zinc, silver, tin and lead. A treatment method that has been investigated and reported to be effective for certain nickel complexes is precipitation at high pH (11.6 to 12.5) utilizing lime. The drastic increase in pH is believed to prompt a shift in the complex dissociation equilibrium to produce uncomplexed metal ions which can then be precipitated.<sup>13</sup>

### **5.7.2 Carbon Adsorption**

Sometimes it is necessary to pretreat a wastewater stream prior to discharge to a POTW. Activated carbon adsorption is occasionally used to remove contaminants (usually organic compounds) from such streams. Most carbon-adsorption systems use granular activated carbon (GAC) in flowthrough column reactors. Since the adsorption process is reversible, it is common to remove the adsorbed contaminants and regenerate the carbon for reuse. It is important to determine if carbon adsorption can produce



an effluent of acceptable quality and price for a specific process. For additional assistance for specific waste management applications, consult with an engineering consulting firm, professional trade association, and/or a major activated carbon manufacturer.<sup>13</sup>

## 5.8 Wastewater Control Technology

Wastewater is generated in the nickel plating industry as a byproduct of:

1. Process tank rinses
2. Servicing filters
3. Clean-up of equipment and floor spills

These sources of wastewater are also the primary targets for source reduction, recovery, recycle and reuse. Most of the emphasis on recovery technology has been on rinsewater since it constitutes the majority of the flow leaving an operation and necessitates expensive treatment. Bath dumps are generally of low volume and occur infrequently. Often bath dumps are collected and transported by a waste service provider for final treatment and disposal, but more and more baths are being treated on-site for regeneration and reuse of the bath chemicals. Floor spills include both accidental and intentional waste sources, such as tank overflows, drips from workpieces, leaking tanks or pipes, chemical spills, salt encrustations, washdown water and oil drips-spills from equipment during the operation, transport and handling. Floor spills are managed by the application of good housekeeping, maintenance and operating practices, combined with appropriate operator training.<sup>13</sup>

Wastewater treatment following P2 and recovery/recycle/reuse options can be accomplished using one of five general approaches:

- On-site treatment system
- On-site treatment using a mobile treatment system
- Pretreatment followed by discharge to POTW

- Off-site treatment by a centralized waste treatment facility
- Transport of wastewater to an off-site treatment/disposal facility

Maintaining and operating an on-site treatment facility can be labor intensive and expensive and is usually not a good option for small nickel plating companies. A mobile system can also be expensive for a small plater. Mobile systems are generally used for infrequent site clean-up requirements and are not commonly used by nickel platers. Pretreatment followed by discharge to a POTW is a wastewater control option for many platers who are also active in recovery/recycle programs. Off-site treatment by a centralized waste treatment facility works when several platers are located in the same vicinity, usually in large metropolitan industrial areas. A typical option for most small waste generators is storing the hazardous waste in accordance with RCRA requirements until it is economically sound to have the waste transported to an off-site treatment and disposal facility.<sup>13</sup>

## 5.9 Air Emissions Control Technology

Air emissions are created when hydrogen gas ( $H_2$ ) is produced in the electroplating or EN plating process with air bubbles from air agitation systems in these processes escaping and carrying some of the nickel plating solution with each release. Emissions escape from the blind holes of parts being plated and during the chemical process of the nickel deposition at the surface of the part. Capturing these emissions with hoods or a general ventilation system and routing them to a wet scrubber is the most common control technology for nickel plating air emissions. If the rest of the United States follows the lead of California and its regulation declaring all soluble nickel compounds to be carcinogenic, it will be necessary for all nickel platers to install High Efficiency Particulate Air (HEPA) filters to control emissions from small, medium, and large plating tanks. Since most new tanks are not designed with ventilation systems and the HEPA filters work best in combination with a scrubber or mist eliminator, the estimated cost for achieving compliance could range from about \$20,000 to \$140,000 per tank, depending on the size of the tank and design of the facility.<sup>12</sup>

## 6. Conclusions and Recommendations

In summary, this capsule report has compiled information from reports, articles, books, guides, web sites, and manuals that address nickel plating emission issues, pollution prevention, and control technologies. The report's primary purpose is to assist the metal finishing community in the management of nickel plating environmental issues by providing technical information and practical examples of cost-effective, environmentally acceptable practices. The nickel plating industry is described as part of the larger metal finishing industry in the United States, sharing similar problems and solutions. The technical descriptions provided in this report focused on both the nickel electrodeposition process and the electroless nickel deposition processes. Special attention was given to incorporating issues and factors to the processes regarding environmental releases, costs, technology, and environmental regulations. Life-cycle stages of source reduction, recycle/recovery, pretreatment, treatment, and control technologies were integrated into considering environmental management options.

Nickel plating practitioners are constantly making decisions that affect their production and processes. One of the purposes of this report was to provide a viable reference for making informed choices. It is recommended that decision-makers within the nickel plating community embrace the opportunity for partnerships in solving shared technical problems and coordinating difficult environmental issues. Partnerships with professional and trade associations encourage industry professionals in meeting these challenges. The *National Metal Finishing Resource Center (NMFRC)*, <http://www.nmfrc.org>; *American Electroplaters and Surface Finishers Society, Inc. (AESF)*, <http://www.aesf.org>; and *National Association of Metal Finishers (NAMF)*, <http://www.namf.org> are examples of metal finishing organizations where partnerships are working. EPA offers a number of hotlines and web sites regarding environmental information. EPA's Small Business Ombudsman Office (OSBO), <http://www.epa.gov/sbo> addresses small business issues, problems, and needs. The "Small Business Ombudsman Update" provides EPA web pages and hotlines, the status of high visibility actions, and a variety of assistance references including state contacts.

It is recommended that individuals engaged in nickel plating consider integration of their options for environmental compliance when determining a practice for their specific facility. This requires the nickel plater to gather information, analyze the data regarding facility needs and consider all of the factors before making an informed decision. The plating

shop owner/operator best knows his or her facility and processes and, therefore, should be able to make the appropriate decision. The information and examples provided herein were designed to help support decisions. By integrating pollution prevention and control technology options to meet the challenges of economic and regulatory drivers, the decision-maker can take advantage of all the tools available and avoid concentrating on a single approach, or following examples not tailored for their facility. Generic environmental solutions should be used only for generic environmental problems. Most nickel plating small-shop problems are site-specific and require site-specific solutions. Approaches should be tailored to meet the individual nickel plater's needs. Partnerships make good business sense, but the responsibility for environmental compliance and business success remains with the plating shop owner/operator.

### Major environmental issues:

- Economically achievable pollution prevention and control technology options are needed to meet changing regulations.
- The playing field for environmental compliance between jurisdictions needs to be leveled within the United States and globally.
- Continued research and development are needed to develop and transfer technology to reduce waste generation through process changes, material substitution, water use reduction, metals recovery/recycle, bath life extension.
- Continued government-industrial partnerships are needed with trade and professional organizations and environmental groups to jointly consider regulatory limits and solutions to environmental problems.
- Long-term research and development planning by the industry should attempt to identify what is needed 5 years and 10 years from now to enable companies to address environmental issues while remaining competitive within a global economy.

### Major recommendations:

- Facilities should continue to conduct environmental audits and pollution prevention opportunity assessments for identifying where P2 and compliance can be accomplished.

- Industry must continue to pursue approaches that encourage life-cycle assessment, ISO 14000, pollution prevention, and activity-based costing.
- Government, industry, trade and professional associations and academia should enhance technology transfer that meets the needs of the nickel plating practitioner to improve production and reduce environmental impacts.
- EPA and industry should continue to enhance partnerships for out-year planning with specific goals to be more competitive on the global market, while reducing environmental impacts and improving production.
- More efficient plating solutions need to be developed that utilize lower concentrations of nickel in the electroplating and EN plating processes and produce lower levels (preferably zero levels) of air emissions.

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