The Do’s and Don’ts of Operating An Alkaline Zinc-Nickel Plating Process

by

Adam Walsh
Dipsol of America Technical Sales Representative
The Trends Towards High Zinc-Nickel

Automakers face competition with warranty length
  • Extending service and functionality timeline

Applications are calling for a higher level of corrosion protection
  • 1000 hours + beyond what typical Zinc finishes can provide
NSS Corrosion Performance

Zinc & Zinc Alloy NSS Corrosion Hours

- White Rust Hours
- Red Rust Hours

NSS Hours

- Zinc
- ZnFe
- ZnNi Low
- SnZn
- ZnNi High

Plated Finish
Discussion Roadmap: Zn/Ni overview

A brief Introduction to Electroplating

- How Electroplating Works
- What is Zinc/Nickel Plating?
- The Benefits of Zn/Ni Alloy Plating

The Chemical Components of an Alkaline Zn/Ni bath

- The Alkaline Electrolyte Solution
- Zinc, its role in corrosion resistance
- Nickel’s contribution to the sacrificial coating
- Nickel Complexer
- Brightener
Discussion Roadmap: The Chemistry

• The Alkaline Electrolytic Solution
  □ Effects of high and low caustic soda

• Zinc and Nickel Concentration
  □ Metal concentration, appearance, and efficiency

• Nickel Complexer
  □ Efficiency and Nickel deposit

• Brightener
  □ Overall appearance and efficiency
Electroplating is the process in which an electric current is used to reduce dissolved metal cations in a plating solution to form a coherent metal coating on a desired electrode.

Electroplating changes the chemical, physical, and mechanical properties of the workpiece.
- Improved Corrosion Resistance
- Outward Appearance Change
- Change in Tensile Strength or Surface Hardness
A Brief Introduction to Electroplating

Plating provides protection over steel (Fe)

The plated layer is a more active metal on the electro-galvanic scale (corrodes preferentially).

• Creates a sacrificial coating
A Brief Introduction to Electroplating
How Electroplating Works

The concept of electroplating.....
• Passing an electric current through an electrolyte solution
• Multiple terminals (electrodes) are dipped into the electrolyte solution
  – Each electrode is connected to a power supply, completing a circuit
  – The Positive electrode is known as the **Anode**
  – The Negative electrode is known as the **Cathode**

The electrodes and electrolyte solution are made from carefully chosen elements or compounds.
A Brief Introduction to Electroplating
How Electroplating Works

When the electricity flows through the circuit....

• Positively charged metal ions in the electrolyte solution are attracted to the negatively charged cathode (workpiece)

  — The positive metal ions slowly deposit on the cathode, creating the protective outer layer

  — The speed of the plating deposit largely depends on the current strength and electrolyte concentration
A Brief Introduction to Electroplating
Rack and Barrel

Rack Plating
• Large, complex, or fragile parts
• Kept mostly still during plating
  – Sometimes cathode rockers are used
• Typically faster than barrel plating

Barrel Plating
• Small and durable parts
  – Fasteners and small stampings
• Rotating, perforated barrel
  – Uniform finish
• Low cost
• High part volume
Alkaline Zn/Ni Plating Cell

- Nickel Anodes
- Alloy metal additive
- Brightener Additive
- DC Rectifier
- Metal Complexor

Oxidation Reaction at Anodes: ZnOH

Reduction Reaction at Cathode: Zn Metal

NaOH

Zn Generator Tank

Alloy metal additive
Brightener Additive
Metal Complexor

Copyright(c) Dipsol of America, Inc. All Rights Reserved.

http://www.dipsolamerica.com
Process Flow

- Soil Removal
- Surface Activation
- Alkaline Plating Bath
- Passivate
- Optional Top Coat
- Dry
Cleaning and pretreatment before plating is half the battle…..

- Properly cleaned parts accept the metal ions and plating more readily

Dirt and Oils on the parts prior to entering the plating bath may cause…

- Poor appearance
- Adhesion issues
- Blistering
- Failure to initiate plating on the workpiece
The Hull Cell Test is used to replicate the electroplating deposit at various current densities

- The test is often used in routine bath maintenance, establishing operating parameters, or improving the plating process

- The small chamber is filled with the plating solution, an anode at the straight end, and a test panel as a cathode at the angled end
  - Accurately duplicates a production-plating size tank
A Brief Introduction to Electroplating
Hull Cells and Current Density

Plating the test panel cathode at an angle in the Hull Cell chamber replicates any variables across the range of operating current densities.

……What is current density?
Current density is the amount of DC current per the surface area of the workpiece(s)

- DC Current is commonly measured in Amperes (A)
- Surface area is commonly measured in square feet, square inches, square centimeters, square decimeters, etc.
  - Examples: A (Amperes) /ft² (Square Feet)…..A/dm²
- HCD = High Current Density    LCD = Low Current Density

[Diagram showing Hull Cell chamber with anode and cathode]

Alkaline Zinc Nickel Hull Cell Panel
Now that we know about.....
• The basics of electroplating
• The plating process
• Hull Cells and current density

Let's move on to Alkaline Zinc Nickel plating!!!
Alkaline Zinc Nickel plating characteristics….

- 12-17% Nickel in the plating deposit
  - Significantly improves the resistance of the sacrificial coating
- Coating thickness of 8-14µm
  - NSS performance 3-4 times that of Zinc over the same substrate
- Readily accepts trivalent chromate and topcoat

Diagram:
- Top Coat layer (.5-1 µm)
- Passivate Layer (100-350 nm)
- Zn/Ni layer (8-14 µm)
- Substrate
The Alkaline Zinc Nickel Chemistry

Alkaline Zinc Nickel plating bath components

- Alkaline Electrolyte solution
- Zinc metal in solution
- Nickel metal in solution
- Nickel Complexing Agent
- Brightener Additive
The Alkaline Zinc Nickel Chemistry

The Alkaline Electrolytic Solution.....

• Key component to the Alkaline Zinc Nickel bath
• Allows Zinc metal to stay in plating solution

Explaining the chemistry.....

• Zinc is insoluble in water where the pH is fairly neutral
• The solubility of Zinc increases when the pH is above 11
  • The addition of alkaline chemicals raises the pH allowing Zinc to exist as Zn\(^{2+}\) in the plating solution
    • Sodium Hydroxide (NaOH)
The Do’s and Don'ts: The Alkaline Electrolyte Solution

Typically referred to as the amount of “Caustic Soda” or “Caustic” in solution

• Plating chemical suppliers recommend an optimal concentration range based on the proprietary bath ratio

• We will refer to the concentrations as “Too High”, “Too Low”, or “Optimal” for the sake of today’s discussion
Troubleshooting: Caustic Soda

- Levels of caustic may be out of the optimal range for a variety of reasons
  - Bath dilution
  - Drag in/out
  - Incorrect additions

What it looks like……

Some 4A/20 minute long Hull Cells
The Do’s and Don'ts: The Alkaline Electrolyte Solution

High Caustic

Optimal Caustic

Low Caustic
The Do’s and Don'ts: The Alkaline Electrolyte Solution

As you can see there is little to no appearance difference on the panels....

High Caustic

Optimal Caustic

Low Caustic

.....but what about the deposit
The Do’s and Don'ts: The Alkaline Electrolyte Solution

Thickness Comparison

Low vs. High Caustic Thickness

Loss in Thickness and plating efficiency

Ni% Comparison

Low vs. High Caustic Nickel Deposit

Loss in Ni% uniformity in LCD
The Do’s and Don'ts: The Alkaline Electrolyte Solution

Maintaining the caustic concentration……..

High caustic levels
  • Uneven throw across current densities

Low caustic levels will not permit Zn\(^{2+}\) ions in solution to plate readily
  • Loss of plating efficiency
  • Loss of uniformity in LCD

Be mindful of other chemical additives that may contain some caustic soda.

The most efficient way to monitor caustic levels is through a simple titration analysis that can determine the caustic concentration of the bath*

*Note: Carbonate levels need to be considered
Zinc and its role in corrosion resistance

- Zinc makes up 83-88% of the plating deposit
- More corrosion resistant than steel in most natural atmospheres
- Often regarded as most economical means of corrosion resistance
- Provides a sacrificial coating on the workpiece
Concentration of Zinc may be out of the optimal range for a variety of reasons:

- Consumed during plating
- Drag in/out
- Dilution of the bath
- Improper replenishment
- Generator tank issues
The Do’s and Don'ts: Zinc Metal in Solution

High Zinc

Optimal Zinc

Low Zinc
The Do's and Don'ts: Zinc Metal in Solution

High Zinc

Optimal Zinc

Low Zinc
The Do's and Don'ts: Zinc Metal in Solution

When the Zinc concentration is not optimal, some issues are noticeable on the parts…

High Zinc

• Dull grey deposit

Optimal Zinc

• Streaks in the middle current area

Low Zinc
The Do’s and Don'ts: Zinc Metal in Solution

Thickness Comparison

Low vs. High Zinc Thickness

- Thickness (µm)
  - Low Zinc
  - High Zinc
  - Optimum Zinc

Distance from HCD Edge

Huge variance in plating efficiency

Ni% Comparison

Low vs. High Zinc: Nickel Deposit

- Nickel %
  - Low Zinc
  - High Zinc
  - Optimum Zinc

Distance from HCD Edge

Loss of Nickel uniformity
The Do's and Don'ts: Zinc Metal in Solution

Maintaining the Zinc concentration......

When the zinc concentration is lower than optimal

• Deposit thickness decreased throughout panel
• % Ni codeposition increased throughout panel
  • May cause ductility loss

When the Zinc concentration is higher than optimal

• Gray deposit appeared in HCD area
• Deposit thickness increased throughout panel
• % Ni codeposition decreased throughout panel

What to do....

• Maximize or limit Zinc generator use
• Add or remove Zinc sources (balls)
• Dilution (too high)
• Over the side additions (too low)

Regulating Zinc Concentration....

• Frequent bath analysis
  • Atomic Absorption spectroscopy (AA)
  • Titration
The Alkaline Zinc Nickel Chemistry

Nickel’s contribution to the sacrificial coating

• Nickel makes up 12-17% of the deposit
  • Nickel has superior corrosion resistance due to its slow rate of oxidation

• A Zinc-Nickel plated part performs 3-4 times better in Neutral Salt Spray testing than Zinc plated parts

1. At a co-deposit of 12-17% Ni: Corrosion potential is closer to Fe than to Zn

   Less Noble  Zn  Zn-Ni  Fe  Noble

   -1.1 V   -1.0 ~ -0.8 V   -0.6 V

Therefore, alloy dissolution SLOWER than rate of Zinc alone
Troubleshooting: Nickel Metal Concentration

- Concentration of Nickel may be out of the optimal range for a variety of reasons
  - Consumed during plating
  - Drag In/Out
  - Dilution of the bath
  - Improper replenishment
The Do’s and Don'ts: Nickel Metal in Solution

High Nickel

Optimum Nickel

Low Nickel
The Do’s and Don'ts: Nickel Metal in Solution

When the Nickel concentration is not optimal some issues will be noticeable on the parts…

High Nickel

Optimum Nickel

Low Nickel Panel

• HCD area gray deposit
• LCD dullness/haziness
The Do’s and Don'ts: Nickel Metal in Solution

Thickness Comparison

High Nickel can result in higher thickness throughout

Ni% Comparison

Variance in the Nickel deposit

Copyright(c) Dipsol of America, Inc. All Rights Reserved.  http://www.dipsolamerica.com
The Do’s and Don'ts: Nickel Metal in Solution

When the nickel concentration is lower than optimal

- Gray deposit appeared in HCD area
- % Ni codeposition decreased throughout panel
- Dullness/haziness developed in LCD area

What to do....

- Closely monitor Ni replenishments
  - Atomic Absorption Spectroscopy
  - Hull Cell XRF measurements

When the nickel concentration is higher than optimal

- Deposit thickness increased throughout panel
- % Ni codeposition increased throughout panel
  - Loss of ductility

 Nickel concentration can be difficult to determine

Maintained through consistent additions through Amp/Hour feeders.

- When the Nickel % in the deposit is outside of the optimum range corrosion performance will decrease
The Nickel Complexer Additives

- Proprietary chemical additives
- Stabilizes the Nickel ions in solution
The Do’s and Don’ts: Nickel Complexing Agent

Troubleshooting the Nickel complexing additive

- Concentration of Nickel complexing additive may be out of the optimal range for a variety of reasons
  - Broken down due to excess heat
  - Drag Out
  - Dilution of the bath
  - Improper replenishment
  - Low anode current density

What it looks like……
The Do’s and Don’ts: Nickel Complexing Agent

High Complexer

Optimum Complexer

Low Complexer
The Do’s and Don’ts: Nickel Complexing Agent

High Complexer

Optimum Complexer

Low Complexer
Low and high concentrations of Nickel complexer show some change in appearance:

- High Complexer
- Optimal Complexer
- Low Complexer

In the Mid to Low Current areas
- Dullness and haziness
The Do’s and Don’ts: Nickel Complexing Agent

Thickness Comparison

Low vs. High Complexer: Thickness

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Distance from HCD Edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Complexer</td>
<td>High Complexer</td>
</tr>
<tr>
<td>Optimum Complexer</td>
<td></td>
</tr>
</tbody>
</table>

Ni% Comparison

Low vs. High Complexer: Nickel Deposit

<table>
<thead>
<tr>
<th>Nickel %</th>
<th>Distance from HCD Edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Complexer</td>
<td>High Complexer</td>
</tr>
<tr>
<td>Optimum Complexer</td>
<td></td>
</tr>
</tbody>
</table>

Less uniform Nickel codeposition when not optimal
The Do’s and Don’ts: Nickel Complexing Agent

Less than Optimal.....
• % Ni codeposition decreased throughout the panel
• Dullness/haziness developed in MCD area

Higher than Optimal....
• % Ni codeposition increased throughout panel
• Dullness/haziness developed in MCD and LCD areas

What to do....
• Closely monitor complexer replenishments
  • Hull Cell XRF measurements

Can be analyzed with…
• UV/Vis or HPLC

Maintained through consistent additions through Amp/Hour feeders.
The Alkaline Zinc Nickel Chemistry

The Brightener Chemical Components….

• Additional proprietary chemicals

• Maintenance of appearance
  • Helps to maintain uniformity in appearance
  • Typically added in small amounts by a feeder system

….a little goes a long ways
The Do’s and Don’ts: Brightener

The performance of the brightener addition may be affected by the following:

- Consumed during plating
- Drag Out
- Dilution of the bath
- Over/Under replenishment

What it looks like......
The Do’s and Don’ts: Brightener

<table>
<thead>
<tr>
<th>Brightener Type</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Brightener</td>
<td><img src="image1.jpg" alt="High Brightener Image" /></td>
</tr>
<tr>
<td>Optimal Brightener</td>
<td><img src="image2.jpg" alt="Optimal Brightener Image" /></td>
</tr>
<tr>
<td>Low Brightener</td>
<td><img src="image3.jpg" alt="Low Brightener Image" /></td>
</tr>
</tbody>
</table>
The Do’s and Don’ts: Brightener

High Brightener

Optimal Brightener

Low Brightener
Too much or too little brightener additions will result in some appearance change

**High Brightener**
- Bright deposit throughout

**Optimal Brightener**

**Low Brightener**
- Dull deposit throughout
  - HCD prevalent
The Do’s and Don’ts: Brightener

Thickness Comparison

Low vs. High Brightener: Thickness

High Brightener can drastically lower plating efficiency

Ni% Comparison

Low vs. High Brightener Nickel Deposit

High brightener will lower LCD Nickel deposit
The Do’s and Don’ts: Brightener

When the brightener concentration is less than optimal

• Dullness throughout the panel
• Rough HCD deposit

What to do….

• Tightly monitor feeder rates

When the brightener concentration is higher than optimal

• Deposit thickness decreased in HCD area
• Brightness of deposit increased throughout panel

What to do….

• Visual testing
  • Adjustments via Hull Cell

Some other issues that may occur…

• Excess brightener
  • Brittleness or cracking

Another case of low brightener
The operating temperature of an Alkaline Zinc Nickel bath is often overlooked.

The following are examples of a bath that is optimally ran at 25°C/77°F
- High at 90°F
- Low at 60°F
The Do’s and Don’ts: Temperature

High Temperature

Optimal Temperature

Low Temperature
The Do’s and Don’ts: Temperature

High Temperature

Optimal Temperature

Low Temperature
The Do’s and Don’ts: Temperature

Some minor changes in appearance……

High Temperature

Optimal Temperature

Low Temperature

High Temperature
• Streaking in HCD Area

Low Temperature
• LCD Dullness
The Do’s and Don’ts: Temperature

**Thickness Comparison**

Low vs. High Temperature: Thickness

![Graph showing thickness comparison between low and high temperature](image)

**Ni% Comparison**

Low vs. High Temperature: Nickel Deposit

![Graph showing nickel percentage comparison between low and high temperature](image)

Direct relationship between temperature and plating speed

Can change uniformity of Ni deposit
The Do’s and Don’ts: Temperature

When the temperature of the bath is not closely monitored, here’s what can happen…

**High Temperature**
- Streaking in the HCD area
- Deposit thickness increased throughout the panel
- Lower Nickel codeposition throughout

**Low Temperature**
- Lower Thickness and Nickel codeposition throughout
- LCD dullness

Low Temp….

…..Low Speed
So today we briefly explained the importance of process control for Alkaline Zinc Nickel.

A brief introduction to electroplating:
- The process itself
- Hull Cells
- Why Zinc Nickel?

The Chemistry:
- Alkaline Electrolyte Solution
- Zinc
- Nickel
- Nickel Complexer
- Brightener
- Bath Temperature

What to look for when troubleshooting:
- High and Low conditions
- Appearance Issues
- Thickness
- Nickel Deposit
People, goods, eco-friendly world
Sophisticated Company of Metal Surface Finishing Treatment.
New Innovation and technologies are created / developed by DIPSOL.

Thank you. Questions & Discussion