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Session B: Nickel Plating—Basics and Applications

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Nickel Plating—Basics and Applications
Session B

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Nickel Plating—Basics and Applications
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Nickel Electroplating Technology and Applications

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NICKEL ELECTROPLATING TECHNOLOGY AND APPLICATIONS

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This paper reviews nickel electroplating technology and its applications in order to provide electroplaters with some of the information needed to produce high-quality nickel-plated parts at lowest cost. Some of the advancements in nickel electroplating technology are pointed out in the course of reviewing the subject. These advancements in nickel electroplating technology have made it possible to control and vary the appearance and other properties of electrodeposited nickel over broad ranges and hence, to satisfy the requirements of diverse applications. The applications fall into three categories - decorative, engineering and electroforming.

The electroplater must understand the basic principles of the nickel electroplating process, he must know the main features of the processes used in various applications, and he must control the processes and the quality of the finished products.

BASIC PRINCIPLES

The electroplating process operates by the passage of direct current between two electrodes that are immersed in a conductive, aqueous solution of nickel salts. The flow of direct current causes one of those electrodes (the anode) to dissolve and the other electrode (the cathode) to become coated with nickel.

Electrochemical Reactions

The nickel in solution is present in the form of divalent positively charged ions (Ni^{++}). When current flows, the positive ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni) at the cathode surface. The reverse occurs at the anode where metallic nickel dissolves to form divalent positively charged ions which enter the solution. The nickel ions discharged at the cathode are replenished by those formed at the anode. The overall reaction in simplest terms is:

$$Ni^{++} + 2e^- \rightleftharpoons Ni^\circ$$

The reaction is electrochemical because electrical energy is used to transform the chemical species at electrode surfaces.

Average Nickel Thickness

The amount of nickel deposited at the cathode and the amount dissolved at the anode are directly proportional to the product of the current and time. The proportionality constant is a fundamental quantity; i.e., 96,500 coulombs will deposit (reduce) or dissolve (oxidize) one electrochemical equivalent of any substance at 100 percent current efficiency. If more than one reaction occurs at the electrode, the current efficiency of each reaction must be known to calculate these amounts.

The proportionality constant is equal to M divided by nF, where M is the molecular weight, n is the number of electrons involved in the electrochemical reaction, and F is equal to 96,500 coulombs (ampere-seconds). For nickel, the constant is 1.095 grams per ampere-hour and calculations can be made from the following expression:

$$m = 1.095\ a\ I\ t \quad \ldots\ldots\ldots \quad (1)$$

where,

m = the amount of nickel deposited (or dissolved) in grams.
I = the current in amperes.
t = the time in hours.
a = the cathode or anode efficiency ratio for the reaction of interest.

Under practical plating conditions, only one reaction occurs at the anode (a=1). The oxidation of hydroxyl and chloride ions may occur at passive nickel anodes but these reactions do not take place under normal conditions. At the cathode, however, deposition of nickel is accompanied by the reduction of hydrogen, and this secondary reaction consumes a small amount of the current. The cathode efficiency ratio for nickel deposition may vary from 0.92 to 0.99 depending on deposition conditions. An average value that is used in making calculations is 0.955. The cathode current efficiency for nickel deposition is the ratio of the actual weight deposited to the weight calculated from the above expression when it is assumed that a=1. The efficiency of anode dissolution is determined from weight-loss data.

It is possible to estimate the average thickness of the nickel coating from the weight deposited and from the area of the cathode (the component being plated). The average thickness, s, in micrometers equals the weight of nickel, m, in grams, divided by the product of the area, A, in square decimeters, and the density, d, of nickel. The density of nickel is 8.907 g/cm^3.

That is:

$$s = \frac{m}{Ad} \times 100$$

Combining with (1), the above becomes, for nickel:

$$s = 12.99\ a\ \frac{I}{A}\ t$$

The quantity, I/A, is the current density, amperes per square decimeter. Thickness is a function of current density.

The nickel electrodeposition date in Table 1 are calculated from the above relations assuming a cathode efficiency ratio of 0.955. Factors useful in making calculations are given in Table 2.

Table 1 Nickel electrodeposition data (based on 95·5 per cent cathode efficiency)

Deposit thickness	Weight per unit area	Electrical requirement		Time (minutes) to obtain deposit at current density (A/dm²) indicated										
µm	g/dm²	Ah/dm²	A min/dm²	0·5	1	1·5	2	3	4	5	6	8	10	12
2	0·18	0·17	10	20	10	6·8	5·1	3·4	2·6	2·0	1·7	1·3	1·0	0·9
4	0·36	0·34	20	41	20	14	10	6·8	5·1	4·1	3·4	2·6	2·0	1·7
6	0·53	0·51	31	61	31	20	15	10	7·7	6·1	5·1	3·8	3·1	2·6
8	0·71	0·68	41	82	41	27	20	14	10	8·2	6·8	5·1	4·1	3·4
10	0·89	0·85	51	100	51	34	26	17	13	10	8·5	6·4	5·1	4·3
12	1·1	1·0	61	120	61	41	31	20	15	12	10	7·7	6·1	5·1
14	1·2	1·2	71	140	71	48	36	24	18	14	12	8·9	7·1	6·0
16	1·4	1·4	82	160	82	54	41	27	20	16	14	10	8·2	6·8
18	1·6	1·5	92	180	92	61	46	31	23	18	15	11	9·2	7·7
20	1·8	1·7	100	200	100	68	51	34	26	20	17	13	10	8·5
40	3·6	3·4	200	410	200	140	100	68	51	41	34	26	20	17
60	5·3	5·1	310	610	310	200	150	100	77	61	51	38	31	26

Table 2 (continued) Conversions for nickel plating (at 100 per cent cathode efficiency)

To convert	to	multiply by
A min/dm² (continued)	oz/ft²	0·00598
	µm	0·205
	10⁻³ in	0·00807
A min/ft²	Ah/dm²	0·00179
	Ah/ft²	0·0167
	A min/dm²	0·108
	g/dm²	0·00196
	oz/ft²	0·000644
	µm	0·0221
	10⁻³ in	0·000869
g/dm²	Ah/dm²	0·913
	Ah/ft²	8·49
	A min/dm²	54·8
	A min/ft²	509
	oz/ft²	0·328
	µm	11·2
	10⁻³ in	0·442
oz/ft²	Ah/dm²	2·79
	Ah/ft²	25·9
	A min/dm²	167
	A min/ft²	1550
	g/dm²	3·05
	µm	34·3
	10⁻³ in	1·35
µm	Ah/dm²	0·0813
	Ah/ft²	0·755
	A min/dm²	4·88
	A min/ft²	45·3
	g/dm²	0·089
	oz/ft²	0·0292
	10⁻³ in	0·0394
10⁻³ in	Ah/dm²	2·06
	Ah/ft²	19·2
	A min/dm²	124
	A min/ft²	1150
	g/dm²	2·26
	oz/ft²	0·741
	µm	25·4

Table 2 Conversions for nickel plating (at 100 per cent cathode efficiency)

To convert	to	multiply by
Weight of $NiSO_4 \cdot 7H_2O$	Weight of Ni contained	0·21
$NiSO_4 \cdot 6H_2O$		0·22
$NiCl_2 \cdot 6H_2O$		0·25
nickel carbonate		0·46
Ah	A min (ampere minutes)	60
	g nickel deposited	1·095
	oz nickel deposited	0·0386
A min	Ah	0·0167
	g nickel deposited	0·0183
	oz nickel deposited	0·000644
g nickel deposited	Ah	0·913
	A min	54·8
	oz nickel deposited	0·0353
oz nickel deposited	Ah	25·9
	A min	1550
	g nickel deposited	28·35
Ah/dm²	Ah/ft²	9·29
	A min/dm²	60
	A min/ft²	557
	g/dm²	1·095
	oz/ft²	0·358
	µm	12·3
	10⁻³ in	0·484
Ah/ft²	Ah/dm²	0·108
	A min/dm²	6·46
	A min/ft²	60
	g/dm²	0·118
	oz/ft²	0·0386
	µm	1·32
	10⁻³ in	0·052
A min/dm²	Ah/dm²	0·0167
	Ah/ft²	0·155
	A min/ft²	9·29
	g/dm²	0·0182

Current and Thickness Distribution

Every solution has an electrical resistance and nearly every component to be plated has prominent surfaces which are nearer the anode than recessed surfaces. Current flow from the anode to the prominent surfaces is greater than that to recesses. That is, the current density in amps per square decimeter is greater at prominences because the anode-to-cathode distance is shorter and therefore has lower electrical resistance than is the case at recesses. The apportioning of the plating current in this manner is called the 'current distribution', see Figure 1. Inevitably this means that the recessed areas receive a thinner nickel deposit than the prominent areas.

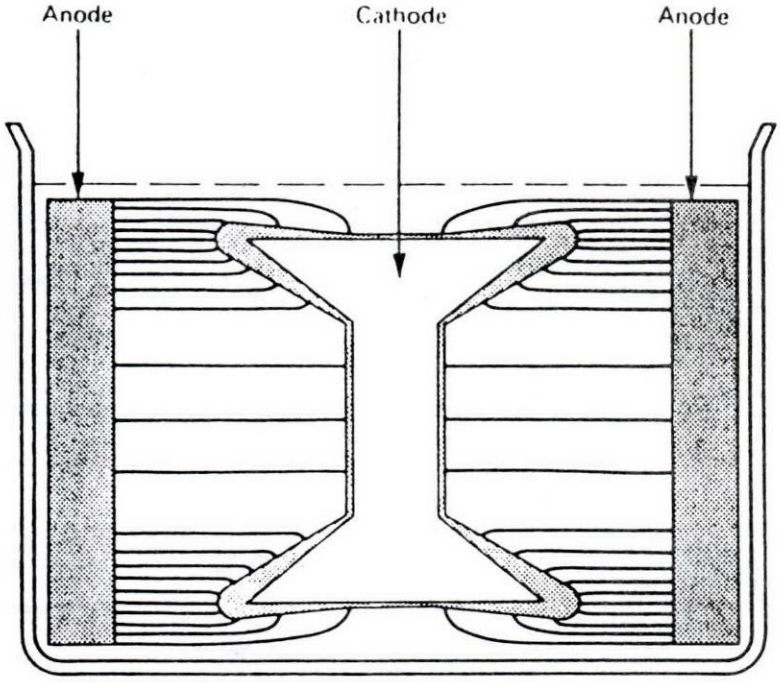


Figure 1. Current distribution is not uniform over a shaped article. Areas remote from the anode will receive a smaller share of the available current than areas near to the anode.

Throwing Power

The relationship between current distribution and thickness is more complex than indicated in the preceding section. Although the geometric factor (shape, positioning of anode and cathode) is important, current distribution is influenced by the electrochemical characteristics of the plating solution. The complex relationship between metal distribution and the conductivity of the solution, cathode polarization, cathode efficiency and geometry is termed throwing power. Throwing power is a measure of the extent to which a solution will produce deposits that are more uniform than those which would be produced in the absence of polarization and deposition efficiency effects.

Cathode polarization is the general name given to a number of factors which increase the difficulty of converting nickel ions to metallic nickel at the cathode. Since polarization causes a rise in tank voltage, it is one measure of the difficulty of electrodeposition. The higher the current density, the greater will be the resistance to deposition set up by cathode polarization. This effect works to the advantage of uniform plating because it means that there is a built-in system which reduces the high current densities at prominent surfaces of a component, and increases current in recesses. Another factor favoring uniform deposition of some metals is that the efficiency of deposition at high current densities is less than that at low current densities, but this is not important when plating nickel.

To increase the throwing power of nickel plating solutions, reduce the current density; increase the conductivity, pH, and temperature.

Practical Implications

These basic principles have practical implications. The nickel processes that are described in the following sections are basically alike because they have the same electrochemical reaction in common. The reaction is controlled by laws that make it possible to calculate the weight of nickel deposited and the average thickness of the nickel coatings. These estimates can be made precise by taking into account variations in cathode efficiencies. The actual thickness at any point on a shaped article depends on the current density at that point. In practice, coating thicknesses must be measured on representative parts and adjustments made to the operating variables and/or the racking before thickness can be controlled within specified ranges. Improving the uniformity of coating thickness enhances the quality of plated parts and saves money by conserving nickel. Understanding these basic principles makes control of electroplating possible.

DECORATIVE NICKEL PLATING

The technology of decorative nickel plating has been improved continuously over the years. The introduction of bright and semi-bright plating solutions, the development of multi-layer nickel coatings, and the use of conventional, microporous and microcracked chromium in combination with multi-layer nickel coatings are prime examples.

Decorative Solutions

The solutions used for decorative plating differ from those used for other purposes in that they contain organic addition agents which modify the growth of the deposit to yield fully-bright, semi-bright or satin-like surfaces. The basic constituents - nickel sulfate, nickel chloride, boric acid and water - serve the same purposes as they do in the Watts solution (Table 3). Nickel sulfate is the principle source of nickel ions; nickel chloride improves the dissolution of non-activated forms of nickel and increases solution conductivity; boric acid buffers the solution pH and helps to produce smoother, more ductile deposits. Water is required to dissolve these basic constituents, and should be pure. Anionic anti-pitting and wetting agents are needed to eliminate pitting due to the clinging of hydrogen bubbles to the parts being plated. Non-foaming wetting agents which lower surface tension are available for air-agitated solutions.

The composition and operating conditions given in Tables 3 and 4 for the Watts solution are typical of many decorative nickel plating solutions, but wide variations in the concentration of nickel sulfate and nickel chloride are possible. For example, higher deposition rates can be used when the nickel chloride to nickel sulfate ratio is raised. Some proprietary bright nickel solutions are available in "high-speed" versions which contain high levels of nickel chloride.

TABLE 3
Typical Composition of a Watts Solution

Nickel Sulfate	240-300 g/l
Nickel Chloride	40-60 g/l
Boric Acid	25-40 g/l

TABLE 4
Operating Conditions for Watts-type Solutions

Temperature	25-50°C
Agitation	air
pH	4.0-5.0
Usual cathodic current density	3-7 A/dm² 30-70 A/ft²
Anodes	Nickel
Mean deposition rate	40-90 um/h

Bright Nickel Solutions

The majority of decorative nickel plating is carried out in solutions containing organic addition agents which modify the growth of the nickel deposit so that a fully bright finish is obtained suitable for immediate chromium plating without mechanical finishing.

Several organic substances are used at appropriate concentrations in these solutions in order to give brightness, levelling and control of deposit stress. Portions of the addition agent molecules are incorporated in the deposit, resulting in a hard, fine-grained coating which usually contains incorporated sulfur. The sulfur causes the deposit to be electrochemically less noble than pure nickel deposits. Hence bright nickel deposits have somewhat reduced resistance to corrosion compared with sulfur-free dull or semibright deposits. Bright nickel deposits may contain 0.05 to 0.10 per cent sulfur.

Modern solutions contain a brightener system comprising several additives which together enable bright deposits to be obtained over a wide range of current densities such as that occurring over a component having a complicated shape with deeply recessed areas.

Brighteners are broadly divided into primary brighteners and secondary brighteners. Primary brighteners have a powerful effect on the deposit and are normally used at low controlled concentration. Primary brighteners often, especially at higher concentration, affect the mechanical properties of the deposit adversely.

Secondary or carrier brighteners have a milder effect on the deposit when used alone, and modify the effect of primary brighteners. Judicious combination of primary and secondary brighteners gives fully bright but relatively ductile deposits having low internal stress.

Most electrodeposits have appreciable internal stress. This means that a thin, perfectly flat sheet is, after plating, slightly concave on the plated side if the deposit stress is tensile, or slightly convex if the deposit stress is compressive. Stress is usually measured by observing the bending induced by plating one side only of a metal strip. Many organic substances used as secondary brighteners also reduce the tendency for the internal stress in the deposit to become tensile. In the absence of primary brighteners, they are able to give zero or even compressive stress in nickel deposits, and thereby find wide application in electroforming where accurate control of deposit stress is vital.

Semi-Bright Nickel Solutions

Semi-bright nickel solutions contain nickel sulfate, nickel chloride, boric acid and a leveling agent such as coumarin or acetylenic alcohols. As implied by its name, the process yields deposits that are semi-lustrous. The deposits are smooth and have a columnar structure unlike the banded structure characteristic of fully bright deposits.

The solution was developed to facilitate polishing and buffing; i.e., semi-bright nickel deposits are easily polished to a mirror finish. Efforts to eliminate the need for polishing led to the combination of semi-bright and bright nickel deposits. This resulted in the greater use of multilayer nickel coatings, not only to minimize polishing, but to improve corrosion performance of decorative nickel coatings.

Single and Multilayer Nickel Coatings

Single-layer bright nickel coatings are decorative and are suitable for use in mildly corrosive service using a nickel thickness of about 5 to 12 micrometers. They are unsuitable for severe service conditions; in these, double-layer nickel coatings are required.

Double-layer nickel coatings have an undercoat of highly-leveled sulfur-free nickel covered with sufficient bright nickel to give a fully bright finish with minimum requirement for expensive mechanical finishing of the substrate.

Because the undercoat of sulfur-free, semi-bright nickel is electrochemically more noble that the final bright nickel above it, corrosive attack is preferentially directed towards the bright nickel and a flat-based pit is formed. This effectively retards the pitting action since, before it can penetrate the coating further, a considerable portion of the bright nickel layer must be removed. In service, double-layer systems show a marked improvement in corrosion resistance over single-layer systems.

Microdiscontinuous Chromium

Electrodeposited chromium coatings are applied over single and multilayer nickel coatings to prevent the tarnishing that occurs when nickel is exposed to the atmosphere. The chromium coating is relatively thin compared to the nickel because electrodeposited chromium is not intrinsically bright and will become dull if thickness is increased beyond certain limits. Brightness is not affected if the chromium thickness is about 0.3 micrometers.

In surfaces plated with nickel plus chromium, corrosion of the nickel begins at a crack or pore in the chromium. The exposed nickel acts as the anode and the surrounding chromium surface as the cathode. Because the area of the chromium cathode is greater than that of the exposed nickel anode, a considerable current is drawn from the anode with the result that penetration to the basis metal may occur at a few small points.

There are few cracks or pores in conventional chromium top coats. Therefore, when corrosion takes place at a crack or pore, the large cathode surface surrounding it results in current being drawn from a small area of nickel underneath and pitting may occur at a significant rate. In microporous chromium a large number of pores are deliberately induced in the chromium top coat so that corrosion can start at many sites. The

corrosion current now has to be spread over these sites on the nickel so that the amount passing to each site is small, and at none is the rate of corrosion enough to cause more than relatively superficial damage after long periods of service. The cracks or pores are too small for the eye to see and the appearance of the chromium is bright.

To produce a microporous chromium coating, the chromium is deposited on to a special, additional thin layer of nickel which incorporates inert solid particles. The particles induce a large number of pores in the chromium. The usual nickel undercoat or coats are used below the special deposit of nickel.

The corrosion protection afforded by microcracked chromium is similar to that of microporous chromium but the discontinuities in the chromium are tiny cracks. One procedure is to deposit a thin layer of highly stressed nickel over the usual nickel layers. This layer produces a fine crack pattern in a deposit of chromium of conventional thickness which may be unacceptable in some applications. This tendency can be reduced by increasing the thickness to 0.5 micrometers.

Microdiscontinuous chromium coatings, either microporous or microcracked, greatly improve corrosion performance. For example, a uniform double-layer nickel coating 40 micrometers thick electroplated either with microporous or microcracked chromium on steel resisted corrosion in severe service for 16 years. What is not often appreciated is that the improvement in the corrosion performance has been accomplished without increasing the thickness of the nickel coatings. This has kept decorative nickel plating practical and cost competitive.

Standards and Recommended Thicknesses

ASTM Standard B456 and ISO Draft International Standard 1456 are excellent sources of information on specific requirements for decorative nickel plus chromium coatings to achieve acceptable performance under different conditions of service. The standards give several classes of coatings that differ in thickness and type, and classifies the various coating systems according to their resistance to corrosion. Copies of the complete standards should be consulted.

In essence, the available standards covering electrodeposited, decorative coatings of nickel plus chromium summarize many years of corrosion experience which have shown that:

1. Multilayers nickel coatings are significantly more corrosion resistant than single-layer bright nickel coatings.

2. Microdiscontinuous chromium coatings provide more protection than conventional chromium coatings; and,

3. The corrosion protection afforded by the use of decorative electroplated nickel plus chromium coatings is directly proportional to the thickness of nickel.

Decorative Applications

More than 140 million pounds of nickel are consumed annually in the non-communist world in electroplating mostly for decorative applications. The major applications are given in Table 5.

TABLE 5
Decorative Nickel Electroplating Applications

Automotive - Hardware and Trim; Bumpers; Wheels
Furniture - Office, Household, Schools
Hand Tools - General Hardware, Fasteners
Wheel Goods (Non-Automotive) Bicycles, Lawn Mowers, Toys, Motorcycles, Jewelry, Silverware, Flatware, Personal Hardware
Sporting Equipment, Luggage, Toys and Carriages
Office Appliances - Computing Accounting
Plumbing and Plumbing Fixtures
Cutlery, Flatware, Holloware and Kitchen Utensils
Electric Lighting Equipment - Lamps and Fixtures
Major Appliances - Ranges, Ovens, Refrigerators, Freezers, Washers, Dryers
Electric Houseware - Toasters, Flatirons, Fans, Clocks
Fabricated Wire Products - Baskets, Shopping Carts, Kitchen Wire Products, Displays
Medical Instruments and Supplies

ENGINEERING AND ELECTROFORMING

Nickel coatings are used in engineering applications to modify or improve surface properties such as corrosion resistance, hardness, wear and magnetic characteristics. Although the appearance of the coating is important and the plated surface should be defect-free, the lustrous mirror-like deposits described in the preceding section are not usually required.

Nickel electroforming is a specialized use of the nickel plating process. Electroforming is the production of products by electroplating onto a mandrel which is subsequently separated from the deposit.

Solutions

The two most popular solutions for depositing engineering nickel coatings and for use in electroforming are the Watts solution and sulfamate solution. The Watts solution is a relatively inexpensive, simple solution which is easy to control andd keep pure.

Sulfamate solutions have distinct advantages, however, and are extremely popular for electroforming. The advantages of sulfamate solutions are low internal stress in the deposit, high rates of deposition and superior throwing power. The basic formulation normally contains between 250 and 450 g/l nickel sulfamate together with about 30 g/l boric acid and 10 g/l nickel chloride. To this may be added organic compounds to control pitting caused by hydrogen bubbles, to modify the internal stress - even to the extent of making it compressive - and to increase hardness and strength by reducing the grain size of the deposit. Typical operating conditions for conventional nickel sulfamate solutions are given in Table 6.

The extra cost of using chemicals that are as pure as possible to prepare the solution is more than offset by savings in the preliminary purification procedures necessary for all nickel sulfamate solutions. It is particularly important that the heavy metal, ammonium, and sulfate content of the chemicals should be low. Lead must be rigorously excluded from all equipment used for sufamate solutions.

TABLE 6
Typical operating conditions for nickel sulfamate solutions

Maxiumum current density at 25°C	15A/dm² (140A/ft²)
Maximum current density at 70°C	32A/dm² (300 A/ft²)
pH	3.0 - 5.0
Operating temperature	25 - 70°C

Conventional plating rates for electroforming thick deposits of nickel occupy expensive plant and raise problems of maintaining conditions favorable to electrodeposition over long periods of time. The 'Ni-Speed' process permits increases in deposition rates up to 1mm per hour when current density is uniform. Even when deposition is on complex shapes, deposition rate can be increased by 2-3 times over those of conventional processes. This represents a large reduction in production times. The composition and typical operating conditions for the 'Ni-Speed' solutions are given in Tables 7A and 7B.

The advantages of the 'Ni-Speed' solution and process are: very high rates of deposition, internal stress can be controlled over a wide range from compressive to tensile without use of organic addition agents, deposits have good mechanical properties and can be made moderately hard (about 250 HV) without addition agents.

TABLE 7A
Composition of the 'Ni-Speed' Nickel Plating Solution

Constituent	Optimum concentration g/l	Normally acceptable range g/l
Nickel Sulfamate	600	550 - 650
Nickel Chloride	10	5 - 15
Boric Acid	40	30 - 40

TABLE 7B
Typical Operating Conditions for the 'Ni-Speed' solution

Current Density	up to 90A/dm² (800A/ft²)	Depends on shape of article, solution temperature and degree of agitation
pH value	3.5 - 4.5	Excessively low pH causes hydrolysis and should be avoided. pH adjustment is made by adding nickel carbonate or sulfamic acid.
Temperature	normally 60 or 70°C	The higher temperature permits higher current densities and approximately doubles the maximum plating rate. It also reduces stress. It should not be exceeded by more than a few degrees due to danger of hydrolysis. Lower temperatures, down to room temperature, may be used.
Main anodes	Sulfur activated nickel in titanium baskets.	When current densities above 16A/dm² (150 A/ft²) are required, activated nickel is necessary to avoid passivity. It may be necessary to draw off the anolyte continuously to avoid salt crystallization at very high current densities.

The solution has good throwing power and freedom from the co-deposited sulfur associated with organic hardening or stress-reducing additives, which would embrittle the deposit if it were heated above 400°C, when welding or brazing, or even above 200°C over long periods of time.

The solution is given a two-stage initial purification using a non-activated nickel anode:

> Electrolysis with a current density of 0.5 A/dm² (5 A/ft²) on both cathode and anode.
>
> Electrolysis using an anode current density of 0.5 A/dm² (5 A/ft²) and a cathode current density of 4 A/dm² (40 A/ft²)

The treatments are carried out until a test deposit made at 5 A/dm² (50 A/ft²) and 60°C in a correctly treated solution is lustrous and the stress compressive at 50 ± 15 MN/m2 (7000 ± 2000 lbf/in²).

In use, the solution should be continuously electrolysed in a separate tank using a non-activated anode in order that deposit stress may be controlled. Deposits having zero internal stress can be obtained over a range of current densities by varying solution temperature, as shown in Table 8.

TABLE 8

Relationship between solution temperature, current density and plating rate for the zero stress condition in deposits using the 'Ni-Speed' process

Temperature °C	35	40	45	50	55	60	65	70
Current density								
A/dm²	1.1	2.7	4.3	8.1	13.5	17.8	21.6	32
A/ft²	10	25	40	75	125	165	200	300
Plating rate,								
approx. um/h	12	31	50	94	156	206	250	375
10^{-3} in/h	0.5	1.2	2	3.7	6.2	8.2	10	15

PROPERTIES

Typical properties of electrodeposits from Watts-type solution are shown in Table 9. The mechanical properties of the deposits are affected by the pH and temperature of the solution and by the cathodic current density. The variations in internal stress, tensile strength, ductility and hardness are illustrated in Figures 2, 3 and 4 and using data reported by V. Zentner,

A. Brenner and C.W. Jennings (Plating, 39, 365, 1229; 1952). The variations of these properties associated with increasing ratio of chloride ions to sulfate ions in the solution is shown in Figure 5.

TABLE 9
Typical properties of deposits from Watts-type solutions

Appearance	Dull
Macrohardness	130-200 HV
Internal Stress	150 MN/m^2
	$22x10^3 lbf/in^2$
Tensile strength	410 MN/m^2
	$60x10^3 lbf/in^2$
Elongation	22-30 per cent

Typical properties of deposits from conventional sulfamate nickel solution are given in Table 10.

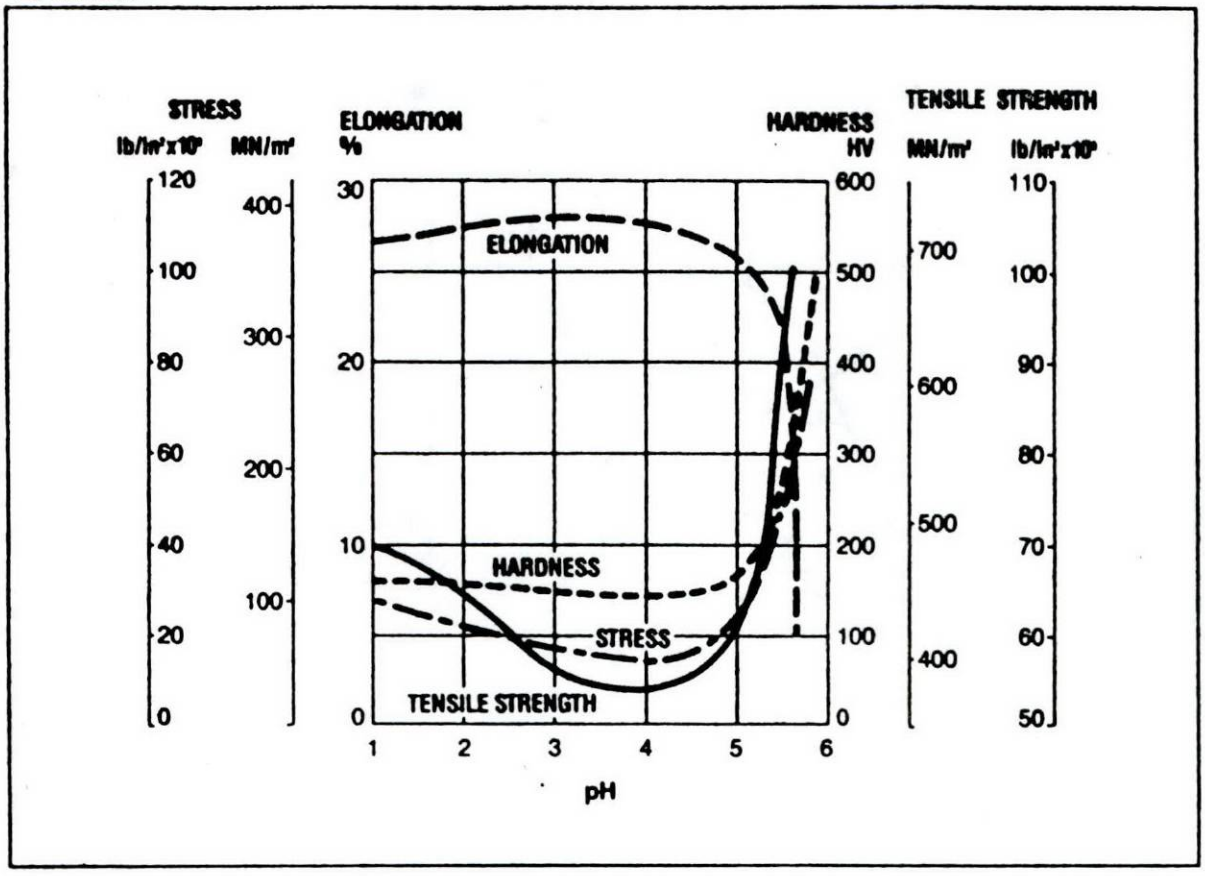
TABLE 10
Typical properties of deposits from nickel sulfamate solutions

Hardness*	150 HV for the simplest solution 450 HV for solutions with chloride and special additives
Tensile strength*	400-550 MN/m^2
	60-80 $10^3 lbf/in^2$
Elongation	20-30 per cent
Anodes	Preferably sulfur-activated nickel in baskets

* A combination of high pH value and the lower of the operating temperature quoted in Table 6 produces the highest hardness and tensile stength.

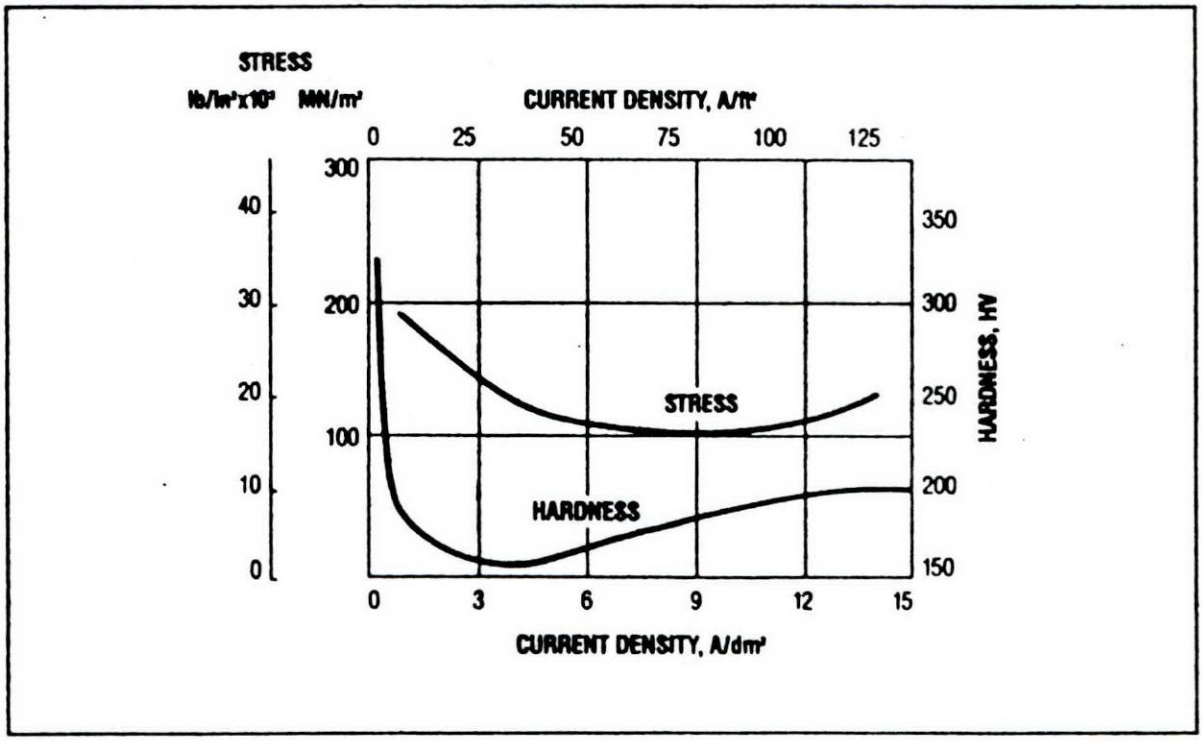
These are but a sampling of some of the important properties of electrodeposited nickel coatings. A comprehensive collection of physical and mechanical property data on nickel, nickel alloy and nickel composite coatings are collected in "The Properties of Electrodeposited Metals and Alloys - A Handbook" by W.H. Safranek, second edition, published by the American Electroplaters and Surface Finishers Society, 12644 Research Parkway, Orlando, Florida 32826.

FIGURE 2



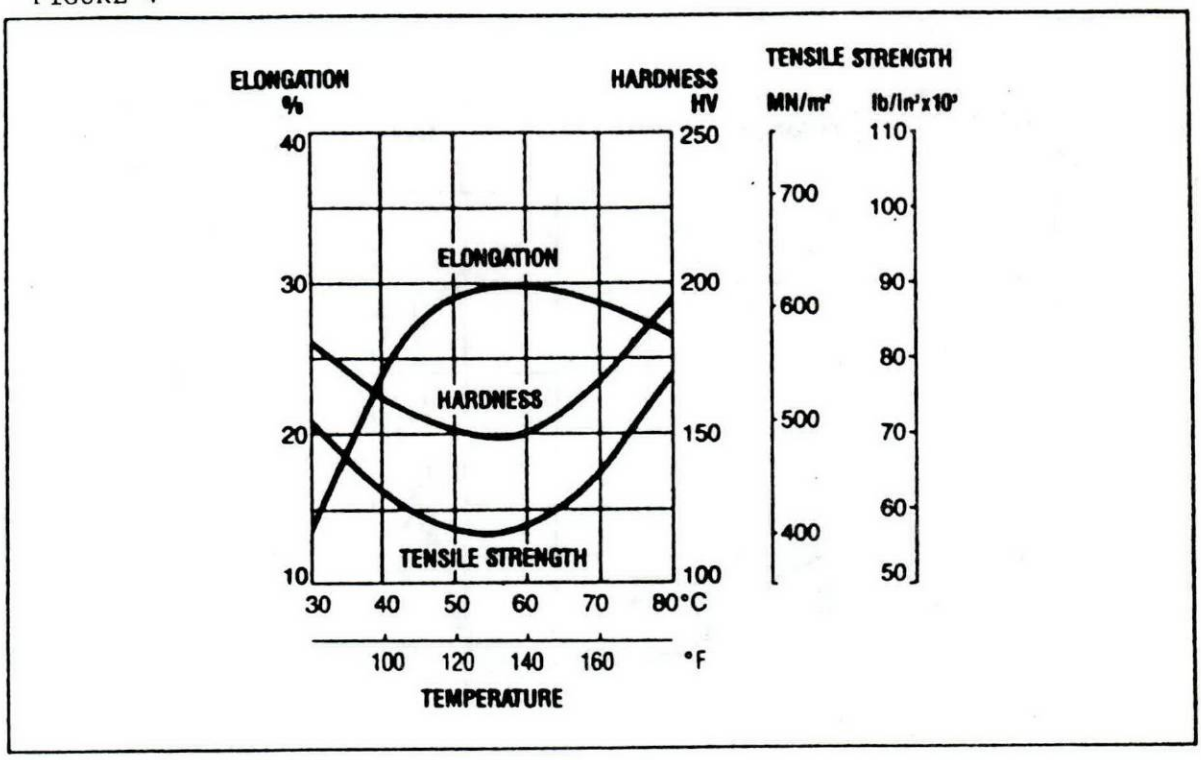
Variation in internal stress, tensile strength, ductility and hardness with pH. Watts bath 54°C and 5 A/dm²

FIGURE 3



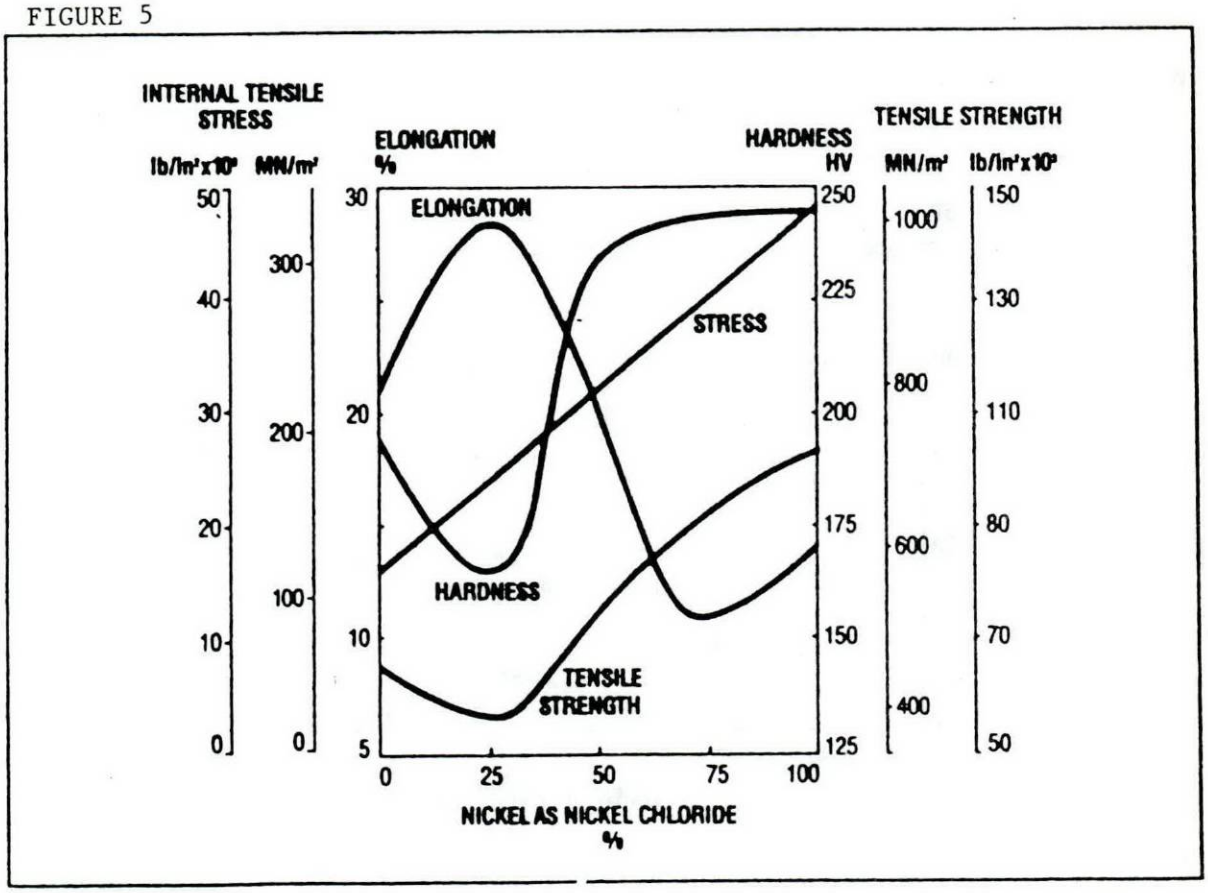
Variation in internal stress and hardness with current density. Watts bath 54°C and pH 3.0.

FIGURE 4



Variation in elongation, tensile strength and hardness with temperature. Watts bath pH 3.0 and 5 A/dm².

FIGURE 5



Variation in internal stress, elongation, tensile strength and hardness with chloride content in deposits from Watts-type solutions operated at 55°C, pH 3.0 and 5 A/dm².

Applications

Engineering nickel coatings are applied in the chemical and petroleum industries to prevent corrosion of equipment and to maintain product purity. Engineering nickel coatings are widely applied in electronics applications as underlayers for gold, palladium, palladium-nickel and other deposits, where the nickel not only prevents interdiffusion of metals, but, also improves the performance of electronic components. Traditional applications are in repair and salvaging of work or mis-machined parts for heavy-duty machinery and tools.

Electroforming provides unique tools that are indispensable for operation in the textile, aerospace, communication, electronics, automotive, photo-copying and other industrial sectors. Specific examples include textile printing screens, components of rocket thrust chambers, nozzles and motor cases; molds and dies for making automotive arm-rests and instrument panels; stampers for making phonograph records, video discs, and audio compact disks; mesh products for use in batteries and porous electrodes, filters and razor screens; optical parts, bellows and radar wave guides.

The engineering and electroforming applications of nickel plating will continue to increase in the years ahead.

NICKEL ANODE MATERIALS FOR TITANIUM ANODE BASKETS

Nickel from the anode is converted into ions which enter the plating solution and replenish those discharged at the cathode. In addition, the anode completes the electrical circuit, distributes current to the parts being plated, and influences metal distribution.

The ideal anode would dissolve uniformly without introducing impurities into the plating solution and without forming any residues. It would be operative over wide ranges of solution composition and current density with low anode polarization. Polarization at the anode is a measure of the difficulty of converting nickel metal into its ions. An anode that exhibits low polarization is more active than one displaying a high polarization. Anode activity is a relative term and its measurement involves comparing anodic polarization characteristics; for example, by determining current-voltage curves.

Under practical plating conditions in chloride-containing solutions, nickel dissolves at 100% anode efficiency. This means that 1.095 grams of nickel dissolve per ampere-hour. Since anode efficiency is greater than cathode efficiency, the nickel ion concentration and pH of the plating solution slowly increase with time. The reverse, a decrease in pH and metal content, is indicative of improperly functioning anodes.

The simplest way to satisfy anode requirements is to suspend nickel bars from hooks placed on an anode bar, so that the nickel, not the hook, is immersed in the plating solution. Nickel anode materials are encased in cloth anode bags to prevent even small amounts of insoluble residues from entering the solution and causing roughness at the cathode. The use of bar anodes is still practiced, but it is not as popular as it used to be.

The way electroplaters utilize nickel as an anode was revolutionized in the 1960's by the introduction of titanium anode baskets. The baskets used in nickel plating are generally made of titanium mesh strenghthened by solid strips of titanium at tops, bottoms and edges. The baskets are suspended on the anode bar by hooks that are an integral part of the baskets. The baskets are loaded with small pieces of nickel. The mesh facilitates the free-flow of plating solution.

The adoption of titanium anode baskets led to a search for improved nickel anode materials. Active forms of electrolytic nickel and forms with unique shapes specifically for use in baskets were introduced. These forms of nickel used in conjunction with baskets come close to meeting the requirements of the ideal anode. The use of nickel in baskets improves quality and helps to conserve nickel.

Today electroplaters have a wide range of anode materials to choose from. The effective utilization of nickel as anode in titanium anode baskets is discussed in the next section which deals with quality.

QUALITY CONSIDERATIONS

Achieving high nickel plating quality at lowest cost involves the following:

1. Maintaining the purity of plating solutions;
2. Preparing surfaces prior to electroplating;
3. Improving the uniformity of deposit thickness;
4. Eliminating rejects;
5. Utilizing nickel in titanium anode baskets effectively;
6. Testing electrodeposits.

Purification of Solutions

Very small amounts of metallic and organic impurities in solution impair the appearance or mechanical properties of the deposit. For good quality plating solutions must be maintained in a state of high-purity.

A few of the many sources of metallic impurities include: 1) drag-over from preceding treatments; 2) components which have fallen off racks and are not removed from the tank; 3) corrosion products from surrounding equipment; 4) tools dropped into the tank, and 5) impure nickel salts and anodes. Metallic contamination is usually from zinc, copper, and iron which have undesirable effects even in small amounts.

A few of the sources of organic contamination are: 1) breakdown of leveling or brightening agents; 2) lubrication oils or greases from overhead equipment; 3) oil-contaminated compressed air supply; 4) extracts from rubber tanks and hoses; 5) rack coatings; filter cloths and anode bags; and, 6) buffing media.

The maximum concentration of impurities normally permissible and treatments for their removal are summarized in Table 11.

TABLE 11
Maximum Concentration of Impurities and Purification Treatments

IMPURITY	MAXIMUM CONCENTRATION PPM	TREATMENTS (DETAILS BELOW)
Iron	150	2 or 1 (0.5 ASD)
Copper	40	2 or 1 (0.2 ASD)
Zinc	50	2 or 1 (0.5 ASD)
Lead	2	1 (0.2 ASD)
Aluminum	60	2
Cr+6	10	2
Calcium	when calcium sulfate precipitates	use demineralized water
Organic Sulfur Compounds	*	3 and 1 (0.2 ASD)
Excess Peroxide	*	maintain bath hot 12 to 24 hours
Excess Wetting Agents	*	3 for 1-2 hours
Organic Impurities	*	3 for 2-3 hours

* the maximum concentrations of organic impurities are process and product related and cannot be specified in a general way.

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1. Electrolytic: Use as large a cathode area as possible and then electrolyze at 0.2 or 0.5 amps/dm². Corrugated cathodes are used to give a wider current density range. The plating solution should be warm and well-agitated. At 0.2 amp/dm² the impurities should be removed after 0.5 to 1.0 ampere-hours per liter treatment; at 0.5 amp/dm², a 1.5 to 2.0 ampere-hour per liter treatment should be enough.
2. High pH: The solution should be tranferred to a separate treatment tank. Raise the pH of hot and well-agitated solution to at least 4.5 with a slurry of nickel carbonate. The amount of carbonate will vary, but 6 grams for each liter of plating solution should suffice. About 0.75 g/l of ferrous sulfate are then added. About 0.8 ml of 30% hydrogen peroxide are added to oxidize the iron. Agitate the bath for an hour or more and then allow to stand hot with no agitation overnight. Filter through filter aid.
3. Activated Carbon: Transfer the plating solution to a separate treatment tank. About 15 to 60 grams of activated carbon are used per liter of plating solution. The solution is agitated for 1 to 2 hours and then filtered through filter aid. (The high pH and activated carbon treatments are sometimes combined for convenience.)

When starting up a new bath, high pH, activated carbon, and electrolytic purification treatments should be performed sequentially. After the pH is adjusted to the desired operating value the quality of the deposit should be checked.

Preparing Surfaces for Plating

Nickel plating for all uses requires a sound bond between the substrate and the coating. The coating should adhere tightly to the basis material. A sound metallurgical bond may be achieved on most materials.

The selection of grinding, polishing, pickling and conditioning treatments for a variety of basis metals varies from one material to another, and depends on the initial surface condition of the metal. The activating treatments which follow polishing and cleaning operations are listed in Table 12 for the basis metals most commonly plated. The ASTM standards referred to provide additional information.

Non-conductive plastics can be plated by metallizing the material, using etching and catalyzing techniques. The mechanism of adhesion between metal and plastic involves mechanical "locking" or "keying" at the plastic to metal interface which provides a moderately adherent deposit. Further information on plating of plastics may be obtained from ASTM Standard B727.

Improving Deposit Distribution

Improving the uniformity of deposit thickness can result in a major improvement in the performance of electroplated parts in service. It can also help to control costs; by avoiding overplating to meet specified thicknesses in low current density areas, nickel is used effectively and not wasted.

Methods of improving deposit distribution arise from the plating process itself. The throwing power of nickel plating processes is influenced by current density and by the distance between the anode and cathode. Reducing the current density improves deposit distribution. Increasing the distance between the anode and the cathode, also, improves deposit distribution. Either or both of these techniques may be useful in some cases, but have practical limitations. It is difficult to justify lowering the current density in a plant that is operating at capacity. The spacing between the anode and cathode is generally predetermined in a given installation.

The use of properly designed support frames or racks can improve deposit distribution. Racks help to control the current density reaching each component being plated, avoid wire marks and assure positive contact with the work.

Racks of mounted components should be suspended adjacent to each other in the plating tank so that they present an unbroken array of components to the anode. When racks are widely separated there is a

TABLE 12

ASTM Recommended Practices for Preparing Metals for Plating

		Conditioning Step 1		Conditioning Step 2 (if needed)		
Basis Metal	**ASTM Desig.**	**Solution**	**Operation**	**Solution**	**Operation**	**Final Rinse Before Plating**
Aluminum Alloys	B 253	Alkaline Zincate	Immerse long enough to deposit .02 to .05 mg Zn/ sq cm	Rochelle Type Copper strike. pH 10.2 to 10.5	Deposit Cu at 258 a/m² (24 asf) for 2 min then 129 a/m² (12 asf) for 4 min.	Double rinse or spray
Copper Alloys	B 281	Sulfuric or hydrochloric acid soln.	Acid dip			Single rinse or spray
Iron Castings	B 320	Sulfuric or hydrochloric acid soln. Room temp.	Brief dip Cold water rinse	Anodic clean	Anodic at 646 to 1076 a/m² (60 to 100 asf) to remove smut	Rinse, acid dip, then cold water rinse
Lead Alloys	B 319	Fluoborate dip 10% HBF_4	Dip 10 to 15 seconds			Cold water rinse and spray
Nickel	B 343	Acid nickel chloride soln. 240 g/l (32 oz/gal) plus HCl 94 ml/l (12 fl oz/gal)	323 a/m² (30 asf) anodic 2 min cathodic 6 min			None
Stainless Steels	B 254	65% H_2SO_4	Cathodic 2 min	Acid nickel chloride 240 g/l (32 oz/gal) plus HCl 94 ml/1 (12 fl oz/gal)	Cathodic 2 min at 1614 a/m² (150 asf)	None
Steels, low carbon	B 183	Alkaline anodic clean	Anodic at 6 volts for 1 to 2 min. Cold water rinse	4 to 10 vol. per cent H_2SO_4	Dip at room temp. for 5 to 15 sec.	Cold water rinse
Steels, high carbon	B 242	Smut removal Sodium cyanide soln.	Dip or short anodic treatment. Rinse	H_2SO_4 250 to 1000 g/l (34 to 134 oz/gal) plus 125 g/l (17 oz/gal) Na_2SO_4 Keep below 25 C (77 F)	Anodic at 1076 to 4304 a/m² (100 to 400 asf) for not more than 60 sec.	Fast rinse
Zinc Alloys	B 252	Copper strike soln. Rochelle type	Deposit 1.3 μm (50 millionths inch) Cu	Cyanide copper plating bath	Copper plate 5 μm (0.2 mil) thick	Cold water

tendency for the components at the edges of the racks to be plated with thicker nickel. This tendency can be controlled by mounting the components at the edges closer together than those in the center. It is also possible to lengthen mounting prongs in the center of the rack so that the work is closer to the anode.

These techniques are not always satisfactory and sometimes the best arrangement is to use individual shields for each rack or for each component to be plated. Individual shields attached to the rack may be two vertical pieces of plastic. The surface of the solution may act as a shield. Anode baskets can be shielded by placing a plastic sleeve between the anode and the anode bag extending about 25 mm below the topmost row of components; this controls the current density at the top of the rack.

The backs of components are not generally plated to the same specification as for significant surfaces. The overplating of the backs is avoided by placing components back to back on double-sided racks.

Achieving adequate deposit thickness in recessed areas may require the use of auxiliary or bipolar anodes. Auxiliary anodes are placed close to the rack itself, and draw current from a separate circuit. The current reaching the recessed area can thus be adjusted to improve deposit thickness uniformity. A bipolar anode is a piece of bagged nickel placed so that one end is directed toward the anode and the other towards the recess but it is not connected to a current supply. When the plating current flows, the bipolar anode acts as a low-resistance path, so that the end facing the work becomes anodic and the opposite end becomes cathodic. Additional current is then directed into the recess.

By using a combination of methods a relatively uniform distribution of nickel over a rack of components can usually be achieved.

Effective Utilization of Nickel in Titanium Anode Baskets

The use of titanium anode baskets has virtually become standard practice because of three major advantages: 1) a basket full of nickel ensures a uniform anode area giving constant current distribution to the work and consistent deposit distribution; 2) anode maintenance is simplified; and 3) conforming anode baskets are possible. As discussed, the effective size of baskets can be adjusted by using plastic shields.

Titanium is the preferred material because it is not attacked by most nickel plating solutions. Corrosion can arise if the basket is not kept filled with nickel. Nickel anode materials that settle uniformly avoiding the formation of "bridges" are preferable. Titanium anode baskets must not be used with nickel solutions containing any fluoride ions.

Bags for baskets must be durable, must fit tightly, and be of the right length. More metallic residue and sludge form when loose anode bags are employed. Anode bags can be accidently damaged and consequently, many electroplaters use double anode bags for greater safety. The outer bag should be more loosely fitting than the inner so that slight movement of the bag under solution agitation will help diffuse away the concentrated solution produced within the basket by anodic dissolution of the nickel. Anode bags for nickel plating may be made from cotton and polypropylene. In double bagging, it is common to use a polypropylene inner and a cotton outer bag, although double cotton or double polypropylene bags work satisfactorily.

Anode baskets should be removed slowly from the tank to avoid disturbing the anode residue and forcing it through the bag into the plating solution. Anode baskets should be suspended from hooks and not stood on the floor to prevent damage to anode bags. In the tank, anode baskets should always be placed so that the tops of the baskets are above the solution level. It is bad practice to overfill the plating tank when water lost by evaporation is replaced. This will avoid washing residues into the plating solution.

The effective use of nickel in titanium anode baskets can improve the quality of nickel plated parts and control costs.

Eliminating Rejects

Since electroplaters may lose 5 per cent of their output due to rejects, an effort to eliminate rejects is always worthwhile.

Rejects arise mainly from the following defects:

1. Roughness
2. Pitting
3. Blistering
4. High stress and low ductility.
5. Discoloration or poor mechanical properties at low current density areas
6. Burning at high current density areas.

These defects, probable causes and methods of avoiding them are summarized in Table 13.

TABLE 13
Probable Causes and Elimination of Defects

Probable Cause	Elimination
ROUGHNESS	
1. Incomplete polishing of metals so that slivers protrude from surface	1. Improve inspection and control of metal and polishing operations.
2. Incomplete cleaning and failure to remove soil from surface.	2. Improve inspection and control of cleaning operations and, if necessary, modify operations.
3. Detached flakes from racks.	3. Good maintenance of racks and contacts. Strip nodules, etc. periodically.
4. Dust from metal polishing operations and other sources.	4. The surface preparation and metal polishing operations should be physically separated from the plating area. Provide adequate air supply. Keep the area near and above the tanks clean.
5. Insoluble salts in solution.	5. Maintain the composition of the plating solution within specified limits by regular analysis. Use demineralized water to avoid calcium sulfate precipitation.
6. Metallic anode residue.	6. Use good anode bags. Do not disturb anode baskets and bags. Do not raise solution level above the tops of the baskets. Do not drop pieces of nickel into the bottom of the tank. Withdraw anode baskets from solution alowly.
PITTING	
1. Solution chemically out of balance.	1. Maintain chemical composition by regular analysis.
2. Too low a pH.	2. Check pH frequently and make necessary changes.
3. Inadequate agitation.	3. Increase air agitation to remove hydrogen.
4. Incorrect racking of complicated parts.	4. Rack so that all parts receive adequate solution agitation.
5. Organic contamination.	5. Remove oil/grease by carbon treatment.
6. Presence of copper and other inorganic contaminants.	6. Remove metallic impurities by high pH and electrolytic treatments.

TABLE 13
(continued

PROBABLE CAUSE	ELIMINATION
7. Too low a concentration of wetting agent.	7. Control concentration of wetting agent.
8. Incomplete cleaning of the basis metal.	8. Check adequacy of cleaning procedure.
9. Incomplete solution of coumarin and other leveling agents.	9. Can form oily globules on the surface which causes wide, shallow pits. Dissolve the additive in plating solution removed from the tank.
BLISTERING	
1. Poor adhesion	1. Use standarized methods of preparation for metals and plastics.
2. Incomplete removal of grease, oil or oxides.	2. Check adequacy of degreasing and surface activation procedures.
3. Films of silica from cleaning solutions.	3. Check rinsing between cleaning steps.
4. Chromate trapped in rack coatings that are damaged & reused.	4. Maintain integrity of rack coatings.
5. Incorrect application of intermediate deposits.	5. Use correct techniques for applying cyanide copper, acid copper, and acid nickel chloride "strike" deposits.
High Stress And Low Ductility	
1. Addition agents out of balance	1. Maintain addition agent concentrations.
2. Organic or inorganic impurities.	2. Maintain solutions in a state of high purity by high pH, carbon and electrolytic treatments.
Discoloration	
1. At low current densities, usually caused by metallic contamination of the solution.	1. Remove metallic impurities by high pH and electrolytic treatments.
2. Burning at high current density may be caused by high current flowing to the bottom of the rack as it is being lowered into the solution.	2. Ramp the current to prevent burning at the bottom of a rack.

Testing Electrodeposits

The regular testing of nickel-plated parts and components is essential for controlling quality and the costs of plating. Good quality protects the user, as well as the electroplater. It is essential that the appearance of the plated articles is satisfactory. Surfaces must be free from visible defects such as blistering, pits, roughness, cracks or unplated areas. Surfaces must be free from stains and discolorations, and must be bright, dull, or satin-like as specified.

Nickel plating thickness must always be controlled and measured. Adequate nickel thickness is the prime requisite for assuring that plated parts give satisfactory performance in service. Thickness and other tests useful for quality control are summarized in this section.

Thickness Testing. The most precise methods of measuring nickel thickness are destructive methods. The microscopical method, involving measurement of a cross-section under a microscope, is described in ASTM Standard B487. The coulometric method, which can be used to measure the chromium thickness, nickel thickness and thickness of any copper undercoat, is described in ASTM Standard B504. The coulometric test measures the amount of electrical energy used to deplate a small and carefully defined area of the component under test. A cell is sealed to the test surface, filled with electrolyte and a cathode inserted. The component is made the anode and the circuit connected to the power supply via a coulometer. By integrating time in seconds with the current passing, the coulometer provides a direct reading in coulombs. The completion of the de-plating is shown by a marked change in the applied voltage at which point the number of coloumbs used is related to the thickness in micrometers. For routine control of production, it is usually more convenient to measure nickel thickness non-destructively with a magnetic gauge, calibrating the gauge at intervals using standard samples. This method is described in ASTM Standard B530.

The Step Test. The Simultaneous Thickness and Electrochemical (STEP) Test is similar to the coulometric method of determining thickness. By including a reference electrode in the circuit, however, it is possible to measure the electrochemical potential of the material being dissolved. The test was developed to help control the quality of multilayer nickel coatings. For example, with double-layer nickel coatings, a relatively large change in potential occurs when the bright nickel layer has dissolved and the underlying semi-bright nickel layer begins to be attacked. The potential difference is related to the overall corrosion resistance of the double-layer nickel coating. The test has been standarized by ASTM and is being applied in the automotive and other industries. See ASTM Standard B764.

Corrosion Testing. The only truly satisfactory test of a plated component is an in-service test. Once a satisfactory plating system has been established for a component, the performance of components plated to that system can be tested in an accelerated corrosion test apparatus. The time

taken to break down the plating is established and then used in control tests on subsequent production. The CASS and Corrodkote tests are two examples.

Copper Accelerated Acetic Acid Salt Spray Test (CASS). Acidified sodium chloride solution causes corrosive attack on a number of metals including nickel, and the addition of some copper salt to the solution increases the rate of attack on nickel considerably. This mixture then is a useful solution for control tests on nickel-chromium plated parts.The standard solution contains 50 g/l sodium chloride and 0.02 g/l cupric chloride, and is acidified to pH 3.2 using acetic acid. The solution is applied to the plated parts in the form of a spray inside a fog cabinet or room made or lined with glass, rubber or resistant plastics. See ASTM Standard B368.

Corrodkote Test. The Corrodkote test is an attempt to reproduce the corrosive attack on plated automotive parts that is produced by road mud containing corrosive salts. The synthetic 'mud' is a slurry made up from Kaolin plus ferric chloride, copper nitrate and ammonium chloride. The slurry is brushed onto the plated samples and dried. Corrosive attack is then induced by placing the test specimens in a humidity cabinet. The test is described in ASTM Standard B380.

Ductility Test. The ductility test is used in decorative nickel plating mainly to check that semi-bright nickel has an elongation greater than 8%, and also to check that bright nickel solutions are in good working condition, since the bright deposits often become brittle otherwise.

The test is conveniently carried out by cutting a test strip 150mm long, 10 mm wide and 1 mm thick from a larger sheet, usually soft brass, which has been plated with 25 micrometers of the nickel deposit. The test strip is bent, with the plated surface outermost, through 180°C over a mandrel of 11.5 mm diameter until the two ends of the test strip are parallel. If no cracks pass completely across the convex surface, the plating has an elongation of a least 8%. See ASTM Standards B456, B489 and B490.

Adhesion Tests. Two tests are recommended in ISO 1456. The first is a simple file test in which a piece of the plated article is held in a vise and a coarse file applied to the cut edge in such a manner as to raise the plated coating. Filing is done from the basis metal to the coating at an angle of 45°. Poorly adherent deposits are easily raised. The second test involves heating the sample or component in an oven (to 300°C for steel, 150°C for zinc alloy), followed by quenching into water at room temperature. The rapid contraction of the metal detaches any poorly adherent deposit. Also see ASTM Standard B571.

Adhesion testing of electrodeposited nickel plus chromium coatings on plastic substrates is carried out by means of thermal cycling over temperature ranges of 75°C to either 20°C, -20°C or -40°C. Details are given in ASTM Standard B553.

SUMMARY

The basic principles of nickel electroplating and the essential features of the processes used for decorative, engineering and electroforming purposes have been reviewed. Many of the advancements in nickel electroplating technology have taken place within the past fifty years. In decorative plating, buffed Watts nickel coatings were made obsolete by the introduction of plating processes that yield mirror-bright deposits directly from solution. Multilayer nickel coatings with improved corrosion performance evolved from single-layer bright nickel coatings. Microcracked and microporous electrodeposited chromium coatings were introduced and have substantially increased the corrosion resistance of multilayer nickel coatings. We have witnessed a revolution in the way electroplaters satisfy anode requirements. The use of titanium anode baskets led to the development of active forms of nickel with unique shapes made at the refinery level. The commercialization of sulfamate processes added a new dimension to nickel electroforming. Underlying many of these advancements is a greater understanding of the electrochemical principles of corrosion.

A commitment to quality assures continued progress in the technology and application of nickel electroplating. The commitment is required to produce high-quality plated parts at lowest cost.

B-2

Nickel Plating—Basics and Applications
Session B

Analysis of Nickel Plating Solutions

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ANALYSIS OF NICKEL PLATING SOLUTIONS

By
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With today's emphasis on quality, the plating supervisor needs to monitor the components and impurities in his plating bath closely. In nickel plating, high or low levels of additives may result in burned or highly stressed deposits. The presence of impurities such as copper or zinc will result in discolored surfaces.

The plating chemist needs methods of analysis that will provide accurate information. These methods should be quick, precise, simple, and hopefully, inexpensive. To reduce turn-around time, he should be able to perform them within their own facility. If not, he should know what equipment is required to provide the necessary information.

For many bath analytes, there are several methods of analysis. Some methods may require intensive manipulation of the sample to reach the end result while other methods will give the same result in less time and labor but require expensive equipment. Also some methods have been automated. A decision on cost, labor, and accuracy must be made.

Titrimetry

Titrimetric analysis is a quick and accurate method of measuring the concentration of a substance in solution. The analysis is performed by slowly adding a solution of known concentration that reacts rapidly with the analyte whose concentration we wish to determine.

The chemical reaction is represented by the following:

$$aA + bB \rightarrow A_a B_b$$

Where A is the titrant, B the substance to be determined and a + b the number of moles in each. When enough A has been added to react to with all of B present, the endpoint of the titration has been reached.

The endpoint can be determined visually with an indicator color change or measured potentiometrically with a pH meter.

Titrimetric methods require the least investment of capital for analysis of the major components of the bath, titration provides the most accurate results. With proper procedure and technique, errors are in the order of 1 to 0.1%.

The following methods are available for nickel solutions:

Major Components

1. Nickel - Titration with EDTA. Simple, interfence-free visual endpoint. Highly recommended.
2. Nickel - Titration with copper EDTA or Copper Diethylene-triamine. Endpoint detected with copper specific ion electrode. Good method for automatic titrators. Recommended.

3. Chloride - Titration with silver nitrate. Simple, interfence free, visual endpoint. Highly recommended.
4. Boric Acid - Titration with sodium hydroxide after pH adjustment and reaction with mannitol. Endpoint either visual or with pH meter. Adjustment of initial pH is important for proper results. Rest of procedure is simple. Highly recommended.

Additives

1. Saccharin - Sample is acidified and extracted into ethyl acetate and titrated with sodium hydroxide to a visual endpoint with methyl red or bromophenol blue indicator. This procedure is affected by acids carried over in the extraction process. Errors can be in the order of plus or minus 20%. Recommended.

Impurities

1. Calcium and Magnesium Hardness - Nickel is masked with cyanide and hardness is titrated with EDTA and Eriochrome Black T to a visual endpoint. Endpoint may be somewhat difficult to detect. Results are excellent in the 300 - 2000 ppm level. Recommended.

Potientiometry

Potientiometry uses an electrode that responds to the activity of a particular group of ions in solution but not to others. The classic example is the glass electrode for the hydrogen ions. Other electrodes are available now that respond to chloride, fluoride, fluoborate, etc.

Potentiometric methods measure the activity of the ion which is related to its concentration in solution. This not the same as the concentration. In the case of a solution containing Cl^- and $CuCl^+$ only the free Cl^- would be measured with a chloride electrode.

With proper selection of conditions these interferences can be eliminated.

The specific ion electrodes can be used for standard addition analysis or as indicator electrodes for endpoint determination.

The following methods are available.

Major Components

1. Chloride - Standard addition with sodium chloride or titration with silver nitrate.
2. Boric Acid - Conversion into tetrafluoroborate ion with hydrofluoric acid[1] and standard addition with sodium tetrafluoroborate.

Additives

Not applicable.

Impurities

Not recommended.

Voltammetry

Voltammetry involves applying a potential to a sample in a electrochemical cell and plotting the current as a function of the applied potential. When the analyte undergoes reduction or oxidation, there is a change in current and the potential where this occurs indentifies the species. Platinum, gold, and glassy carbon and mercury are used as working electrodes. The technique is referred to as polarography when the working electrode is mercury. Organics as well as metals can be determined by this method.

A number of different techniques such as differential pulse, square wave, and cylic stripping voltammetry are available. These methods allow greater sensitivity and faster analysis than conventional direct current polarography.

Most instruments are computerized which results in ease of data recording and use. Sample preparation is, in most cases, minimal. The bath sample can be analyzed either directly, diluted, or extracted before analysis. Calibration curves can be prepared or standard addition analysis can be used. The use of standard addition analysis is recommended if there are high concentrations of wetting agents.

Major Components

Requires large dilutions for analysis. Not recommended for boric acid.

Additives

1. Pyridine Derivatives - 0.2 ml sample added to 0.2M Na_4EDTA. Analyze by square wave or differential pulse. Differential pulse requires addition of surfactant. Highly recommended.[2]
2. Saccharin - Acidify with HCl - extract with methylene chloride. Evaporate and dissolve in 10 ml 0.1M sodium hydroxide. 0.5 ml sample in 10 ml of 0.5M HCl - 1.06V. Analyze with square wave or differential pulse. Highly recommended.

Impurities

1. Hexavalent Chromium - 0.5 ml sample in 10 ml 0.1M NH_3 NH_4CL -0.35V. Analyze by differential pulse. Square wave may give total chromium in some instances.
2. Cu, Pb - 1 ml sample in 10 ml 0.2M acetate pH 4.5 deposit for 30 seconds then strip Cu -0.1V Pb - .4V
3. Fe - 1 ml in 0.1M Oxalate pH 4.5, -0.23V.
4. Class I Brighteners by Cyclic Voltametric Stripping - working bath is added to blank nickel solution and change in nickel stripping potential is observed.

Spectrophotometry

Colorimetric and spectrophotometric procedures are based on the absorption of radiant energy by a solution. This can be visible or ultraviolet light. The amount of energy absorbed is proportional to the concentration of absorbing material in solution. Absorption can be determined with a spectrophotometer or in some cases visually with the use of a set of color standards.

These methods are usually used for low-level concentrations from trace levels to 1 or 2%. The number of dilutions required to analyze most major components can result in large errors in the final result. For example, boric acid can be analyzed photometrically but it is easily determined by titration.

Substances that have little or no color can be determined after reaction with a reagent that forms a highly colored product. By comparison with a series of standards, the original concentration can be found.

This reaction product may also allow for an analysis that otherwise could not be done. For example, many pyridine derivatives absorb light at the same wavelengths that saccharin and its break down products. Reaction with barbituric acid and cyanide results in a colored product whose properties eliminate this problem.

Standards need to be prepared for a calibration curve. Also a standard should be run with each new reagent solution as a check for accuracy.

The following methods are available:

Major Components

1. Nickel - Can be measured at 675 nm after dilution. Recommended.

Additives

1. Saccharin - Subject to interference from breakdown products of brighteners. Not recommended.
2. Pyridine Derivatives - Reaction with barbituric acid, cyanide, and Chloramine T. Requires 1 hour reaction time and low levels must be extracted with amyl alcohol. Recommended.
3. Anionic surfactants - Extraction with chloroform after reaction with methylene blue. Recommended.

Impurities

1. Cr^{+6} + Cr^{+3} - Reaction with 1,5 diphenyl carbazide. Simple, interference free. Cr^{+3} determined after oxidation with bromine water. Highly recommended.
2. Ammonia - Reaction with phenol. Simple interference free. Highly recommended.

3. Copper - Requires extraction from bath with chloroform after reaction with thiocyanate. Requires attention to technique. Recommended.
4. Zinc - Extraction with chloroform after reaction with dithiozone. Recommended.
5. Iron - Extraction with chloroform after reaction with bathophenanthroline. Cu will interfere. Recommended.

Atomic Absorption and Atomic Emission Spectroscopy

These methods are based on the absorption or emission of light. In atomic absorption analysis, light from a hollow cathode lamp is passed through a flame and into a monochrometer and photomultipler detector. The lamp is specific for the element that its cathode is constructed from. The sample is aspirated into the flame where it is reduced to neutral atoms. Atoms of that element present absorb a portion of light proportional to its concentration. The linear absorbance range is usally 1 to 2 orders of magnitude.

There are two sources of interference with atomic absorption analysis, matrix or chemical effects and spectral interference.

For some elements, such as iron, absorbance is affected by the sulfate and chloride in the matrix of the sample. In some cases this can be eliminated by using a nitrous oxide/actylene flame instead of the cooler air/acetylene flame. In other cases matrix matching must be used for proper results. These can be corrected for with deuterium arc, Smith-Hieftje, or Zeeman background correction.

One of the drawbacks of atomic absorption spectroscopy is the lamps used. Each element to be analyzed requires its own lamp. The cost per lamp is about $250 - $300. Also ventilation must be provided for the flame. Due to the high dissolved solids content, nickel bath samples should be diluted to prevent clogging the burner. Cost for instrumentation is about $15,000 to $20,000.

Major Components

Not recommended.

Additives

Not applicable.

Impurities

Highly recommended.

For emission spectroscopy, the inductively coupled plasma emission spectrometer is available. Excitation is provided by inductive coupling with a load coil to ionize the sample after it is aspirated in a stream of argon gas. The sample

is heated in the plasma and the elements present emit light at their characteristic frequencies. The light passes into a monochrometer and into a detector. The elements can be analyzed sequentially or simultaneously depending on the design of the instrument.

In the plasma, the sample is completely ionized so no matrix effects occur as in atomic absorption spectroscopy. Also the linear working range is 4 to 5 orders of magnitude compared to 1 to 2 in atomic absorption. The only interferences that occur are when the wavelength of two elements over lap. These interferences can be found by consulting a line coincidence table of wavelengths. All metallic elements can be analyzed as well as non-metallic elements such as boron, sulfur, phosphorus, and silicon.

Cost for the instrumentation starts around $60,000. Also ventilation is required and air conditioning is required for the room wher the instrument will be situated.

Major Components

Nickel and boron can be determined. Recommended.

Additives

Not applicable.

Impurities

Highly recommended.

Chromatographic Analysis Spectroscopy

These techniques include high performance liquid chromatography (HPLC) and ion chromatograph (IC). The analytes are separated with an eluent on a chromatographic column based on either their polarity (HPLC) or ionic charge (IC). However, with the advent of new column materials and eluents the distinction between these methods is becoming obscured.

These methods allow the determination of multiple analytes in one sample. For example in the analysis of saccahrin, its breakdown products toluene sulfonamide and benzamide can be determined. Multiple contaminant metals in nickel solutions have also been done by IC in one analysis. There is also a choice in detection. Conductivity, ultraviolet-visible spectrometry, and electrochemical detection are the most common. This allows for very selective detection in the presence of other analytes.

These units can cost from $30,000 to $50,000. Attention must be paid to proper maintenance of the equipment. However, most of the previously-mentioned low level analytes can be determined on these instruments with changes in analytical columns, eluents, and detectors.

Chromatography

Major Components

Not recommended.

Additives

Highly recommended.

Impurities

Highly recommended.

TABLE I

	Major Components	Additives	Impurities
Titrimetry	Highly Recommended	Recommended	Recommended
Potientometry	Recommended	Not Applicable	Not Recommended
Voltammetry	Not Recommended	Highly Recommended	Highly Recommended
Spectrophotometry	Recommended	Recommended	Recommended
Atomic Absorption	Not Recommended	Not Applicable	Highly Recommended
Atomic Emission	Recommended	Not Applicable	Highly Recommended
Liquid Chromotography	Not Recommended	Highly Recommended	Highly Recommended

TABLE II

	Cost	Support	Training
Titrimetry	$25	Minimal	Technician
Potientometry	$1,000	Minimal	Technician
Voltammetry	$15,000	Moderate	B.S. Degree
Spectrophotometry	$1,000	Moderate	Technician
Atomic Absorption	$8,000	High	B.S. Degree
Atomic Emission	$60,000	High	B.S. Degree
Liquid Chromatography	$30,000	High	B.S. Degree

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B-3

Nickel Plating—Basics and Applications
Session B

Troubleshooting Bright Nickel Plating Installations The Practical Way

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Trouble Shooting Bright Nickel Plating Installations the Practical Way

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Bright nickel plating enjoys the distinction of being the world's most well documented finishing process. More research has been done on the application of nickel deposits and more has been written about it than any other process. Why, then, is there so much mystery that surrounds servicing and trouble shooting bright nickel plating installations? There are several reasons:

1. Bright nickel is seldom used by itself as a final finish. It is almost always applied in combination with one or more other coatings. This multiplicity of deposits and processing steps contributes to the complexity.

2. The bright nickel electrolyte itself contains several ingredients - including multiple addition agents - and, as any statistician can attest, the difficulty of controlling a process increases as does the number of components comprising the process.

3. Many faults that occur early in the processing cycle are not detectable on parts until they are at, or near, the end of the complete cycle. The most obvious example of this is inadequate cleaning that is not evident on a part until after it is nickel plated. This "lag effect" complicates the task of pinpointing the true source of trouble.

4. The same plating defect can result from several different sources. Of course, all electrolytes exhibit this to some degree, but none to the extent of a bright nickel plating solution. For nickel, there are almost always several possible sources that can produce any given imperfection. Thus, matching problems with their causes is not as simple as picking a given problem from column A and pairing it up with its unique cause from column B.

5. At times suppliers have not been especially open in passing on control and technical service information to finishers. When this occurs, it is generally a throwback to the days when suppliers only passed on a minimum amount of operating information to customers, thinking it would increase their worth and importance in the customers' eyes.

6. Bright nickel plating is a sensitive and non-forgiving process. Many minor faults that are invisible to all but the most discriminating eye have a significant effect on the quality of the final finish. Likewise, the electrolyte has no inherent cleaning ability of its own, so there is very little room for error in the pretreatment cycle, compared with many other finishing processes.

7. Some problems can go undetected for quite some time before they affect quality to the point where rejects occur. For example, it may take several days before a deficiency in the cleaning cycle can drag or carry enough soil into the nickel plating solution to cause rejects. Delayed effects like this make it very difficult to identify the real source of trouble.

None of this, of course, is revolutionary information. Previous articles dealing with the servicing of bright nickel plating installations have already mentioned most of these ideas. Nevertheless, very few articles have properly emphasized what should be done to overcome the natural complicating effect these considerations have on service situations. Instead, the articles usually consist of extensive lists of faults, causes, and remedies that apply to bright nickel processing lines.

This does not mean this information is not important. It must be used in all problem solving situations. However, attempting to use it without first narrowing the scope of investigation is very inefficient. Narrowing the scope of investigation amounts to generating a check list of key questions to help initiate investigative service efforts at the spot in the total processing cycle that is the most probable location of difficulty. A secondary benefit of this approach is that is organizes the thought process in a manner that eliminates much of the mystique involved with servicing bright nickel plating installations.

Since no two plating installations are the same, there is no such thing as a universal check list for every nickel plating line. Yes, there are certain questions which would apply in every case, but there are also other questions that only apply to a given installation because of aspects that are unique to that installation. Thus, each plant must generate its own check list that incorporates questions which are universally applicable and its own questions that are unique to the given installation and parts that are processed.

A series of suggested steps follows which should prove helpful in generating such a check list, one that will be most helpful in reducing the time needed to identify and resolve a service problem when one occurs.

1. BE SURE THERE IS A PROBLEM. Do not mistake random occurrences of defects for typical production performance.

2. Once there has been confirmation there is a problem, identify the extent to which the problem exists. Is it evident to the same degree on all processed parts, or just a few? Rarely does a problem occur on every piece. When this happens, it usually results from a single major fault, such as one of the rectifiers being turned off, or a temperature being too low or too high in one of the processing tanks.

   It is also important to determine where on the part the defect can be seen. Everywhere, or just on horizontal surfaces, or just on vertical surfaces? The more evident the problem is on all surfaces, the more likely it is the result of a single cause. Likewise, problems that only

2. continued:

occur on horizontal surfaces usually result from solids in one of the processing tanks - generally either the copper tank (if one is a part of the line) or the nickel tank. Another possibility is the roughness is caused by lifting parts through a layer of soils that has collected on the top of one of the processing tanks - most likely one of the cleaners.

It is also important to determine at what current densities the problem is most apparent. Can it be seen at all current densities? Just at high current densities, or just at low current densities? As a rule, problems that are evident at all current densities are due to faults in a processing step other than one of the plating tanks.

Likewise, if parts are rack processed, where on the rack does the defect occur? At the top, at the bottom, at the center, at the corners? If the problem occurs at a corner of plating rack, is it the corner that exits the various processing tanks first (i.e., the leading edge), or last (i.e., the trailing edge)? Problems that occur only on parts taken from the top or bottom of a rack, but which are not necessarily current density specific, usually are the result of insufficient or excessive time in one of the pretreatment steps. Another possibility when a problem is evident only on parts taken from the top of a rack is too low a solution level in one of the processing tanks. Problems that occur only on parts taken from the center of a rack are generally current density related, and usually result from a problem that stems from one of the electrified processing steps - an electrocleaner, an electrolytic activator, or one of the plating tanks.

Problems that occur on parts racked in the leading edge area of a plating fixture generally result from electrical faults in the entry area of the chrome plating tank. Similarly, defects evident on parts racked in the trailing edge area are usually due to electrical problems in the exit area of the nickel plating tank. Reversing the position of a rack after it exits the nickel tank, but before it enters the chrome tank will usually confirm these theories. If a leading edge fault remains in the same area on the rack after reversing the leading and trailing edges, it usually means the problem exists in the chrome tank. But if the location of the problem moves upon reversing the position of the rack, the nickel plating tank is usually the location of the source of the problem.

The above list of questions is, of course, not all-inclusive. However, it should be complete enough to illustrate the type of qualifying questions to ask in order to define the problem so the problem solving efforts of those involved can be properly channeled.

3. The easiest problem to solve is the one that occurs on every processed part, but this rarely happens. Generally, a problem is only evident on a portion of production parts. Thus, be systematic. Identify the first place in the total processing cycle where the fault can be seen, then work backwards from this point, examining each step of the cycle individually to pinpoint the prime location and cause of the trouble.

4. It is also helpful to define the type of problem that is occurring. Despite all the previously mentioned factors unique to nickel plating which complicate service efforts, there are only a limited number of defects that occur on a bright nickel plating line. The following list of problems covers over 95% of them.

   a. Pitting
   b. Roughness, micro or macro
   c. Stains, hazes, dullness, or streaked patterns
   d. Darkness of the plated deposit
   e. Poor adhesion
   f. Poor nickel or chrome coverage in low current density areas
   g. Brittleness and or burning of the plated finishes
   h. Reduced plating efficiency (both cathode and anode)

   Clearly, this is an important step in the total service effort. Indeed, a person has to know the real problem he or she faces before that individual can make any use of the published reference information that lists the various causes and remedies of many plating defects.

5. Write down the results of all tests and observations, including the results of modifications made to the total cycle that have no apparent effect on the problem. Also, label production parts to reflect the differences in processing cycles or steps that are screened, regardless of whether they have an noticeable effect on performance, or not. Remember, it is often just as valuable to know which steps have the least effect on total performance as it is to know which ones have the greatest effect. Also, keep in mind that changing just one or two steps in a long cycle seldom solves most service situations. Usually, several changes must be made before a problem can be accurately identified and the appropriate alterations made to the cycle to eliminate substandard work. This must be done in a step by step manner and the only way to keep track of each modification is to write everything down.

6. Select tests that will provide the maximum amount of information, while jeopardizing the fewest parts. This minimizes costs, and also simplifies data analysis since there are fewer parts to examine and interpret. For example, it is often helpful to switch the position of two racks to determine the effect of skipping a given step in the total cycle. In these cases, it is most efficient to couple the testing of the result of eliminating one step in the total cycle with the effect of doubling the time spent in another processing step. After identifying these two steps, switch the racks from these portions of the cycle.

   Generally, plating defects that are current density specific result from something that is out of specification in one of the processing steps in which current is applied to the parts. The easiest way to test determine if given step in the cycle is causing the current density related problem is to move parts around on the plating fixture while they are in this particular portion of the total cycle. In these cases, of course, it is not necessary to move entire racks. Simply transfer pieces from one

6. continued:

location on a rack to another location on the same rack, such as from a high current density area to a low current density area, or from the front of the rack to the back. If the location of the problem moves as the location of the piece on the rack changes, it is reasonable to assume something happening (or not happening) in one of the electrolytic steps ahead of this portion of the cycle is causing the defect. Likewise, if the problem does not move with the part, but remains in the same location, it is reasonable to assume the processing step in question is causing the difficulty, or at least contributing to it in a meaningfully.

Another useful test is to simply rotate a piece 180 degrees so that what was the top surface before a given step becomes the bottom surface. This is an especially helpful approach in instances where shelf roughness is a problem and the task is to determine the step in the total cycle that is creating or introducing it. In these cases, it is easy to test if a single step is responsible for the roughness by rotating a piece just while it is in the tank associated with the portion of the total cycle that is being evaluated. The part should be examined after it has completed enough of the total cycle to where the defect can be seen. Obviously, this same approach will test specific process steps for pitting tendencies.

Changing the location of a part on a rack, or its position, are not always the best ways to test whether a given step in the processing cycle is causing difficulties. In cases where hazes or cloud patterns are evident on parts after plating, the pretreatment portion of the cycle is often the source of trouble. The most effective way to screen the individual steps of the pretreatment cycle is to partially wipe an area on a part just before it enters the tank being studied. If the hazes or clouds cannot be seen where the part has been wiped, but are still evident in the adjacent areas, it is logical to assume that the pretreatment cycle is not removing a soil or smut whose presence on the parts is responsible for the haze or cloud.

Use a white paper towel or rag so it is easier to see when the hand wiping removes soil or smut. Likewise, begin the wiping process immediately ahead of the first plating tank after which the defect can be seen, and then systematically work backwards from this point to identify the step in the total cycle that is responsible for the residual film.

If wiping with a paper towel or rag has no effect on the haze or cloud, repeat this same process using a clean Scotchbrite pad. If this eliminates the problem, it is safe to assume the interfering film is quite tenacious and a more vigorous pretreatment cycle should be evaluated.

If wiping parts with a Scotchbrite pad does not remove the haze or cloud, it is more than likely that the problem is not a result of anything occurring in the pretreatment cycle. Instead, the plating and post plating portions of the line should be evaluated.

7. One of the most important guidelines to follow is to vary only one parameter at a time. Admittedly, this is often difficult to do in the face of extreme pressure to restore full production capability as rapidly as possible. Nevertheless, changing things one item at a time is the only way to truly solve a problem. Changing several things at once may eliminate the difficulty that is causing the rejects, but it does not provide any useful information to identify exactly which change had what effect on overall quality. This is another way of saying it does nothing that will lead to a permanent solution to the problem. Worse than that, it does nothing that will simplify solving this same problem the next time it occurs.

8. Be objective. Don't approach any service situation with the attitude of already knowing the cause of a particular problem before starting. It is important to make the most efficient use of prior service experiences, but not if it means losing objectivity. To permanently solve a problem, one must identify and treat the cause, not the symptom. This can only be done by maintaining an unbiased point of view.

9. Maintain at least limited production. Problem solving is impossible without processing parts, even when it involves generating a limited number of rejects. Furthermore, servicing is much easier when there is an uninterrupted flow of work processed through the line. Repeatedly filling and emptying a processing line may produce fewer rejected parts, but it also introduces many variables that complicate problem solving. This is especially true in cases due to electrical problems. The only way to properly investigate them is by testing when there is a rack at each station in the line. Operating with a series of open stations will produce entirely different results.

   Another approach to take to restore at least limited production is to go back to a process cycle that has worked in the past. If this cannot be done, experiment with different processing cycles, such as double cleaning or using longer plating times. The extent to which these changes can be carried out depends upon the physical limitations of the line involved. Another possibility is to operate with fewer parts on each plating fixture or workbar.

   Also, there are times when problems are only evident on certain size or configuration parts. In these cases, another possibility is to run as many parts that can be processed without problems as possible, but to also allow processing of a limited number of the parts that exhibit the defect. Otherwise, there is no way to measure progress. Of course, the long term goal is to resume normal production. In the short term, however, operating with an altered cycle that allows limited production is better than losing production entirely.

10. Test as many things off-line as possible. It is faster and less expensive to do this. Off-line testing should include as many steps in the total cycle as possible, including rinse tanks and even drying steps, if they appear to have any effect on the defect that is seen.

10. continued:

The most important consideration is to duplicate production conditions as closely as possible. In particular, match dwell times, hang times above the various processing tanks, and transfer times between tanks. It is also important to try to match the amount of agitation that occurs when processing pieces online.

Often, the easiest way to isolate a single processing step, while duplicating the remainder of the production cycle (including dwell times, transfer times, etc.) is to use a small processing tank, placed next to the production tank that is to be skipped in a given test. Simply remove one or more parts from a rack as it is about to enter the tank in question and put them in the small test tank instead, being careful to match processing times, etc.. As the rack exits the regular processing tank, remove the parts from the test tank and replace them in their original locations on the production fixture. Be sure to mark the location of each piece processed in this manner, and to record the number of the workbar or hanger to which the rack is fixed.

11. Be sure to only use tests that are meaningful and that duplicate the problem that is seen in full production. This will prevent wasting time and effort chasing ghosts. Ideally, when testing, use the regular processing cycle for everything but the individual cycle step under investigation.

If off-line testing does not duplicate the problem using normal test specimens (e.g., Hull cell panels), try running production parts in a small tank. If parts are too large to allow this, try running small sections of production parts, using racking geometry that approximates production conditions. If the problem can be seen at this point, logic suggests the problem cannot be due to any of the processing steps that follow the one under study. Also, since the fault was not apparent on another base metal (i.e., Hull cell stock), a parameter may be of range which only has an effect on certain base metals. An example would be too high a cleaner concentration. It is unlikely this would have a measurable effect on steel base metal parts, but it could have a significant effect when processing brass parts through the same cleaner.

If, on the other hand, off-line testing still cannot duplicate the defect, stop testing in the small scale, off-line tank, and try running known quality base metal parts on the production line in place of regular parts. Hull cell panels are almost always accessible and offer the additional advantage that they allow for the complete elimination of the cleaning cycle. The thin zinc coating on the panels can easily be removed in a small volume of freshly made up acid. Wiping parts with a clean, wet sponge or towel will remove any smut on the surface and provide a part that can be inserted into the production line immediately ahead any of the plating tanks.

11. continued:

    If this is done, and the problem can be seen on Hull cell stock, it is safe to assume the plating tank under study is the source of the difficulty. Similarly, if no problem is evident, it is equally safe to assume that the problem is not coming from the plating tank under study.

12. Remember not all the parameters that can be measured on a processing line have an equal impact on quality. In a nickel plating solution, for example, the parameters that have the greatest effect on performance are those that can change the quickest: pH; temperature; agitation patterns; concentration of the secondary brightener portion of the addition agent system; current to the cathode; entry and exit currents on nickel and chrome plating tanks; etc.. Accordingly, these are the factors to examine first when faced with a trouble shooting situation. Only after examining these aspects is there reason to check the other operating parameters.

    It is also important to keep in mind the degree of change each of these parameters can undergo before it will have a significant impact on performance. For example, a 10% change in pH or temperature will have a much more dramatic effect on quality than will a 10% change in boric acid concentration.

No discussion of trouble shooting concepts would be complete without stressing the importance of preventative maintenance. Is has been proven over and over again that production difficulties and high operating costs are inversely proportional to the degree of control and preventative maintenance that is exercised. In other words, the more time and effort a finisher puts forth catching and solving problems while they are minor, the less difficulty that finisher will have maintaining high quality and an efficient operation. Here are a few simple things that can be done to prevent problems before they happen.

1. Record all additions to every tank in the processing cycle. This should include dates of when tanks are dumped and made up fresh, as well as when the plating tanks are treated to remove various impurities. Having this information is extremely beneficial. It streamlines trouble shooting and also provides very useful cost analysis information, even when there are no problems.

2. Maintain good housekeeping throughout the plant, but especially in the area near the processing line(s). This will minimize the possibility of foreign matter accidentally entering any of the tanks.

3. Keep a reference file of panels and parts that illustrate certain problems and their solutions. Not only are these an invaluable aid during the trouble shooting process itself, they are also very helpful as a training device for new employees.

4. Develop an in-house library of technical articles and trouble shooting reference information. Examples would be V. Guernsey's article, "Those Elusive Little Amperes," published in the February and March, 1976, issues of Plating and Surface Finishing, and Lou Gianelos' article, "Trouble Shooting of Nickel Plating Solutions," published in the August, September, and October, 1977, issues of Plating and Surface Finishing. Both are classic references that can should be kept near at hand since they contain so much valuable information.

5. Routinely check different aspects of the processing line. Most finishers agree that incorporating the following schedule into their plant practices is very beneficial.

Control Item	Frequency of Control
Plating solutions	
Bath analysis	Weekly
Plating tests	Weekly (More often under heavy production situations) (Send to supplier for addition agent analysis and double check of solution analysis monthly)
Pretreatment solutions	Twice weekly
Solution levels	Each shift
Temperature controllers	Each shift
Amp Meters/Volt Meters	Each shift
Addition agent feeders	Each shift
Anode baskets	Twice weekly
pH of nickel solution	Each shift
Flow of solution thru filter	Each shift
Uniformity of agitation	Each shift

In summary, servicing and trouble shooting bright nickel plating installations need not be overly complicated. The single most important consideration is establishing and following a logical procedure in analyzing the total circumstances. Think of it as drawing up a road map that creates a series of forks in the road. At each fork one or more questions should be asked. The answers to the questions dictate which of the two paths to follow. This process can be continued until all the sources of difficulty are identified and all the necessary corrective steps are taken to restore high quality, error-free plating.

B-4

Nickel Plating—Basics and Applications
Session B

Decorative Nickel Chromium Plating On Stainless Steel

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DECORATIVE NICKEL CHROMIUM PLATING ON STAINLESS STEEL

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Introduction

Buffed, chromium flashed stainless steel represents an important segment of the automotive metal finishing market for bright decorative trim applications. The annual usage of stainless steel in automobiles currently exceeds 183,000 tons, most of which is used for decorative trim.[1] While much of the stainless steel trim is untreated, an ample portion of it is chrome flashed to improve corrosion protection and impart its highly desirable blue-white chromium appearance. However, even though stainless steel trim provides outstanding protection and durability, there are drawbacks. For instance, processing expenses can be excessive; the cost of polishing and buffing can, in some cases, exceed the value of the raw piece. Complex parts are very difficult to buff. Parts require special handling and packaging since bright annealing softens stainless steel so that even chrome flashed parts readily scuff and scratch. The finish, as is, or chromium plated, does not match nickel-chromium deposits; it is transparent, and lacks depth of appearance. This is readily apparent when said parts are placed side by side.

Electropolishing of stainless steel automotive trim is now a commercially viable alternative to mechanical finishing prior to chrome flashing.[2] Buffing requirements can be reduced, or even eliminated in some cases, and reflectivity improved. However, electropolishing does not resolve the handling problems nor can it provide an aesthetically perfect match with nickel chromium plated surfaces. Complex shaped parts are difficult to consistently process in large volume applications. Cost can be prohibitive, especially in cases where mechanical polishing and buffing cannot be eliminated or substantially reduced.

An Improved Process

There is a novel way of overcoming all of the above problems - by plating stainless steel with decorative nickel and chromium. Processing is quite simple and with the drastic reduction of mechanical polishing and buffing cost of application is minimized. Thickness requirements are low, compared to those typically required for severe environmental exposure (ASTM Service Condition 4). The substiantially harder nickel-chromium deposit produces a highly scuff and scratch resistant surface, and, of course, perfectly matches adjacent decorative nickel chromium plated surfaces. As will be discussed in detail later, adhesion and corrosion resistance are outstanding. Yet, in spite of all these positive features, perhaps the biggest attribute is specular appearance. Decorative bright nickel hides the surface defects of stainless steel very well and

brilliant, mirror like finishes can be obtained with thicknesses of less than 25 μm (1.0 mil). (See Fig. 1).

Process Cycle

Various cylces are used to prepare stainless steel for a flash of chromium. A typical cleaning cycle for 300 or 400 series stainless steel is described below.[3]

Alkaline Soak

Anodic Electroclean

25-50% Sulfuric Acid Immersion

Chromium Electrodeposit

Depending on the specific application, a dilute cathodic acid can replace the acid immersion and the electrocleaner can be made cathodic.[4] Seyb recommends an acidic rinse comprising 2 to 4 oz/gal of chromium plating solution to prevent surface staining.[5] The acid can even be completely eliminated and the workpiece activated in the chromium bath by making it anodic prior to chromium electrodeposition.[6]

Satisfactory appearance and nominal adhesion of decorative nickel-chromium platings can be achieved with most of the above cycles for some applications. However, to meet the strict adhesion and corrosion requirements demanded by the automotive industry, specialized cleaning and activation cycles are necessary. While both cathodic or anodic acid activation provides reasonably good results, a proprietary anodic activation cycle is the preferred choice since it maximizes adhesion, and provides electrodeposits that will consistently pass the bend, grind-saw and heat-quench tests described by the ASTM.[7]

The fact that the anodic treatment improves adhesion is somewhat of a surprise. One might expect that it would significantly alter the composition and/or oxidize the surface of the workpiece adversely affecting adhesion. However, Energy Dispersive Spectrum analysis indicates that anodic acid activation causes very little compositional change on the stainless steel surface. (See Table 1).

The use of cathodic sulfuric acid activation produced similar results, however, both cathodic activation and immersion produced bonding that was inferior to anodic activation.

Scanning electron microscopy indicates that anodic activation alters the surface morphology of the stainless steel. A comparison of bright annealed 434 SS coupons treated in several ways reveals that anodic activation induces relatively high surface porosity. This is especially true when the proprietary acid is used. (See Fig. 2). Consequently, the improvement in bond may be at least partly due to improved mechanical

anchoring.

The process cycle that produces the most consistent results with respect to appearance, adhesion and corrosion protection is described in Table 2.

As one can see, the cycle is quite simple and can easily be adapted to existing nickel-chromium plating lines. Semi-bright nickel can be incorporated into the cycle, however, preliminary tests indicate that the use of duplex nickel does not offer any additional corrosion protection compared to single layered bright nickel when the substrate is stainless steel.

Corrosion Tests/Results

The use of cathodic acid activation produced corrosion protection that was inferior to that achieved with an anodic treatment. Figures 3 & 4 compare the effect of cathodic and anodic activation on the corrosion properties of various types of stainless steel plated with nickel-chromium. The results make it clear that, regardless of the type of stainless steel tested, anodic activation provides improved corrosion protection.

Panels plated without microdiscontinuous chromium exhibited large surface pits after CASS exposure. Figures 5 & 6 indicate that the use of microdiscontinuous chromium not only elminates the problem of large surface pitting, but also improves the overall corrosion properties in CASS.

Numerous other corrosion tests were made to compare the corrosion properties of conventional and high sulfur nickel. In this case the sulfur content of the conventional bright nickel ranged from 0.04% to 0.06% by weight. The sulfur content of the high sulfur nickel deposit was 0.08% to 0.11% by weight. After one cycle of CASS the higher sulfur nickel appeared to provide better corrosion protection. However, after 2 or 3 cycles, extensive blistering was observed in those panels that did not have microdiscontinuous chromium. These blisters were so small that they were originally mistaken for very fine surface pitting. Microscopic examination (see figure 7) shows that the blister is more a function of corrosion rather than poor adhesion. The photos show that the sacrificial corrosion of the very active nickel deposit to the very noble stainless steel causes undercutting that results in blisters. As corrosion progresses, the nickel flakes off leaving a uniform corrosion crater. The crater grows as corrosion progresses. Notice in Fig. 8 that there is virtually no penetration into the basis metal.

Another phenomenon that was observed in CASS is the ability of stainless steel to "heal" a corrosion site. For example, if test panels exhibit serious corrosion failure after one cycle of CASS exposure, further corrosion at those particular sites can be curtailed. This is accomplished by removing the rust stains at the given sites, and delaying placement of the parts in the CASS cabinet for a few days. Unlike plated carbon steel, rust stains from plated stainless steel can be easily

removed with a magnesium oxide slurry. While new corrosion sites may appear during the second CASS cycle, rust stains rarely recur at the original failure sites. A possible explanation is that, once cleaned, the sites had time to become passive before their subsequent exposure to the very aggressive CASS solution. This is further attested to by the fact that the longer the delay before the next CASS cycle, the less likely the recurrence of rust stain.

This hypothesis is also supported by examining the effect of stress fractured nickel-chromium topcoats on corrosion. Nickel chromium plated 430 stainless steel and carbon steel panels were bent 120°F which caused severe fracturing of the platings. The bent panels were then exposed to one cycle of the CASS two days after they were bent. Results revealed severe base metal failure on the carbon steel control panels, as expected, and only very mild surface staining on the stainless steel panels. Duplicate stainless steel panels that were immediately placed in the CASS test cabinet showed base metal corrosion. It appears that, once exposed to the atmosphere for even a relatively short period of time, the stainless steel underlayer becomes passive enough to prevent rusting.

Static Exposure

A group of test panels were plated for industrial static exposure tests. A description of these panels is given in Table 3. A pair of panels from each set, A through H, were mounted on porcelain fixtures, and exposed to a moderately aggressive industrial environment, in Warren, Michigan. Replicate panels were exposed at Chrysler Motor Company's test site in Highland Park, Michigan. These panels were placed in their "spritz zone", an area where they were sprayed weekly with a 5% neutral salt solution. Consequently, this could be classified as a semi-accelerated test, although Chrysler engineers have found it to be only moderately more aggressive than conventional static exposure. Initial placement was made in November, 1985 at the Warren site, and January, 1986 at the Chrysler site. All panels were removed in late spring, carefully examined and then returned to their respective sites in mid fall.

As of October, 1988, none of the panels have any serious corrosion failure. Set F-1 (low carbon steel substrate) is beginning to show some very mild base metal failure at both sites, the most serious at the Chrysler facility. Here the ASTM ratings average 9/8; at the Warren site, the average is $9/9.^{8}$ All the plated stainless steel panels have a base metal protection rating of 10. Some appearance ratings at the Chrysler facility are as low as 8 due to surface pitting and mild nickel staining. These panels had no microdiscontinuous chromium and incorporated the use of a high sulfur bright nickel.

As was observed in accelerated tests, thin, high sulfur nickel deposits, without microdiscontinuous chromium (Set G-1) exhibited uniform blistering as well as some poor adhesion at the rack contacts. This condition was far more pronounced at the Chrysler test site and, as observed on the CASS test coupons, the blisters are relatively very small, typically less than

50 μm. No blisters are evident on Set H-1 where microporous chromium was used. The cause of the poor adhesion around the rack contacts has not been absolutely determined. However, the fact that they have only been observed on panels from Set G indicate that the very active high sulfur nickel may be a contributing factor.

Commercial Experience

The nickel-chromium plating of stainless steel is being commercially practiced in several shops. All are hoist lines that also plate other substrates. Since the process is new, adhesion is scrupulously examined; in many cases, parts from every rack are checked. Tests typically include the saw-grind and heat-quench methods. The heat-quench test is the more desirable since it is generally non destructive and also more severe. Although some adhesion problems have been experienced, none have been process related. Rather, as can be the case with any type of plating, the culprits were improper processing sequences and equipment failures.

Presently, the vast majority of the work processed is decorative automotive trim. However, marine hardware and hospital supplies are other applications that are gaining acceptance. I conservatively estimate that about 3,000,000 ft^2 of nickel-chromium plated stainless steel will be processed in 1989.

Conclusions

The above data demonstrates that the decorative application of nickel and chromium on stainless steel is not only a viable and practical alternative to the current finishing methods, but also provides a more desirable finish. The finish not only perfectly matches other nickel-chromium plated substrates, such as steel, zinc diecasting or brass, but it also provides comparable adhesion characteristics.

The substrate corrosion properties of either the 300 or 400 series stainless steel do not seem to be appreciably altered by the platings. This is supported by both CASS and static exposure tests. Though incomplete, the static exposure test results are the more significant. Penetration through 25 μm (1.0 mil) of single layered bright nickel can occur in one month at the Warren test site.[9] Consequently, even though significant penetration has taken place, base metal degradation has been absent. Contrary to CASS test results, this is also the case with 434 stainless steel. In fact, at this juncture, there appears to be no significant difference in the corrosion properties of nickel-chromium plated 300 and 400 series stainless steel in static exposure tests.

This observation has recently been confirmed in tests carried out by General Motors at their test track in Milford, Michigan. A detailed description of the results cannot be given at this time since it is still confidential. However, these test results have led General Motors to modify its specification for nickel-chromium plated stainless steel (GM4255M) to include grade 434.

It is apparent that we can now meet the automotive styling demands for the long term durability of stainless steel and the value added aesthetic qualities of decorative nickel-chromium. In addition, these highly desirable qualitites can be achieved with simple and cost effective processing techniques. All of which leaves me to believe that this new finish will soon be the primary choice for automotive bumpers and trim as well as other exterior applications.

Acknowledgments

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TABLE 1

EDS ANALYSIS OF 304 STAINLESS STEEL SURFACES

Element & Line	10% H_2SO_4 (Immersion)		10% H_2SO_4 (Anodic)	
	Wgt %	Atomic %	Wgt %	Atomic %
Cr KA	19.51	20.74	19.28	20.50
Fe KA	71.58	70.87	72.03	71.31
Ni KA	8.91	8.39	8.89	8.19

TABLE 2

PREFERRED PROCESS CYCLE FOR
NICKEL-CHROMIUM PLATING STAINLESS STEEL

SOAK CLEAN	1 - 2 min.
CWR	
ALKALINE ELECTROCLEAN/ACTIVATION	1 - 2 min. @ 4V
CWR	
ACID ACTIVATION	1 - 2 min. @ 25 ASF
CWR	
WOODS NICKEL STRIKE	2 min. @ 20 ASF
BRIGHT NICKEL	Variable thickness
MICROPOROUS NICKEL STRIKE	1 - 2 min. @ 45 ASF
CHROMIUM (HEXAVALENT)	0.25 μm

Table 3

CHRYSLER/OMI STATIC EXPOSURE TEST PANELS

SET #	SS TYPE	BR Ni (mils)	M.P. Ni (mils)	Cr (mils)
A-1	301	0.07	-	0.01
A-2	301	0.65	0.05	0.01
A-3*	301	0.70	-	0.01
A-4*	301	0.65	0.05	0.01
B-1	434	0.70	-	0.01
B-2	434	0.65	-	0.01
B-3*	434	0.70	-	0.01
B-4*	434	0.65	0.05	0.01
C-1*	304	0.70	-	0.01
D-1*	201	0.70	-	0.01
E-1	201	0.70	-	0.01
F-1**				
G-1	304	0.35	-	0.01
H-1	304	0.30	0.05	0.01

* High sulfur bright nickel with sulfur content ranging from 0.08 - 0.11%.

** Low carbon steel - 1.0 mils semi-bright nickel, 0.5 mils bright nickel, microporous nickel strike, 0.01 mils. chromium.

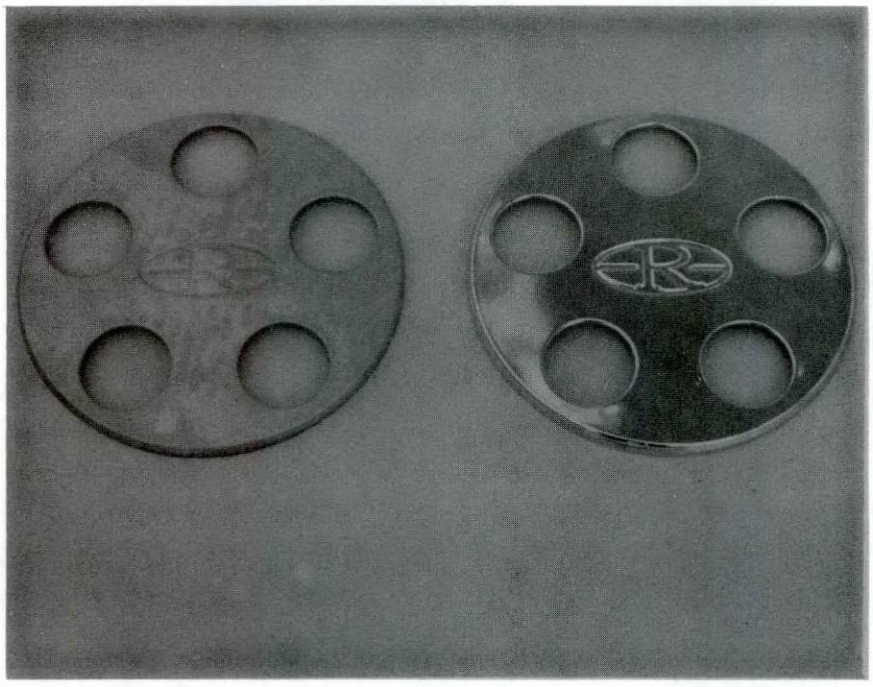
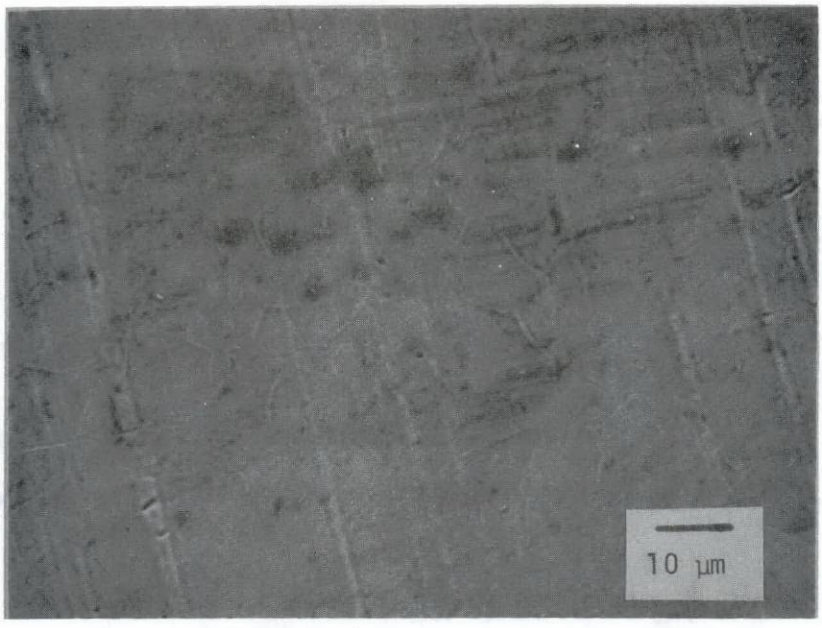


Figure 1 - 30 stainless steel wheel cover assembly before and after nickel-chromium deposition. No metal finishing was employed prior to plating. Average nickel thickness is 20 µm (0.8 mils).



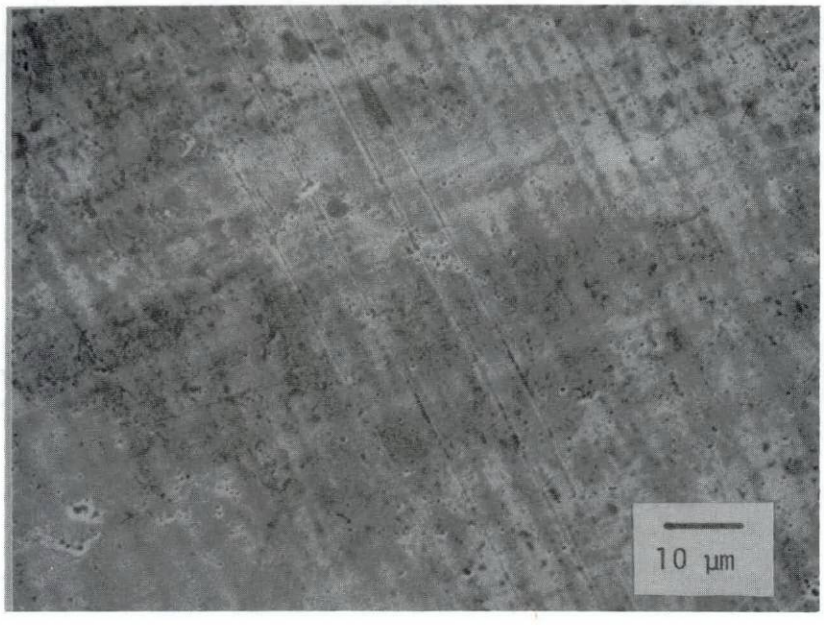


Figure 2 - SEM photograph of 434 stainless steel coupons treated with cathodic acid activation (TOP) and anodic acid activation (BOTTOM). Microporosity caused by anodic acid activation may account for improved adhesion of subsequent nickel deposit.

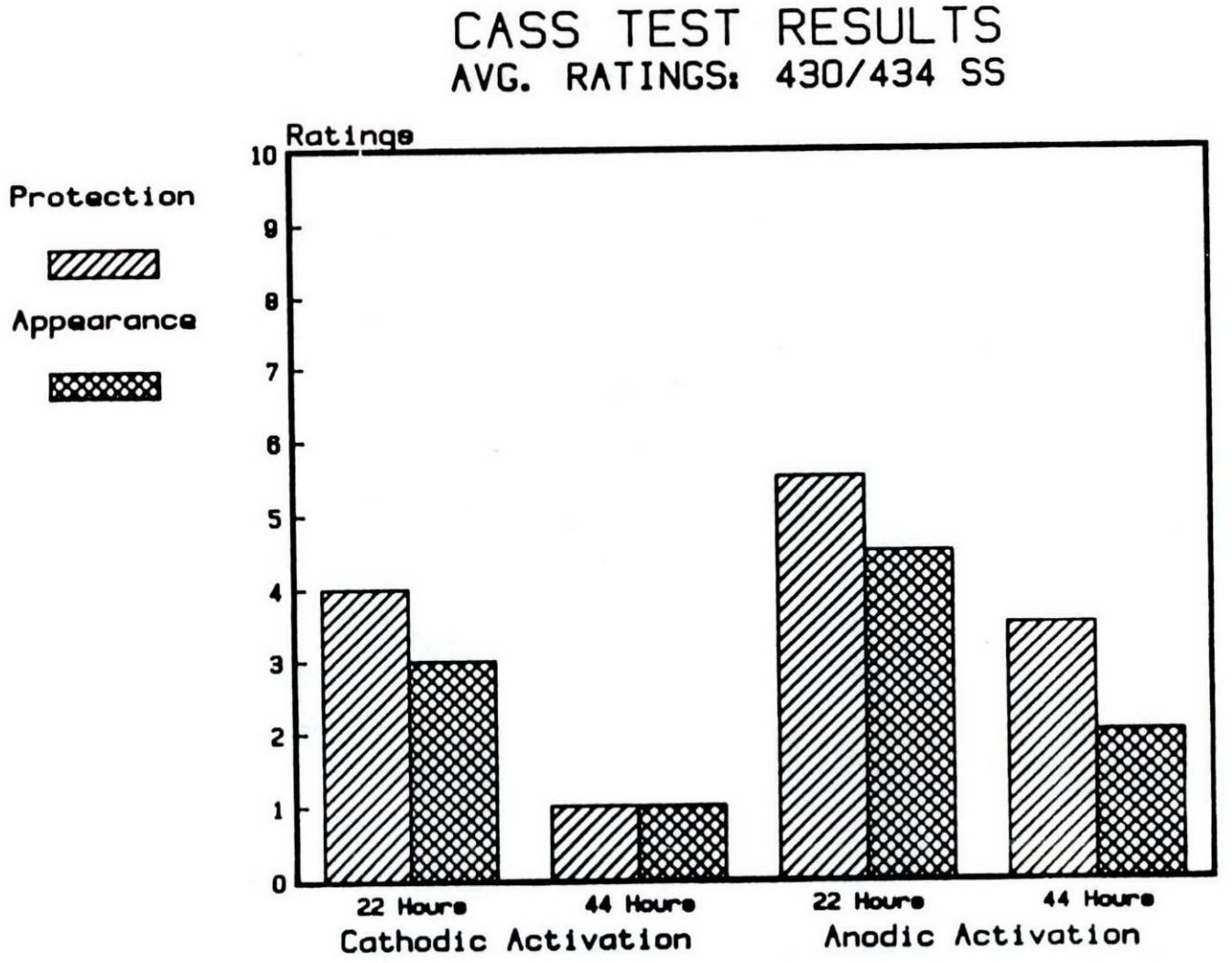


Figure 3 - Average protection and appearance ratings (ASTM Standard B 537) of stainless steel coupons plated with an average thickness of 17.5 µm (0.7 mil) bright nickel and 0.25 µm (0.01 mil) conventional chromium. Results demonstrate advantage of anodic activation.

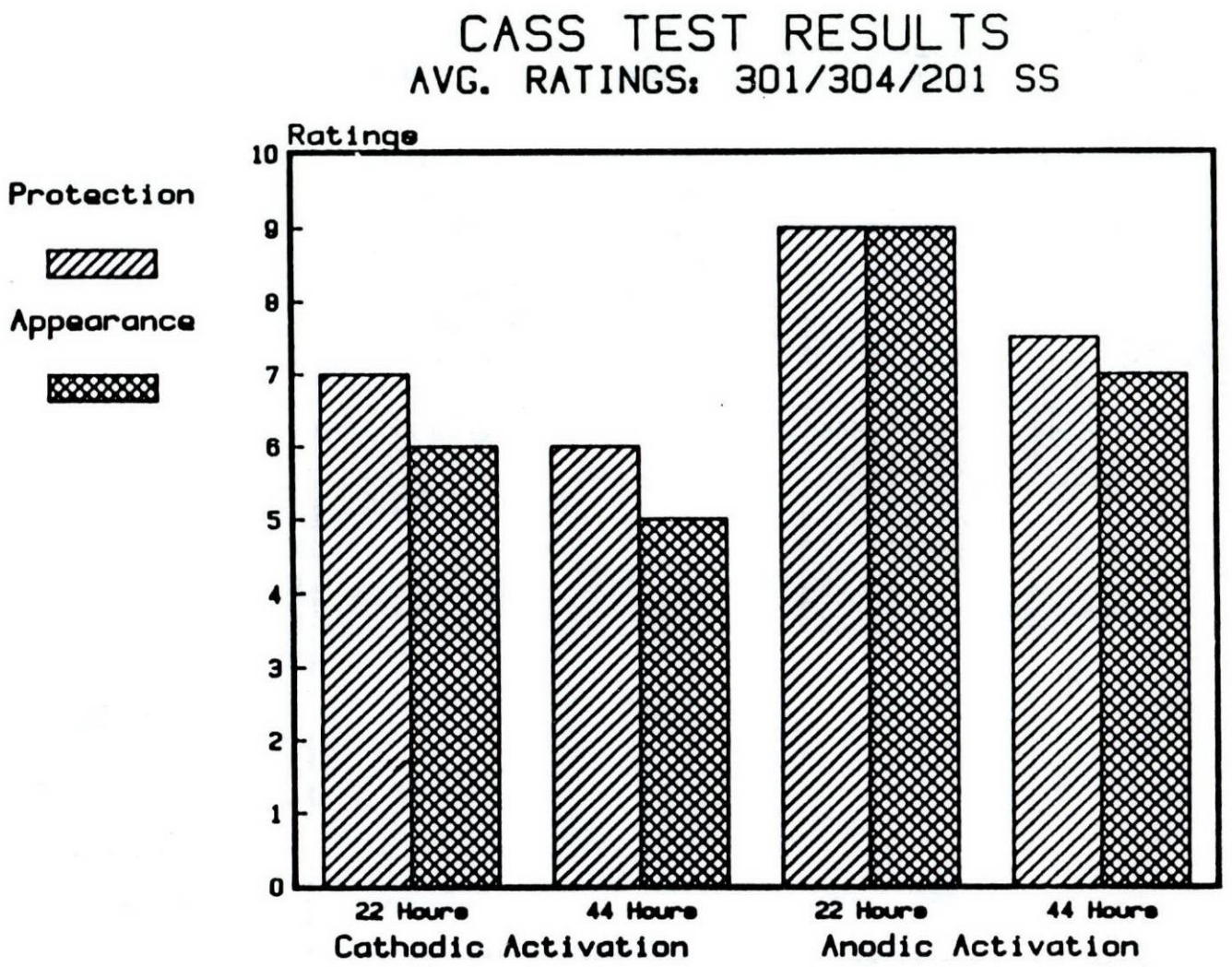


Figure 4 - Average protection and appearance ratings of stainless steel coupons plated with an average thickness of 17.5 µm (0.7 mil) bright nickel and 0.25 µm (0.1 mil) conventional chromium. Results demonstrate advantage of anodic activation.

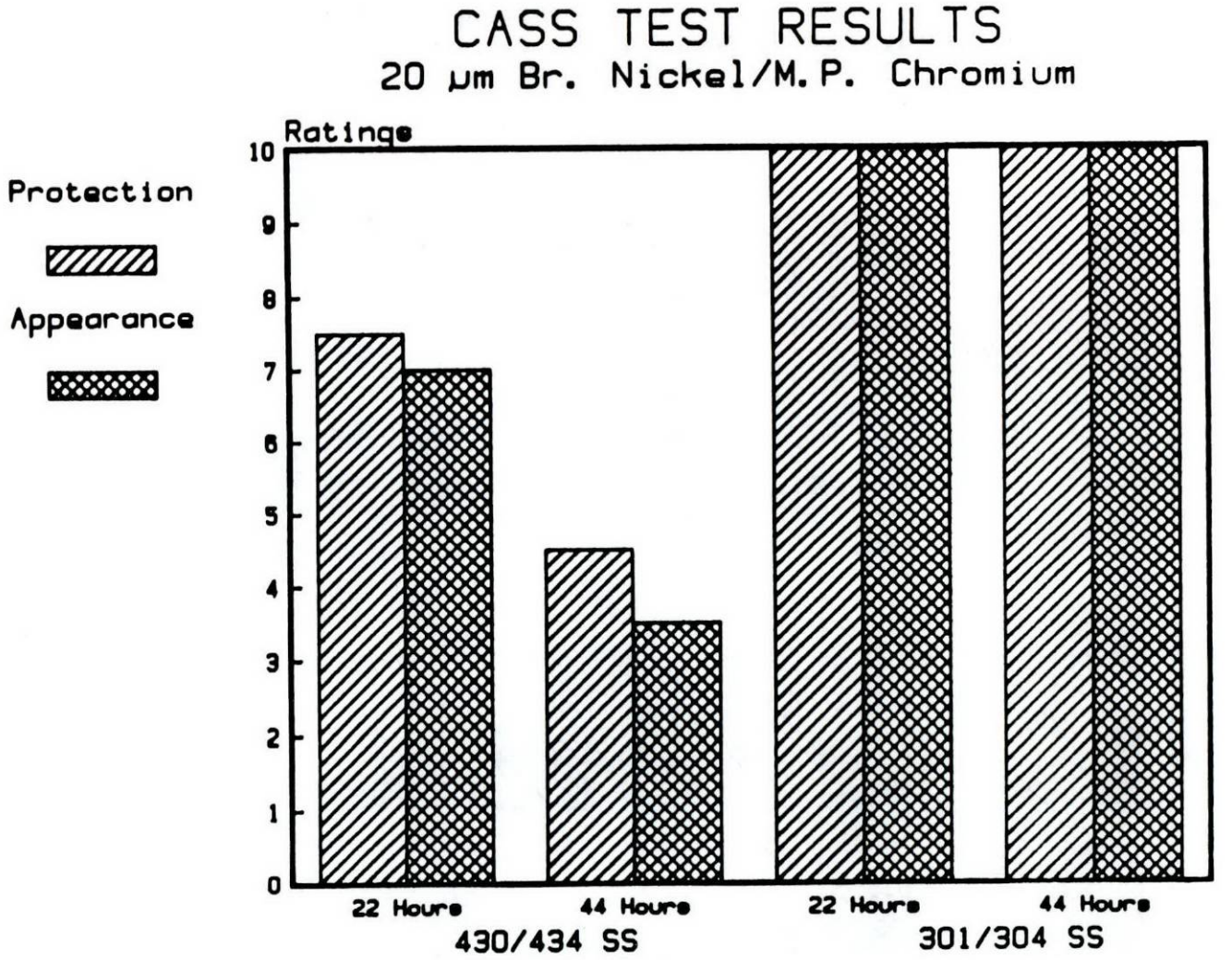


Figure 5 - Average protection and appearance ratings of various grades of stainless steel coupons demonstrate superior corrosion protection of 300 series stainless steel.

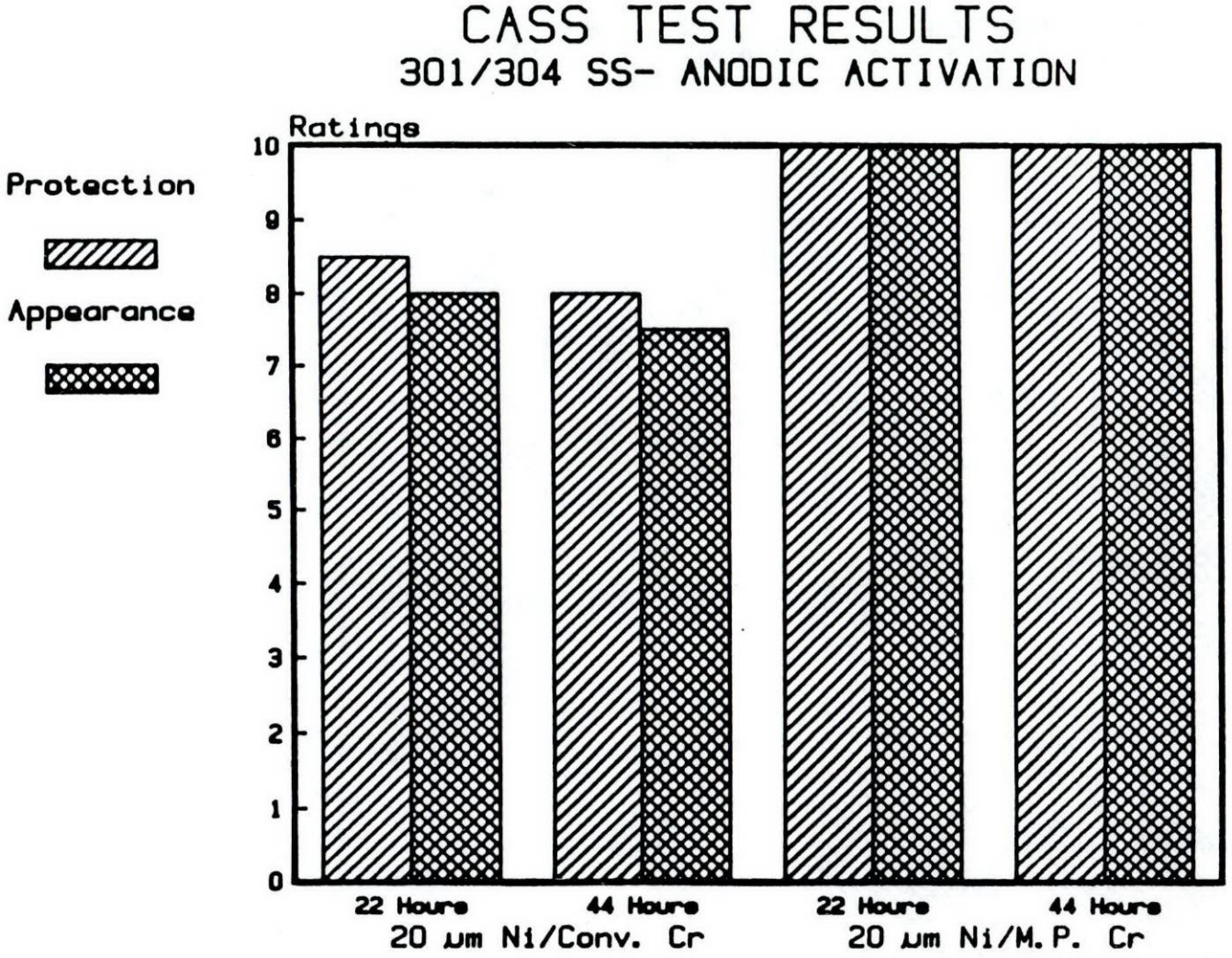
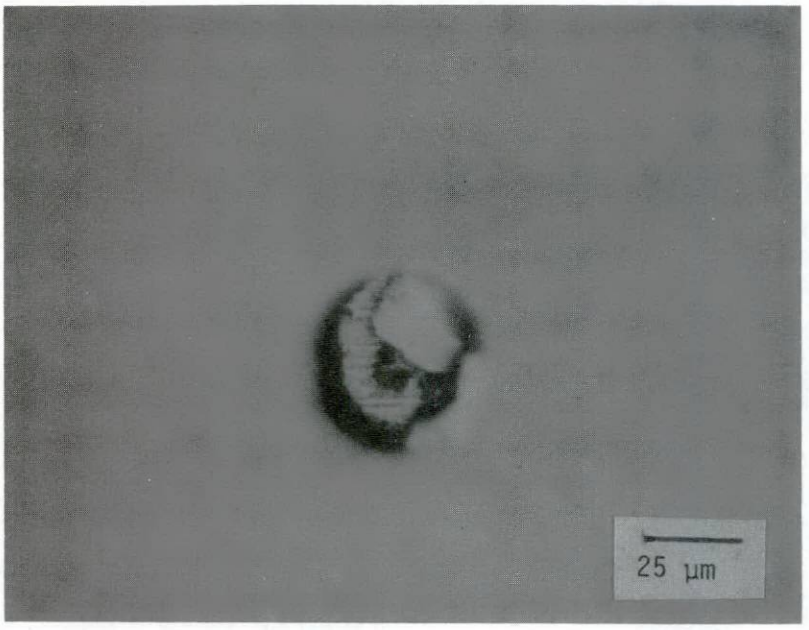


Figure 6 - Average protection and appearance ratings of 301/304 stainless steel coupons show the advantage of microporous chromium.



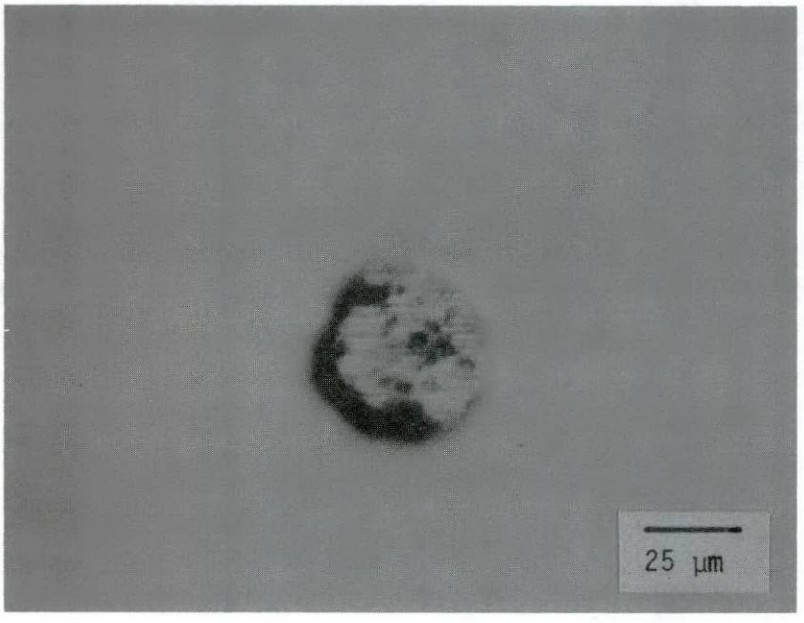


Figure 7 - Progression of corrosion blister in high sulfur nickel coating plated on 304 stainless steel, after 44 hours (TOP) and 66 hours (BOTTOM) CASS.

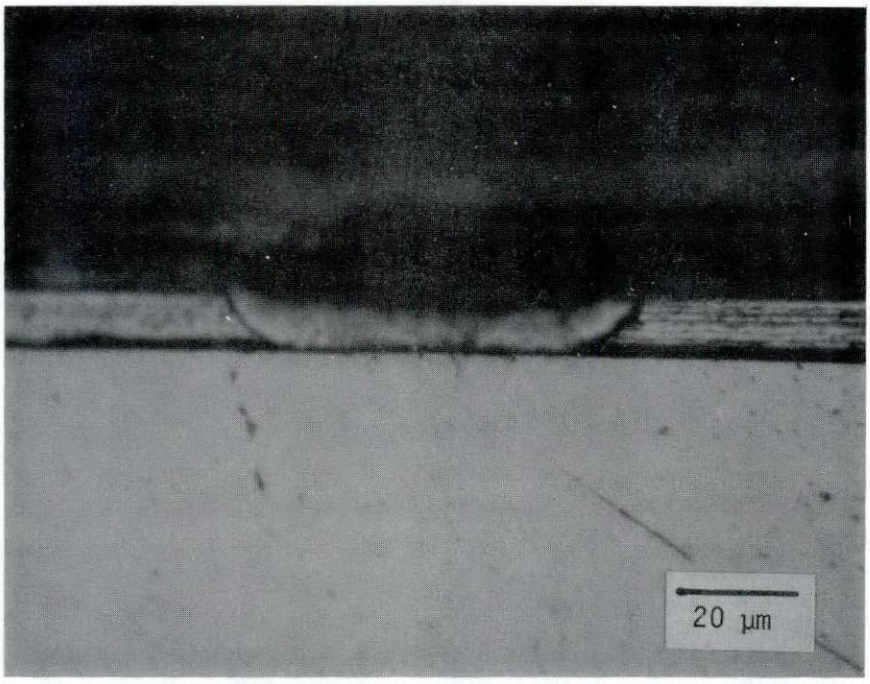


Figure 8 - Cross section of corrosion site of nickel-chromium plated stainless steel coupon shows no base metal attack after 66 hrs. CASS.

B-5

Nickel Plating—Basics and Applications
Session B

Successful Applications of Functional Nickel Plating

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SUCCESSFUL APPLICATIONS OF FUNCTIONAL NICKEL PLATING

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Introduction

Although there has been a very significant reduction in the amount of nickel plating in some traditionally large market areas, the industry has nevertheless experienced considerable strength in the last few years. Consumption of nickel in automotive applications, for instance, has declined seriously in this decade and only North America has provided any real resistance to the world-wide trend to less bright trim. Yet, nickel anode consumption was particularly high in 1987 and 1988 and, consequently, it must be assumed that expansion has occurred in other areas. This is certainly true in electroforming and functional plating, in applications were advantage can be taken of the wide range of properties attainable in electrodeposited nickel. In both areas, this decade has seen some very successful applications. The increased use in functional or engineering applications can be attributed in part, to a greater awareness of the capabilities and versatility of electrodeposited nickel, supported by the very high quality standards now being maintained by most platers. The extent to which stricter process control and improved technical expertise has contributed cannot be underestimated and the promotion of successful applications in providing protection against corrosion, high temperature oxidation, erosion and wear can only enhance the image of the industry. This paper will describe three

examples of functional nickel plating, which are impressive in scale, cost effectiveness and overall performance.

A. Copper Coolers For High Temperature Furnaces

In this application, the high temperature oxidation resistance of electroplated nickel is combined with the excellent thermal conductivity of copper in greatly improving the efficiency of electric furnace operation. The application can be explained by reference to the nickel plating of copper coolers that has resulted in a drastic reduction of refractory erosion in the electric furnaces used in the production of ferronickel by Falconbridge Ltd. in the Dominican Republic.

A serious problem associated with the operation of high temperature furnaces is the erosion of the refractory lining and this can be explained by reference to Figure 1. It shows a partial transverse view through an electric smelting furnace, in which the required heat is introduced as electrical energy through a central electrode. During smelting, charge material is melted and two molten layers are formed - a lower metal or matte layer and a less dense slag layer which receives the energy from the electrode. This molten slag layer contains chemical species which are strongly oxidizing and react readily with the refractory lining, causing the very serious erosion shown in Figure 1. There are several mechanisms by which the erosion can occur, all of which become more serious with an increase in temperature at the refractory surface. Eventually, the erosion reaches a stage which requires the furnace to be shut down for refractory repair or re-lining. It has been shown over a period of several years that the refractory can be protected by placing solid copper coolers through the wall of the furnace and into the lining, so that a short length, which is water cooled, remains outside the furnace, as shown in Figure 2. This design avoids the danger of water entering the furnace. By selecting the size and location of the coolers, sufficient heat can be conducted away to greatly reduce damage to the refractory lining and in some furnaces, up to four hundred coolers may be embedded in the side wall. The success depends to a large extent on the cooling being sufficient to freeze slag in the areas of the coolers, thereby isolating the refractory, as shown in Figure 2.

Copper suffers from having poor high temperature oxidation resistance and, due to the very high oxygen potential in the slag, severe oxidation occurs continuously. This results in a significant change in shape, reduced surface area and loss of cooling capacity. The problem has been resolved by nickel plating.

A typical cooler is made from special high conductivity copper and weighs about 70 kg. Dimensions would typically be 60 cm long and 12 cm diameter, but these can vary, depending on the amount of heat to be conducted away and the acceptable lining temperature. All exterior surfaces are rough machined or as-rolled and the entire length of the coolers to be located inside the furnace must be nickel plated to extend their useful life. A minimum nickel thickness of 250 microns has been specified to provide oxidation resistance and to prevent excessive buildup of nickel around the circumference at the bottom edge, the coolers are roughly chamferred to a radius of about 3 mm.

Excellent bonding of the nickel is required for this high temperature operation and porosity in the nickel that might allow oxidation of the underlying copper is unacceptable. The surface condition of the coolers can be variable but generally they are quite heavily soiled. Two methods of precleaning have proved successful, the first being a cathodic treatment in a solution of 15 g/l sodium carbonate and 4 g/l sodium cyanide and the second a soak clean in a low sodium hydroxide content, proprietary cleaner, which could also be used electrolytically for heavily soiled surfaces. Some inconsistent bonding was obtained after pickling in 10 percent sulphuric acid, but greater reliability was achieved by ensuring the removal of some metal from the surface and, consequently, 3 to 5 percent hydrogen peroxide added to the acid has been beneficial.

After rinsing, the parts were plated in a Watts-type electrolyte at a current density of 3 to 4 A/dm^2. No special fixtures were used to control current distribution, but a series of tests were made initially to ensure minimum thickness was being obtained on the base of the cooler when suspended vertically in the bath. This could be adequately controlled by adjusting the depth of the anode baskets in the tank and once the optimum position was established, thickness requirements could be met consistently. Several plated coolers are shown in Figure 3.

The success of the application of functional nickel plating has been dramatic. Although oxidation of the nickel has occurred in the furnace, the oxide has been protective to the underlying nickel, which has remained intact and prevented damage to the copper. During evaluation of the effectiveness of nickel plating, direct comparison of the plated and unplated coolers was made and the results can be seen in Figure 4. The unplated cooler on the left is shown to have changed shape significantly through oxidation and would continue to do so, but the plated coolers are unchanged except for some surface discolouration. This means that a furnace shutdown to change coolers that have greatly reduced cooling capacity, is no longer necessary if they are nickel plated, and after several years of experience with them, they can only be described as having 'indefinite' life.

B. Marine Engineering Application

One of the largest and most challenging applications for functional nickel plating in this decade was completed in France for The Dutch Water Authority. It was impressive in both the scale and quality control required. The project was an outstanding example of marine engineering, which was designed to protect the Dutch coastline at the mouth of the Ooster Schelde, an area shown in Figure 5, where devastating floods had previously occurred. An indication of the scale of the project can be realized by reference to Figure 6, which shows part of the unique storm surge barrier, with movable sluice gates operated by enormous piston rods. The three kilometer long barrier contains 63 hydraulically operated gates, each 42 m long and weighing 300 to 500 MT. Two hydraulic cylinders, with steel piston rods as large as 18 m long, 500 mm in diameter and weighing 32 MT operate each gate. To ensure reliable operation of these piston rods in the aggressive sea water and salt spray environment, nickel plate was chosen to provide corrosion resistance for the steel and the base for the hard chromium deposit.

The decision to use nickel/chromium plated, low alloy steel for this application instead of stainless steel was based on superior wear resistance, machinability, and mechanical properties, while still providing excellent corrosion resistance in the severe marine environment. A high quality steel was used, which was particularly well suited for plating because of its low inclusion levels. Surface inclusions can have an

adverse affect on corrosion resistance. It was realized at an early stage that if chromium were used alone, cracking in the deposits, either as deposited or induced under stress conditions, would result in premature corrosion of the steel in this application and, consequently, a series of qualification tests were made. Following a thorough examination of deposit properties such as hardness, ductility, microstructure and corrosion resistance, thickness requirements of 120 microns nickel and 70 microns chromium were specified. The significance of the nickel was clearly evident from ISO 4540 salt spray corrosion tests, in which the nickel/chromium combination withstood a minimum of 1200 hours, compared to only 10 to 40 hours for chromium alone at a rating of 10, i.e., no corrosion pits. Uniform microstructure and hardness were required through the thickness of the deposit and a target of 200 VHN was established. After successfully completing preliminary trials and qualification tests, production of the piston rods began.

The success of the project was dependent on the strictest quality control from start to finish and the records maintained on the production of each piston rod were complete in all details. Prior to plating, the steel was ground and polished to diameter and surface specifications. A grinding machine was used with a capability of handling 18 m long cylinders with diameters up to 900 mm.

All processing, except the final chromium plating stage, was in the horizontal position. To ensure good current distribution during the electrolytic steps, the parts were rotated and current was introduced at each end. Standard cleaning and pickling procedures were used with a very high level of control and constant monitoring of all process parameters. The piston rods were vapour degreased, electrolytically cleaned in proprietary alkaline cleaner and pickled in hydrochloric acid. Fresh water was maintained for rinsing and particular care was taken to prevent rusting of the very active surfaces during transfer to the plating tank. A typical piston rod is shown over the nickel tank in Figure 7.

A Watts-Type electrolyte, with no additives other than wetting agents, was used for nickel plating and operating conditions were constantly monitored. Current density was 4 A/dm^2 and deposition time was 2.5 hours. Total current ranged from 1500 to 2500 amperes, depending on the size of each piston rod. Nothing was spared in guaranteeing the condition of the

electrolyte. It was continually carbon-treated and filtered and test samples were plated before and after every part was processed to confirm deposit quality. In addition, samples at both ends of each piston rod were prepared during the actual plating stage for similar assessment. Good current distribution was obtained, which resulted in a thickness variation of <10 microns in the 120 micron thick deposit over the length of the piston rods.

At this stage, the entire surface was checked for imperfections and prior to chromium plating, the nickel was lightly belt polished, alkali cleaned and pickled. The piston rods were then chromium plated in a vertical position to a thickness of 70 microns and, prior to final inspection, the chromium was belt polished similarly to the nickel. Excellent bonding of nickel to steel and chromium to nickel was obtained throughout.

This very large and demanding application for electroplated nickel was proven to be extremely successful and clearly demonstrates the value of functional plating, when operated with strict process control and technical expertise. The production of the piston rods and the plating extended over a two year period and the first rods were installed in 1982. One of a pair of rods installed on one of the 63 gates is shown in Figure 8. No problems have been reported and, in fact, the success of the project has since resulted in similar procedures being used for piston rods on North Sea oil rigs. Satisfactory control of the sluice gates by the plated piston rods in the Ooster Schelde Project now allows the tidal system that controls the ecology of the area to be maintained, while still being capable of preventing a recurrence of the 1953 floods in which 1,000 people died. What better application for functional nickel plating!

C. Copper Molds For Continuous Casting Of Steel.

One of the most successful applications for functional nickel plating in this decade has resulted in significant cost benefit and product improvement in one of our major industries, i.e., the steel industry. During the last 20 years, the steel industry around the world has converted their operations from ingot casting to continuous slab casting for subsequent rolling into strip and nickel plating has participated in this conversion, especially in the last 7 or 8 years. The

major improvements obtained by continuous casting have been in steel quality and production costs and the nickel plating of the copper molds used in the process has contributed greatly in both areas. Improved quality is associated with greater consistency in chemical composition and metallurgical condition, which in turn results in superior, more uniform finished strip. Cost savings result from the elimination of several stages in the ingot route, combined with increased yield and lower energy requirements.

A typical continuous casting machine is shown in Figure 9. Briefly, molten steel is transferred from a ladle into a tundish, which is basically a molten metal reservoir, and then into a water cooled, oscillating, copper mold. While in the mold, sufficient heat is extracted from the steel to form a thin shell with adequate strength to contain the still molten core of the cast slab. In this condition, the slab leaves the bottom of the mold and enters the secondary cooling zone, where it passes through support rolls and more heat is removed by water spraying. Additional rolls then gradually bend the slab so that it leaves the casting unit in a straight, horizontal and completely solidified state. At this point, the casting is cut by torch into slab lengths with typical cross sections of about 200 cm X 25 cm, ready for rolling.

The efficiency of steel production is dependent on the performance and life of the mold. A typical mold for slab casting is shown in Figure 10. It is an open ended, water cooled, copper shell consisting of two side plates and two end plates, which form the desired shape and cross-sectional dimensions of the cast slab. The inside surfaces of the side plates are usually machined with a slight taper and curvature, typically with a radius of about 11 m, and the end plates are usually adjustable to accommodate different slab width requirements. The outside faces of the mold are grooved, so that when assembled in a rigid steel support system or water box, channels are formed for the passage of cooling water.

The performance of the mold is obviously very critical. Heat must be withdrawn at a rate related to pouring temperatures and casting rates, which would typically be 1525°C to 1550°C and 0.6 to 1.2 m/minute, respectively. The high thermal conductivity of copper makes it a natural choice for mold use, even though stresses imposed on the copper during casting are enormous. Two of the major problems with copper molds are in maintaining good surface condition and uniform

side plate spacing, but nickel plating has contributed greatly in reducing both problems. Excessive mold wear will affect side plate spacing, which will create heat transfer problems, as the gap width between the solidified steel shell and the mold increases. This, in turn, could affect the integrity of the steel shell, with disastrous results if it causes a breakout of molten steel. The incidence of surface cracking in the steel also increases with gap width and pickup of copper from the mold is known to cause 'star cracking' or hot shortness in the steel slab. These are the main reasons why electroplating has been used to protect the copper mold surfaces.

The original objective in plating molds was to improve product quality by preventing copper pickup, rather than to increase mold life. Initially, chromium deposits up to 0.25 mm thick were used and experienced some success, but this was slight compared with the benefit now provided by nickel plating and there are good reasons for this. Firstly, the thermal properties of nickel are better matched to those of copper, as shown in Table 1.

Table 1

Thermal Properties Of Copper, Chromium And Nickel

	Thermal Expansion Coefficient ($^{o}C^{-1} X 10^{6}$)	Thermal Conductivity ($cal/cm^{2}/cm/s/^{o}C$)
Copper	16.5	0.94
Chromium	6.2	0.16
Nickel	13.3	0.22

Consequently, the stress on the nickel and on the bond are less and heat transfer through the nickel is better than through chromium of similar thickness. Secondly, at mold operating temperatures, there is no deterioration of the hardness of nickel that might affect wear resistance, whereas chromium plate is not recommended for applications involving wear resistance at elevated temperatures. In addition, nickel plating is a much more efficient process than chromium plating and so better deposition rates and current distribution are possible and these are important factors when

deposit thicknesses up to 3 mm are being used. However, it is the versatility of nickel and the range of physical properties attainable in the plating process that has contributed to its success in this application. Hardness, ductility and stress are described as the most important physical properties of the nickel, as is the case in most applications. Hardness is the only property routinely determined. A hardness of 200 VHN is considered typical and in Watts baths this is obtained in various ways, such as control of electrolyte temperature and pH or chloride and ammonium ion concentration. Successful plating has been dependent on establishing a balance of conditions that will produce acceptable hardness values with ductility and stress levels that will withstand the rigorous conditions experienced during casting.

Preparation of the mold surfaces and the plating procedures themselves are basically those used routinely in nickel plating of copper. They differ mainly in the thoroughness of pre-cleaning, pickling and plating control that is so important in functional plating operations. The cost of fabrication, plating and installation of molds warrants all the time required to ensure excellent bonds and deposit quality and inferior work will have serious effects on steel productivity and metallurgical condition. The following procedures are considered typical:

- Grind or mill copper surface to specified curvature.
- Mask all areas not to be plated, using dip or spray coatings. New molds are plated before mounting on the water box support equipment required during casting but the entire assembly is normally left intact when replating used mold surfaces.
- Install wire "robbers" to prevent excessive edge buildup of nickel.
- Soak clean in proprietary copper cleaner and water rinse.
- Scrub all areas to be plated with a slurry of pumice.
- Wash thoroughly and inspect for water breaks.
- Activate in acid bath by soaking or electrolytic treatment.
- Water rinse and maintain wet surfaces during transfer to nickel plating tank.
- Immerse in plating solution with live entry.
- Deposit nickel at 3 to 4 A/dm^2, until thickness requirements have been met in all areas. About one day is required for 1 mm, so two, three or four day plating times may be required. A typical plated side plate is shown in Figure 11.

Following nickel plating, the molds are machined to final nickel thickness requirements and mold contour, with the final pass producing a surface finish of approximately 30 RMS. At this stage, the molds are again cleaned, the nickel surfaces activated and chromium deposited to a thickness of approximately 0.05 mm. They are then ready for assembly and installation in the continuous casting line.

There are many variables in the continuous casting process that can affect mold performance. These include casting rate, pouring temperature, flux quality, mold surface temperature and oscillating frequency but taking all of these into account, the performance of nickel plated molds in improving steel quality and productivity has been very well proven. Direct comparison between different plants is difficult as all variables cannot be taken into consideration but, nevertheless, the extent of the improvements is generally of the same order.

The improvement in product quality is mostly associated with a reduction in surface cracking of the steel. Cracking results mostly from copper contamination but can also occur as a result of gouges in mold surfaces that can cause small, local differences in cooling rates that establish local stresses and subsequent cracking. Nickel plating has greatly reduced surface gouging. A thorough study made in Europe over a one year period has concluded that nickel plated molds reduce the incidence of surface cracking to less than one third of that reported with unplated molds. In addition, greater consistency in the quality of cast slabs has reduced inspection requirements before hot rolling with resultant lower costs.

Some comparative figures for the life of plated and unplated molds are shown in Table 2 and, although casting rates shown are not constant - and they do have a significant affect on mold performance, the advantage of nickel plating is very obvious.

Table 2

Performance Of Plated And Unplated Molds

Mold Type	Plate Thickness (mm)	Casting Rate (m/min)	Mold Life (MT Steel Cast)
Copper	0	0.6	28,000
	0	1.0	20,000
Chromium Plated Cooper	0.25	0.6 - 1.2	35,000
Nickel Plated Copper	1.2	0.6 - 1.2	165,000
	1.0	1.5	182,000

An increase in casting rate usually results in a shorter life and this is apparent in the two results shown for unplated molds. The life corresponding to casting rates of 0.6 to 1.2 m/minute are average values obtained at various locations in the evaluation of plated molds but the 182,000 MT life result is the most interesting. Not only is it a very impressive value but it was obtained at a high casting rate and it can be considered reliable, as it represents mold performance in a European plant during the whole of 1986. It shows an improvement in life of about 800 percent obtained by a 1 mm thickness of nickel plate on copper molds. Such results, combined with improved steel quality, has made nickel plating standard practice in the production of copper molds for the continuous casting of steel slab.

Summary

Three examples of functional nickel plating have been described. The scale of operations, the process control and the technical expertise used in producing the heavy nickel deposits required for these applications are impressive. The importance of deposit quality in each application cannot be overemphasized, as the consequences of inferior quality are quite obvious. Conversely, the benefits realized by the marine engineering, the process metallurgy and the steel industries have been great. Nickel plating has provided considerable extension of the life of major

copper and steel components, with corresponding large cost savings.

The examples described, although impressive in scale and performance, are not generally well known. It is important for our industry, that the benefits of functional plating are better publicized so that design engineers are well aware of the options open to them through electroplating. Nickel is the most versatile of all the metals plated and there is an obvious, growing awareness of the capabilities of nickel electrodeposition that, if properly promoted, could substantially increase the acceptance and usage of nickel in functional plating. The versatility of nickel in providing protection of other metals and alloys from corrosion, wear and high temperature oxidation is becoming more widely recognized and this recognition is being gained, as a result of the high quality standards being maintained by electroplaters involved in functional plating.

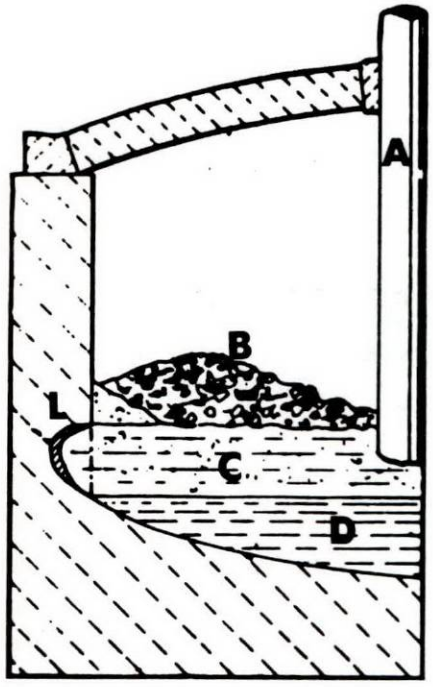

FIG. 1 Electric Smelting Furnace
- A. Electrode
- B. Charge Material
- C. Molten Slag
- D. Molten Metal
- L. Furnace Lining

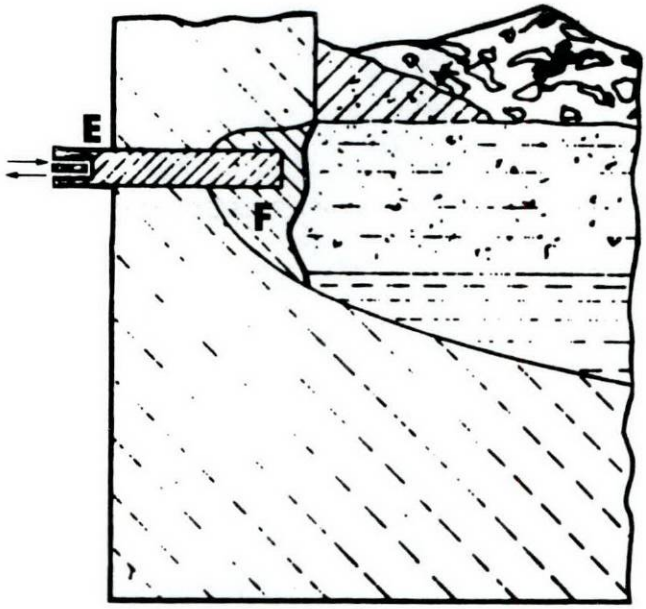

FIG. 2 Installed Copper Cooler
- E. Cooler
- F. Frozen Slag

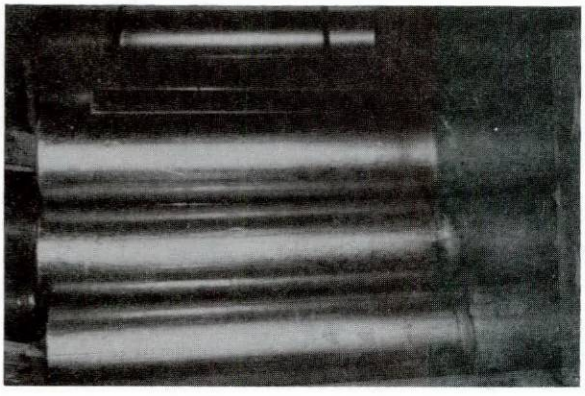

FIG. 3 Plated Coolers



FIG. 4 Comparison of unplated cooler (52) and plated coolers (53, 54)

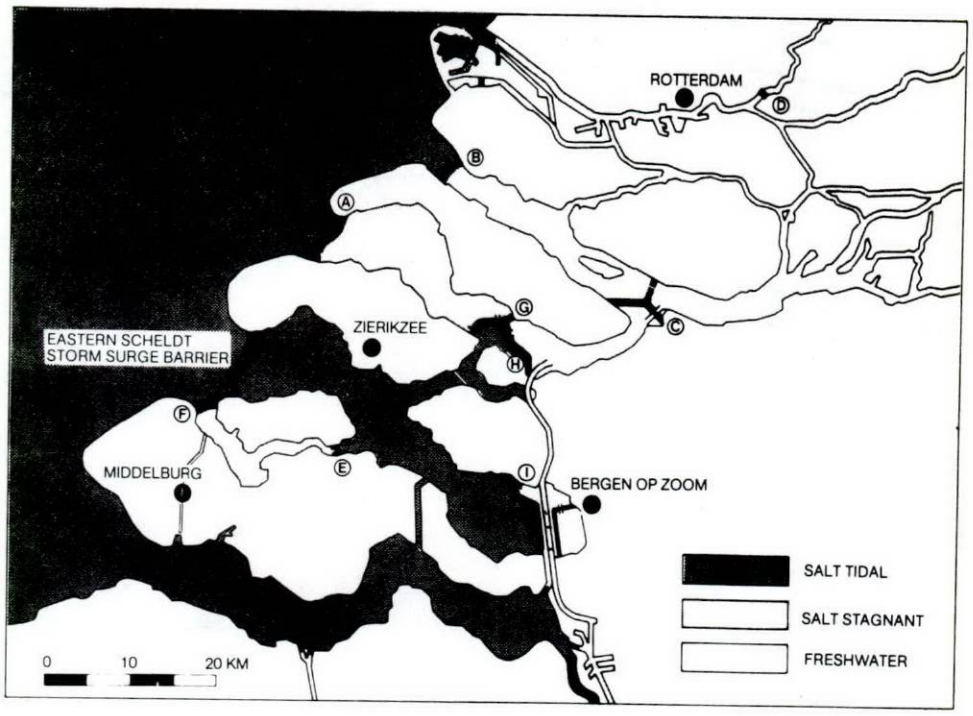

FIG. 5 Site of the Ooster (Eastern) Schelde Project

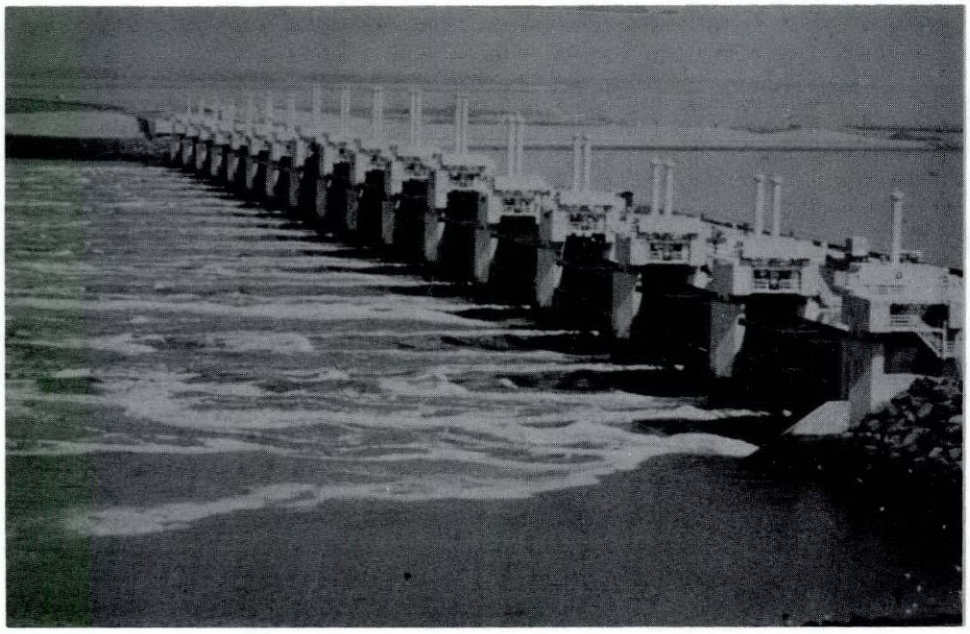

FIG. 6 Part of 3 Km Long Storm Surge Barrier

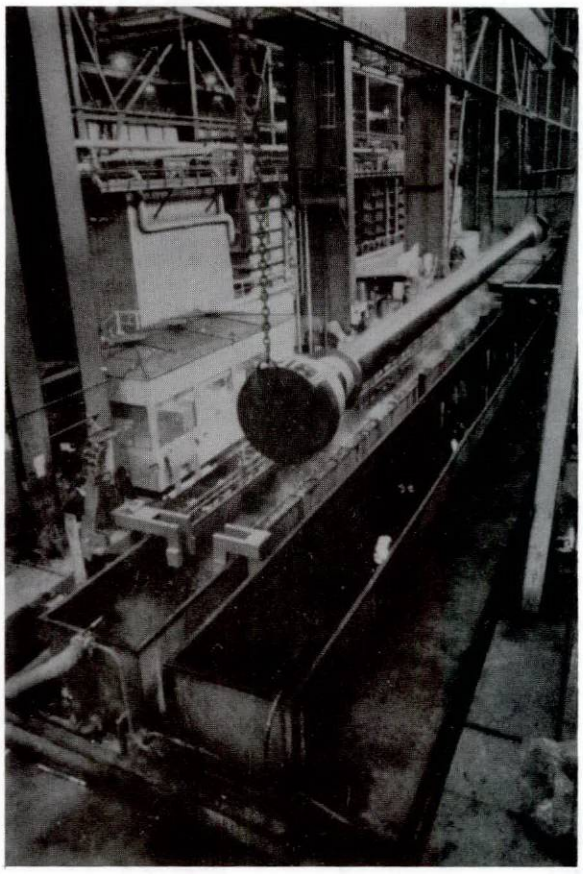

FIG. 7 An 18 mm Long Piston Rod Over Nickel Tank

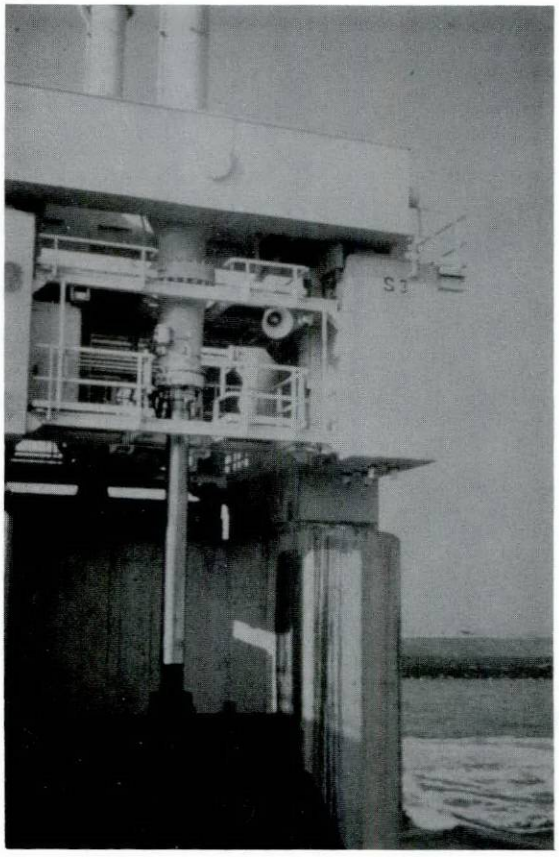

FIG. 8 Installed Nickel Plated Piston Rod

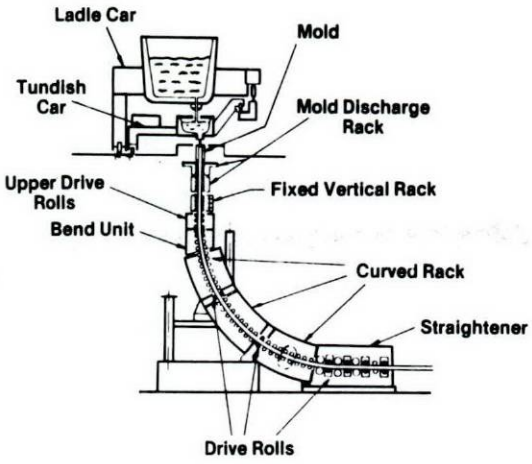

FIG. 9 Continuous Casting of Steel Slab



FIG. 10 Typical Mold for Continuous Casting

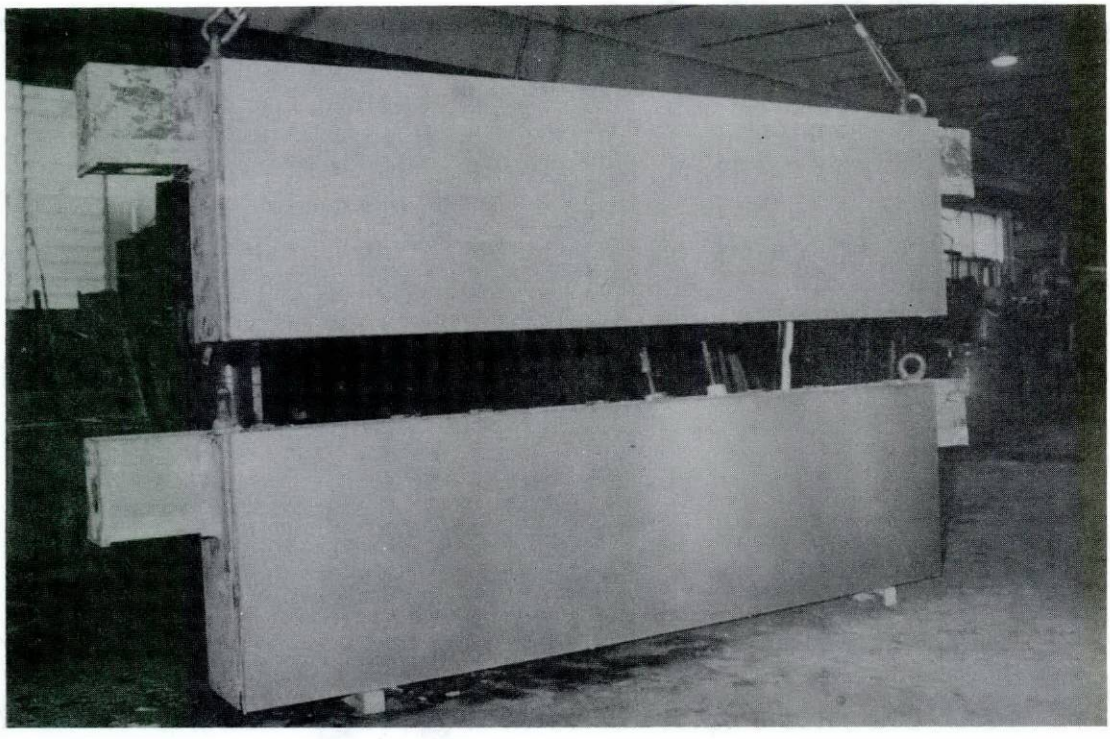

FIG. 11 Large Plated Mold Side Plates

B-6

Nickel Plating—Basics and Applications
Session B

A New Insoluble Nickel Plating Anode For Use With Recovery Systems

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A NEW INSOLUBLE NICKEL PLATING ANODE FOR USE WITH RECOVERY SYSTEMS

by Craig J. Brown
Eco-Tec Inc.

1. Introduction

Stricter pollution control laws, tighter restrictions on land disposal of hazardous solid waste and higher nickel prices have made nickel recovery from rinsewaters a high priority in most electroplating shops. Recovery systems, ranging from evaporators and ion exchangers to simple direct recycle from stagnant rinses, are all being employed with varying degrees of success.

The potential for recovery of nickel salts is often limited because the amount of metal salt additions required to maintain the nickel concentration in the plating bath may be less than the dragout. Often, no metal salts whatsoever are added to the plating bath, so it is not possible to recycle any of the recovered metal salt. Indeed, to prevent a buildup in the metal concentration in the plating bath, it may occasionally be necessary to decant some of the plating solution and replace it with water.

To understand this phenomenon, one must examine the plating process more closely.

The possible electrode reactions in a nickel plating bath are as follows:

anode

Ni_{metal}	$\rightarrow Ni^{++} + 2e^-$	(1)
$2H_2O$	$\rightarrow O_{2(gas)} + 4H^+ + 4e^-$	(2)
$2Cl^-$	$\rightarrow Cl_{2(gas)} + 2e^-$	(3)

cathode

$Ni^{++} + 2e^-$	$\rightarrow Ni_{metal}$	(4)
$2H^+ + 2e^-$	$\rightarrow H_{2(gas)}$	(5)

At 100% anode efficiency, reactions (2) and (3) do not occur and all of the current results in dissolution of nickel anode material. At 100% cathode current efficiency, reaction (5) does not occur and all the current results in deposition of nickel. Therefore, under conditions of 100% cathode efficiency and 100% anode efficiency, nickel is plated out at the cathode at the same rate that it is dissolved from the anode and the pH remains constant. If the effect of dragout is neglected, the concentration of dissolved nickel in the bath should not change.

Under practical circumstances, the anode efficiency does in fact approach 100%, but the cathode efficiency usually falls in the 93-97% range[1]. As a result, the nickel will dissolve from the anode faster than it plates at the cathode and the pH will tend to rise. For example, the 2.8% difference between the mean anode and cathode efficiencies observed for a Watts type solution would lead to a surplus in the solution of 31 grams of nickel ions per 100 ampere hours of electricity passed in the absence of any drag-out. Field observations that this problem is more pronounced with the newer, faster brightening and levelling solutions than the older, more conventional nickel solutions was also substantiated.

Dragout will tend to deplete the nickel concentration in the plating bath. If the dragout rate is high in relation to the rate of nickel plating, there may still be a net decrease in concentration. Under these circumstances it is may be feasible to recycle some recovered nickel salt dragout.

If the nickel plate is relatively thick, as is the case in exterior automotive plating, the depletion effect of the dragout will be balanced to a much greater extent by the poor cathode efficiency, so that the bath will be fairly stable in nickel concentration. Consequently, it will not be possible to recycle very much, if any, of the recovered nickel salt dragout to the semi-bright plating bath.

A material balance on a typical automotive bumper nickel plating operation is shown in Table 1 and Figure 1. In this configuration there is no rinse station between the semi-bright nickel and the bright nickel so than there is no net dragout of nickel from the bright tank. A first look would suggest that the best approach would be to recycle the dragout from the strike and the bright nickel back to the strike and semi-bright tanks. The dragout from the bright tank contains sulphur containing addition agents which would be objectionable in semi-bright. tanks, however some recovery systems[2] have the ability to recover the nickel without the addition agents. A closer look at the nickel material balance shows why this is not feasible.

If no dragout is recycled, we will have a net depletion of nickel in the strike (-5.3 g/m^2 of work plated), while we have a build-up problem in the semi-bright (2.26 g/m^2) and in the bright nickel tank (2.3 g/m^2).

About 96% of the nickel dragout from the strike could be recycled directly back to that tank without causing a buildup problem. *None* of the dragout from the bright nickel tank can be recycled, either to the bright or semi-bright tanks, without causing nickel buildup problems over the long term.

It should be noted that this situation is dependent on the cathode current efficiency, which will vary from plating installation to installation.

Table 1: Nickel Material Balance - Bumper Plating Operation

basis: 1 m^2 (100 dm^2) cathode plated

nickel strike:

bath concentration [Ni]	= 55 g/L
dragout	= 0.1 L/m^2 x 55 g/L x 1m^2
	= 5.5 g
cathode current density	= 4.3 amp/dm^2 (40 amp/ft^2)
current	= 430 amp
plating time	= 50 seconds (0.014 h)
anode dissolution	= 430 amp x 0.014 h x 1.095 g/amp h
	= 6.59 g
cathode deposit	= 430 amp x 0.014 h x 1.095 g/amp h x 97%
	= 6.39 g
nickel balance	= dissolution - deposition + dragin - dragout
	= 6.59 - 6.39 + 0 - 5.5
	= -5.3 g (depletion)

semi bright:

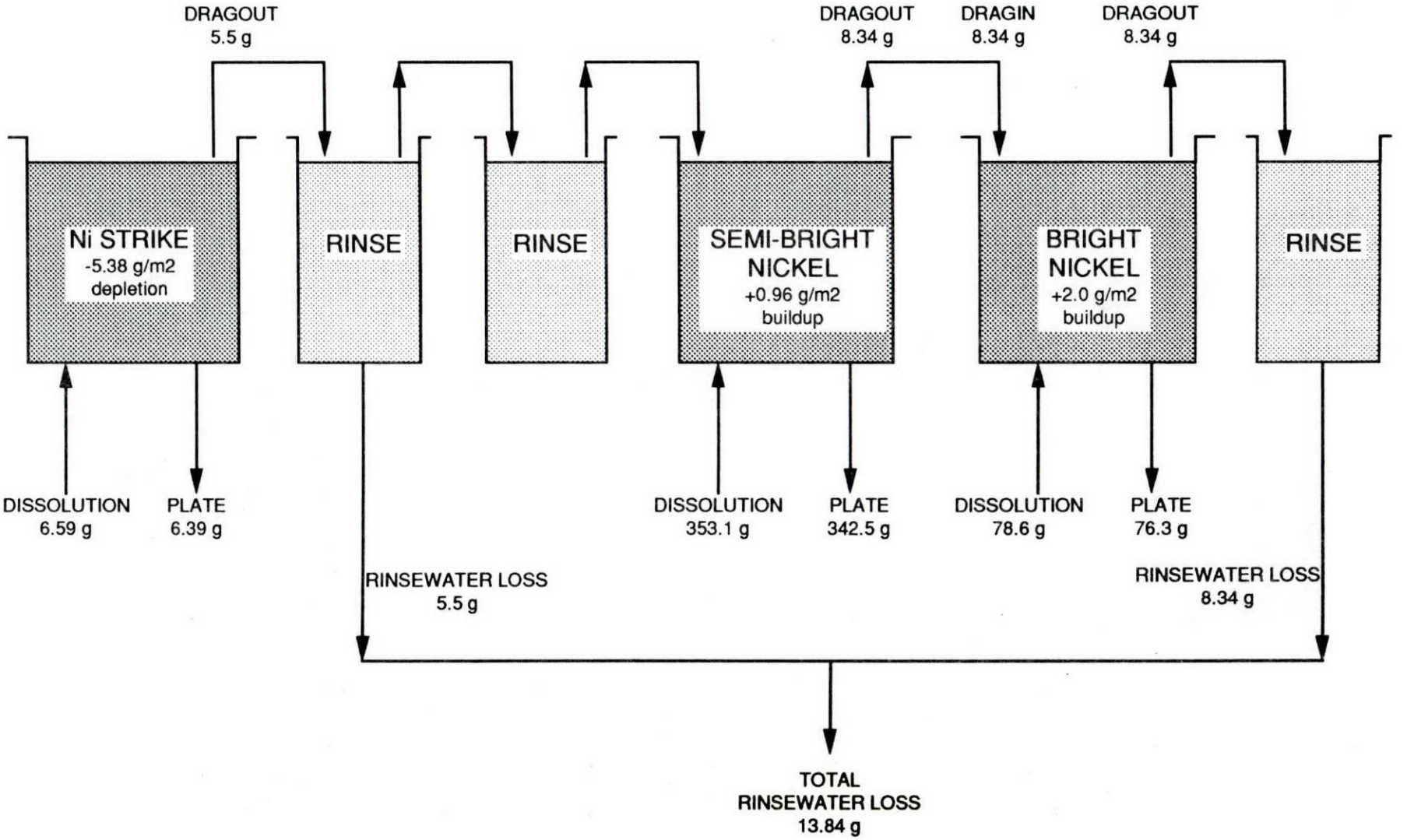
bath concentration [Ni]	= 83.4 g/L
drag-out	= 0.1 L/m^2 x 83.4 g/L x 1m^2
	= 8.34 g
cathode current density	= 4.3 amp/dm^2 (40 amp/ft^2)
current	= 430 amp
plating time	= 45 minutes (0.75 h)
anode dissolution	= 430 amp x 0.75 h x 1.095 g/amp h
	= 353.1 g
cathode deposit	= 430 amp x 0.75 h x 1.095 g/amp h x 97%
	= 342.5 g
nickel balance	= dissolution - deposition + dragin - dragout
	= 353.1 - 342.5 + 0 - 8.34
	= +2.26 g (buildup)

bright:

bath concentration [Ni]	= 83.4 g/L
drag-out	= 0.1 L/m^2 x 83.4 g/L x 1m^2
	= 8.34 g
cathode current density	= 4.3 amp/dm^2 (40 amp/ft^2)
current	= 430 amp
plating time	= 10 minutes (0.167 h)
anode dissolution	= 430 amp x 0.167 h x 1.095 g/amp h
	= 78.6 g
cathode deposit	= 430 amp x 0.75 h x 1.095 g/amp h x 97%
	= 76.3 g
nickel balance	= dissolution - deposition + dragin - dragout
	= 78.6- 76.3 + 8.34 - 8.34
	= +2.3 g (buildup)

Figure 1: Nickel Material Balance

basis: 1square meter cathode work



2. Insoluble Anodes

One way to solve the problem of nickel buildup in the plating bath is to reduce the anode current efficiency so that less nickel is dissolved. Removal of some of the anodes does not accomplish this, as the remaining anodes will simply assume the higher current load and the anode current efficiency will remain at 100%. Hendrickson notes that the anode current efficiency remains at essentially 100%, regardless of current density[1].

A more effective approach is to use of a small percentage of insoluble anodes in the nickel plating bath to lower the overall *effective* anode efficiency (in terms of nickel dissolution). If the amount of insoluble anode is such that the current carried by the soluble anodes which results in the dissolution of nickel is equal to the current that results in actually plating metal at the cathode, there will be no net nickel buildup.

Theoretically this idea does not appear viable. Lyons[3] points out that it is not possible to employ insoluble anodes in copper or zinc sulfate plating baths because the potential required to liberate oxygen is about 1 V more positive than that required to dissolve the soluble anode; consequently all the current will flow from the soluble anodes alone and dissolve them as rapidly as if the insoluble anodes were omitted. In copper and zinc sulfate baths, insoluble anodes cannot carry current unless a higher potential is supplied through a separate circuit.

One would expect a similar situation to occur with nickel plating. In practice it has been observed that platinum anodes do carry some current in nickel baths and the use of auxiliary insoluble anodes for plating recessed areas is quite common. The reported life of insoluble anodes used in this way does seem to be somewhat limited, however.

Reactions (2) and (3) will occur at insoluble anodes in a solution containing sulfate and chloride anions, resulting in production of oxygen and chloride gas, as well as pH reduction. It has been predicted that evolution of chlorine gas will take place if the concentration of chloride ions is above 25% of the concentration of sulfate ions[4]. In a normal Watts nickel plating bath, the chloride is at about this level, so that some chlorine evolution may be expected.

Chlorine may have a tendency to oxidize organic addition agents. This is undesirable as it would significantly increase addition agent consumption and associated operating costs, as well as contaminate the bath with organic impurities. Since nickel plating baths are not customarily ventilated, any discharge of chlorine gas to the atmosphere would be totally unacceptable from a health and safety standpoint.

The qualities required in an insoluble anode for nickel plating are:

1. The anode must not increase the consumption of organic brighteners.
2. It must not adversely affect the chemistry of the bath, either by excessive chlorine evolution or by the dissolution of harmful impurities.
3. The anode must be capable of passing a reasonable amount of current at normal nickel plating voltages.
4. The cost of the anode, amortized over its useful life, must be low in relation to the value of the nickel metal recovered.

Various different anode materials were considered for this purpose. The presence of chloride, because of its corrosive nature, significantly reduces the range of choice. Lead corrodes in chloride solutions and lead contamination in a nickel plating bath is unacceptable. Graphite provides the necessary corrosion resistance, but tends to break down due to oxygen evolution at the current densities employed in nickel plating.

Precious metal coated titanium anodes such as platinum, ruthenium and iridium have good corrosion resistance to chloride and sulfate and are therefore a much better choice. In addition, precious metal coated titanium anodes have very low over-potential for the oxygen evolution reaction - about 0.5 volts lower than lead[5]. It was therefore felt that precious metal coated titanium anodes were the best choice.

3. Preliminary Field Trials

In December 1987, an insoluble anode was installed in a saccharine-containing bright nickel plating bath in a Don Mills, Ontario plating shop. The line was a manual operation.

The titanium anode measured approximately 15 cm by 60 cm and was coated with a precious metal. It was suspended from the anode bus bar and located centrally in the plating tank between two nickel anodes so that the current passing through the insoluble anode could be maximized. The nickel anodes were sulfur-depolarized (0.02%) electrolytic nickel. A parallel plating bath, operating under similar conditions, but employing only soluble nickel anodes was located adjacently. This provided a convenient control for evaluation purposes. It should be noted that a separate power supply was *not* employed for the insoluble anode.

The insoluble anode had an effective area of about 10 dm^2 which represented about 3.9% of the total anode area in the tank. The current carried by the insoluble anode varied from 15-55 amps, depending upon the job, averaging about 30 amps, which represented about 4.6% of the total current in the tank.

During three and one half months of operation, representing 626 hours of plating time, the nickel concentration in the plating bath with the insoluble anode dropped from 96.5 g/L to 94 g/L while the concentration in the control bath increased from 103.5 to 104 g/L. Additions of acid to maintain bath pH were about one half those required in the control tank. Indications were strong that the insoluble anode was doing the required job.

It was noted by the plating manager in passing, that it was necessary to add more brightener to the bath with the insoluble anode than to the control tank. Although detailed records were not maintained, it was estimated that brightener consumption had increased by about 50%. This was later attributed to oxidation of the brighteners by the chlorine evolved at the insoluble anode. No other plating problems were observed.

At this point the insoluble anode was removed from the tank. Visual inspection of the anode revealed discolorations indicative of coating loss. Measurements on the coating indicated that there had been an approximate 60% coating loss, although adhesion was acceptable. A coating activity test revealed that the coating loss was indicative of either a blinding deposit or organic fouling.

Further laboratory testing of this particular anode type in the same bright nickel plating electrolyte confirmed these observations. Accelerated tests conducted at 54 amp/dm^2 resulted in failure after only 70 hours of operation. At the end of the test, only 25% of initial current was flowing through the anode. Analysis of the anode coating revealed a 50% loss of the precious metal in the coating, leading to poor adhesion and almost total passivation.

These findings were not too surprising. It has been noted by others that the presence of specific organic additives may accentuate, sometimes very appreciably, the dissolution rate of platinum from platinized titanium anodes[6].

Based upon these findings it was obvious that use of a simple insoluble anode of precious metal coated titanium of this type was not viable. It was concluded that it was necessary to isolate the anode from the plating electrolyte to prevent oxidation of the addition agents and attack and/or fouling of the anode coating.

4. Ion Exchange Membrane

One way to isolate the anode is by utilization of an ion exchange membrane. In some trivalent chromium plating processes, ion exchange membranes are employed to separate the anode from intimate contact with the plating solution[7]. This prevents oxidation of the trivalent chromium to the hexavalent form. It was felt that a similar approach could be successfully employed for this application.

An anode assembly was constructed consisting of a polypropylene container fitted with cation selective ion exchange membrane on one side and a precious metal coated titanium anode

(see Figure 2). A dilute solution of sulfuric acid was employed as an anolyte inside the compartment.

The anode assembly was suspended in a saccharine containing bright nickel solution as tested earlier. The anode was operated with a nickel cathode at a current density of 5 amp/dm^2 and a voltage of 7V to determine the effectiveness of the membrane in rejecting the brighteners and protecting the insoluble anode. No soluble nickel anodes were employed during these tests.

The test was stopped after 200 hours of operation. Visual inspection revealed no sign of anode corrosion and the organic content of the sulfuric acid anolyte was only 1 mg/L TOC, which is less than 0.1% of the external plating bath solution concentration. This indicated that the ion exchange membrane effectively rejected the brighteners and provided strong indication that the anode was being successfully protected.

The electrical current was turned off. After 64 hours of solution contact with no current the brightener content was found to have risen to only 57 mg/L TOC. This is only 3.5% of the plating bath concentration, indicating that the membrane was very effective in rejecting the addition agents during a shutdown situation.

It was noted that when the current was turned off, the hydrogen ions exchanged with nickel ions across the membrane, as evidenced by a decrease in acid concentration and an increase in nickel concentration inside the anode compartment. The concentrations reverted to their original levels very quickly after the current was resumed, however and no adverse effects were observed because of this exchange of ions.

5. Preliminary Field Trials With the Membrane

Based upon these tests, a prototype membrane insoluble anode was constructed and installed in the field, in a bright nickel plating bath, as before.

Initial current readings were comparable to those observed without the membrane.

Within a few hours of starting up the plating line, the operators complained about fuming in the region of the insoluble anode and it was withdrawn.

Investigation revealed that although the membrane was cation selective, it was allowing passage of some chloride ions from the nickel plating electrolyte into the anode compartment during overnight periods of non-production. This resulted in a flash of chlorine gas from the insoluble anode into the atmosphere when plating resumed in the morning. This chlorine did not contact the plating solution, but it was objectionable from a health and safety standpoint.

The anode design was then modified to address this problem. The membrane was replaced with one bearing a better chloride rejection efficiency and the compartment was sealed and fitted with a vent tube to duct fumes away to a scrubber.

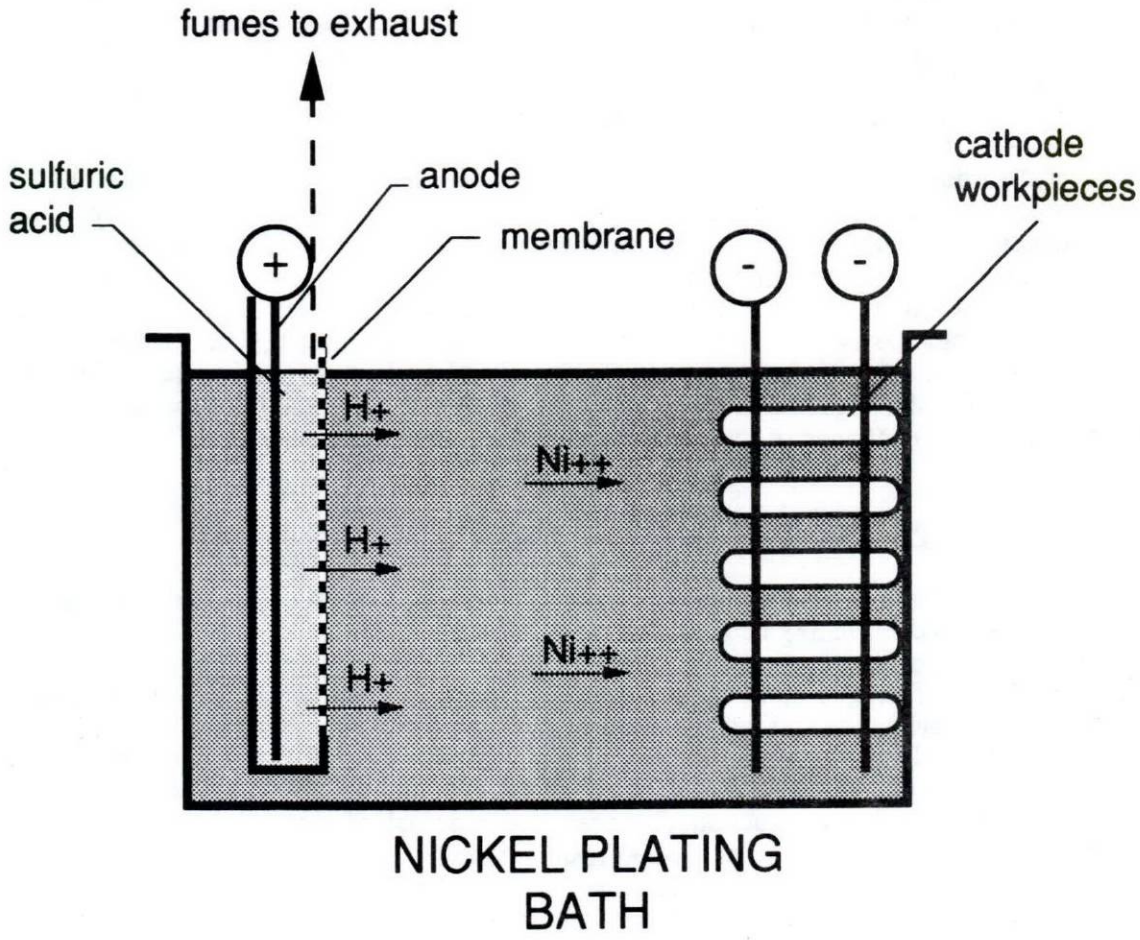


Figure 2: Membrane Type Insoluble Anode

6. Final Field Trials

Various cell designs were evaluated in an effort to provide a simple, yet effective way of sealing the compartment to prevent escape of chlorine gas. Two new prototypes were installed in the field in December 1988.

6.1. Semi-Bright Nickel Plating Installation

The second membrane insoluble anode prototype was installed in a semi-bright nickel plating bath at a large automotive bumper plating, programmed hoist installation. It was located on the end of the anode bus, in the corner of the tank to facilitate service and inspection. (see Figure 3) This location would not maximize the current carried, since it was furthest from the rectifier connection to the buss and was further from the cathode work than most of the other anodes.

The anode compartment was constructed of titanium. The vent for the cell was connected to a small caustic scrubber tower to take care of any chlorine fumes that might be generated. Provision for automatic water makeup to the anode compartment was made.

The insoluble anode had an effective area of 23.8 dm^2. The average current carried by the insoluble anode was 75 amps, giving a current density of 3.15 amp/dm^2. The current measured at the insoluble anode has not changed since installation.

The plating tank contained eight large anode baskets containing electrolytic nickel 'crowns'. Each basket had an anode area of 51.1 dm^2, providing a total area of 409 dm^2. The total current in the tank averaged 2750 amps at a voltage of 17 V, so that the average anode current density was 6.54 amp/dm^2.

The average cathode work load was about 600 dm^2.

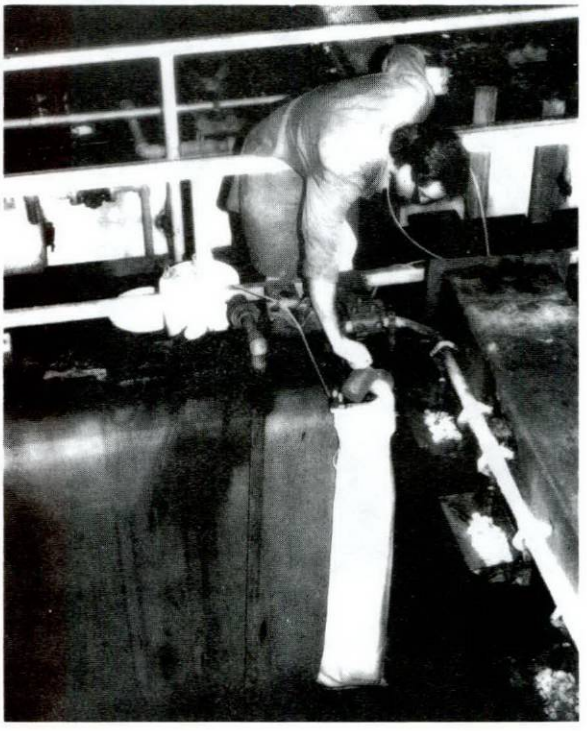


Figure 3: Titanium Insoluble Anode Installed in Semi-Bright Nickel Tank

6.2. Bright Nickel Plating Installation

A third prototype was installed at the initial bright nickel installation. The anode compartment was constructed of polypropylene and is illustrated in Figure 4. The vent for the cell was connected directly to the chrome plating exhaust.

The anode was evaluated in two different locations along the side of the tank were evaluated, about one third of the distance along the anode bus and on the end of the bus.

The insoluble anode had an effective area of 7.9 dm^2. The average current carried by the insoluble anode was 18 amps when located towards the center of the buss, giving a current density of about 2 amp/dm^2. When it was located near the end of the tank, at the end of the anode bus, the current was reduced to 7.5 amps.

The plating tank contained eleven large anode baskets, each with an anode area of 23.2 dm^2, providing a total area of 255 dm^2. The total current in the tank averaged 500 - 550 amps at a voltage of 7.5 V, so that the average anode current density was 1.89 amp/dm^2.

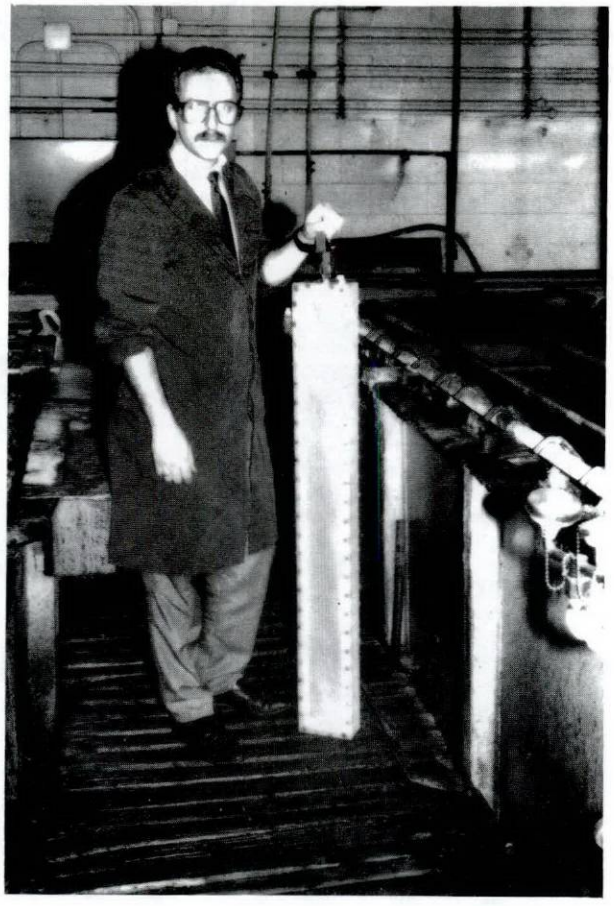


Figure 4: Polypropylene Insoluble Anode Installed in Bright Nickel Plating Tank

7. Discussion

The field results from the three installations are summarized in Table 2.

7.1. Semi-Bright Nickel Plating Installation

The current density on the insoluble anode in the semi-bright tank was approximately 48% of the average current density on the nickel anodes and it carried 2.7% of the total current in the bath. The effective overall anode current efficiency was then 97.3%. Based upon experience at the bright installation, the insoluble anode current density could probably be increased by relocating it closer to the center of the tank.

The plating electrolyte in the tank is recirculated continuously through a large common tank with several other semi-bright nickel tanks. Because of this huge volume of solution, a significant change in solution chemistry is unlikely to be observed.

To date, no plating problems have been observed and no evidence of chlorine fumes has been found.

7.2. Bright Nickel Plating Installation

The insoluble anodes in the bright nickel tank actually carried a *higher* current density than the soluble nickel anodes. The ratio of insoluble anode current density to average soluble anode current density was 1.23 for the bare anode and 1.11 for the membrane anode. This is probably because of its favorable location in the bath, at the center of the anode bus. Some of the soluble anodes at the end of the tank probably carried little current, thereby reducing the overall average.

As with soluble anodes, tank location is a major factor in determining how much current will be carried by the insoluble anode. When located in the center of the tank the membrane insoluble anode carried a current of 18 amps which was 3.33% of the total current. The effective overall anode current density was then 96.6%. This compares to 7.5 amps when it was located near the end of the tank, which was only 1.44% of the total, giving an effective efficienty of 98.6%.

The insoluble anode, without the membrane, carries a current density of 3.0 amp/dm^2 compared to 2.28 amp/dm^2 when the membrane anode was installed in the same location. This reduction is probably due to the electrical resistance of the membrane.

No plating problems have been experience and no further problems with chlorine fumes have been found since installation of the membrane.

Chemical consumption will be observed over the long term. It is expected that the nickel concentration in the tank will drop with time and that the pH will stabilize. The brightener consumption should not increase and will be compared to the adjacent, 'control' tank.

7.3. General

One would expect that the use of pure electrolytic nickel anode material would result in forcing more current through the insoluble anodes. DiBari[8] has shown that the anodic potential for the sulfur bearing anodes used in a the bright nickel plating bath is approximately 0.4 V lower than that for pure electrolytic nickel, such as that use in the semi-bright tank. Because of this reduction in anodic potential, where only soluble nickel anodes are used, it reportedly[9] is possible to use at least 50% more current, before an appreciable liberation of chlorine occurs, using sulfur bearing nickel anodes in place of pure nickel. Where insoluble anodes are used, the higher potential required for the pure nickel dissolution should force the insoluble anode to carry more current.

Although different types of nickel were employed at the two locations, it was not possible to evaluate this phenomenon because of the widely different plating operating conditions and tank locations. A more detailed study on this subject is planned.

In both installations, no plating problems have been experienced that can be attributed to the membrane insoluble anodes.

No deterioration of either membranes or anode coating have been noted in either installation, after several hundred hours of operation. Although no deterioration is expected, long term evaluation of the anodes is currently in progress. Chemical consumptions will also be monitored, to confirm that addition agents are not being degraded and that the nickel concentration in the baths will gradually decrease as expected.

Table 2: Insoluble Anode Operating Conditions

	br. Ni (no membr.)	br. Ni (membrane)	br. Ni (membrane)	sem-br. Ni (membrane)
location	middle	middle	end	end
tank volume (liters)	6433	6433	6433	11355
plating voltage	7.5	7.5	7.5	17
total current (amp)	650	540	520	2750
soluble anode current (amp)	620	522	513	2675
insoluble anode current (amp)	30	18	7.5	75
total soluble anode area (dm^2)	255	255	255	409
soluble anode current density (amp/dm^2)	2.43	2.05	2.01	6.54
insoluble anode area (dm^2)	10	7.9	7.9	23.8
insoluble anode current density (amp/dm^2)	3.0	2.28	0.95	3.15
insoluble/soluble CD ratio	1.23	1.11	0.47	0.48
effective anode current efficiency (%)	95.4	96.7	98.7	97.3

8. Summary and Conclusion

Insoluble anodes will carry a large current load in a nickel plating bath without the requirement of a separate power supply. By installing sufficient insoluble anodes so that the effective anode current efficiency equals the cathode current efficiency, it should be possible to prevent the buildup of dissolved nickel in a nickel plating bath.

Bare, precious metal coated, titanium anodes (without a membrane) have a number of drawbacks including degradation of plating addition agents agents and limited anode coating life. Laboratory and short term field data indicate that utilization of an ion exchange membrane has solved these problems by isolating the anode from the plating electrolyte.

Although membrane anodes do not carry as much current as bare insoluble anodes, this does not present any operational problems. Membrane-type insoluble anode will carry a current density of 48-123% of the soluble nickel anodes in the same tank. The main factor determining insoluble anode current load is probably anode location in the tank, although it is expected that the use of pure electrolytic nickel will force more current through the insoluble anodes than if sulfur-depolarized nickel is used.

Membrane anodes generate small quantities of chloride gas which must be controlled to avoid polluting the plant atmosphere.

Long term field data is now being collected from two production plating installations for evaluation. This should provide information on anode and membrane life.

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