



## Do's & Don'ts

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# Do's & Don'ts for Impurities in Nickel Plating Solutions

Last month, I reviewed the consequences of impurities in nickel baths and their removal. This month, I am covering similar territory, but the perspective is from the consequences of impurities on engineering applications and their deposit properties.

Bright nickel plating solutions are especially sensitive to impurities that can cause numerous defects in the nickel deposit. Likewise, sulfamate nickel plating solutions are very sensitive to impurities that change the physical characteristics of the deposit. The same is true for the Watts formulation used for engineering purposes. Strongly acidic nickel strike solutions that are used for the preparation of stainless steel, titanium and other metals and alloys that require a severe activation process are sensitive to certain impurities.

## Sulfamate nickel plating solutions

The usual formulation for a sulfamate nickel plating solution is as follows:

Nickel as metal (from nickel sulfamate concentrate)	76.5 g/L (10.2 oz/gal)
Chloride or bromide	2.2 g/L (0.3 oz/gal)
Boric acid	45.0 g/L (6.0 oz/gal)
pH	4.0

Chloride and/or bromide are actually impurities that have a negative influence, since the internal stress in the deposit is moved toward a higher tensile stress. In many cases that is not desirable. However, the usual operating data sheet formula tells us that is desirable to add 2.2 g/L of a chloride or bromide. The reason for adding either of these is to help to keep the anodes from polarizing while allowing the use of higher current densities, at the cost of raising the internal stress. If the lowest internal stress is the desired goal, one should lower or eliminate the chloride or bromide. However, if you do that, plating must be at a lower current density than perhaps is desired. My guess is that the current density should be below 60 A/ft<sup>2</sup> (6.45 A/dm<sup>2</sup>). For many applications the lower CD is not a problem, if you are willing to plate a little longer.

A pH of about 5 will result in a harder less ductile deposit. The stress is at its minimum at a temperature of between 35 and 50°C (95 and 126°F).

## Sulfate nickel, Watts nickel and bright nickel

The formula for a nickel plating solution based on the Watts nickel formulation is as follows:

Nickel as metal (using nickel sulfate)	75 g/L (10.0 oz/gal.)
Nickel chloride	60 g/L (8.0 oz/gal.)
Boric acid	45 g/L (6.0 oz/gal.)
pH	4.0

And for a Woods nickel strike:

Nickel as metal (using nickel chloride)	45 - 60 g/L (6.0 - 8.0 oz/gal.)
Hydrochloric acid (22°Baume)	10 - 12 vol%.

The impurities act similarly for all of the above nickel plating solutions.

## Impurities and their consequences

Ammonium ions above 2500 ppm can cause tensile stress and lower ductility.

Cadmium at 1000 ppm, according to Safranek\* produces a dark low CD area and a brittle deposit.

Chromium, starting at 3 ppm of hexavalent chromium or 8 ppm of trivalent chromium, produces extreme stress in the deposits, cracking of the deposit, rough deposits and dark deposits. A Woods nickel strike can tolerate more than 8 ppm of chromium. The amount of chromium tolerated by the nickel strike is dependent on the age of the bath. Nickel will tend to build up in the bath because the anode efficiency is greater than the cathode efficiency. Nickel sulfate may salt out.

Cobalt is sometimes added to sulfamate nickel and to Watts nickels to form a cobalt-nickel alloy. The result is increased tensile stress, but the deposit is also a strong harder alloy that is useful for many applications.

Copper at 50 ppm or more causes dark deposits in the low current density region.

\*W.H. Safranek, *The Properties of Electrodeposited Metals and Alloys: A Handbook*, 2nd Ed., NASF, Washington, DC (1986).

Iron at 300 to 900 ppm whitens the deposit and can cause roughness and reduce ductility. If the pH of the nickel plating solution is kept at or above 3.9, there will be no iron contamination, as it will precipitate in the bath and be removed by filtration. A Woods nickel strike can tolerate more than 900 ppm iron.

Lead causes dark low current density areas and increases tensile stress.

Nitrates above 5 ppm causes tensile stress. Levels above 0.3 g/L result in very high tensile stress.

Organic impurities can cause brittle, dark, pitted deposits. Among the many organic contaminant sources are breakdown products from brighteners; other organic addition agents used to reduce stress, harden the deposit, lower surface tension; and oils from poor cleaning or entrapment in seams, cracks or other recessed areas. Organic impurities take many forms. In bright nickel solutions excess addition of brighteners and/or other addition agents used for brightening and other modifications of the deposit can act as impurities, causing dull, hard, brittle or discolored deposits, even gray to black deposits.

Magnesium has little effect on the deposit properties. However, it can be beneficial, as is manganese, in preventing sulfur from migrating to stress or heated areas of the deposit. Sulfur causes cracking of heated areas and fatigue failure.

Sodium in the amount of 25 to 30 g/L causes brittle deposits. Lower amounts of sodium have little effect.

Sulfur-containing compounds in the range of 25 ppm or higher cause high compressive stress, brittle, fatigue failure and bright deposits.

Tin has two common valence numbers, two and four. Bivalent tin (II) has little effect on the deposit, but tin (IV) can cause high tensile stress.

Zinc is tolerated up to about 250 ppm. Higher concentrations cause dark streaks, burning and brittle deposits. As well, cathode efficiency is reduced.

The alphabet soup of impurities can be removed from nickel plating solutions by various means, the subject of other papers, including last month's Do's and Don'ts Column.

### Do's

- Monitor impurities in your nickel plating solutions.
- Everything in your power to prevent introducing impurities into the plating solutions.
- Be sure that all items to be plated are clean. Watch out for seams, cracks and blind holes that can entrap oil and/or other impurities.
- Maintain the amount of all the constituents of the plating solution to optimum concentration.
- Filter continuously.
- Carbon treat when organics are likely to be present. Follow the supplier's instructions for treating and maintenance.
- Maintain the brighteners in good balance in bright nickel solutions.

### Don'ts

- Over-add brighteners in the bright nickel solutions.
- Add organic materials to Watts or sulfamate solutions if used for engineering, or for the specific properties of the pure deposits (except surfactants that are suitable for nickel plating use.)
- Allow foreign material to fall into the plating tank.
- Allow bus bar cleaning without a protective cover that will prevent anything from entering the plating tank from the bus bars over the tank.
- Don't overheat the plating solutions. High temperature may break down brighteners into organic contaminants. **P&SF**

### Answers to I.Q. Quiz #455 from page 6.

- Two ends =  $2 \times \pi r^2 = 2 \times 3.14 \times (0.75)^2$   
Surface =  $\pi DL = 3.14 \times 1.5 \times 25$   
Total Area  
Current = Area  $\times$  CD =  $0.84 \times 40$   
 $= 3.53 \text{ in}^2$   
 $= 117.75 \text{ in}^2$   
 $= 121.28 \text{ in}^2 = 0.84 \text{ ft}^2$   
**= 33.6 A**
- Acid copper valence  
Atomic weight of copper  
Equivalent weight of copper =  $63.55/2$   
1 Faraday, 96,500 Coulombs yields  
Coulombs =  $33.6 \text{ A} \times 5.0 \text{ min} \times 60 \text{ sec/min}$   
10,080 Coulombs yields  $10,080/96,500 \times 31.78$   
 $= 2$   
 $= 63.55$   
 $= 31.78$   
 $= 31.78 \text{ g copper}$   
 $= 10,080 \text{ Coulombs}$   
**= 3.32 g copper**
- Volume of coating =  $4 \text{ in.} \times 6 \text{ in.} \times (2.54 \text{ cm/in})^2 \times 10.0 \mu\text{m} \times 0.0001 \text{ cm}/\mu\text{m}$   
Density of copper  
Weight of copper =  $0.155 \text{ cm}^3 \times 8.92 \text{ g/cm}^3$   
 $= 0.155 \text{ cm}^3$   
 $= 8.92 \text{ g/cm}^3$   
**= 1.38 g copper**
- 1.38 g of copper is  $10.0 \mu\text{m}$  thick; therefore 3.32 g of copper would be:  
 $3.32 \text{ g}/1.38 \text{ g} \times 10 \mu\text{m}$   
**= 24.0  $\mu\text{m}$**
- Cross-section area of pipe =  $\pi (1.5 \text{ in.})^2/4$   
Velocity = Flow rate/Pipe diameter =  $300 \text{ gal/min} \times 1 \text{ ft}^3/7.48 \text{ gal} \times 1/0.012 \text{ ft}^2$   
 $= 1.77 \text{ in}^2 = 0.012 \text{ ft}^2$   
 $= 3,268.0 \text{ ft/min}$   
**= 37.1 mi/hr**
- 1 US gallon = 0.0925 firkin; 1 fortnight = 20,160 minutes  
**= 559,440 firkins/fortnight**