HAVALLOY Z-N
ALKALINE ZINC-NICKEL ALLOY PROCESS

HAVALLOY Z-N is a functional alkaline cyanide-free process specially designed for plating on complicated shaped parts to obtain high performance zinc alloy deposits containing 13-15% Nickel by weight.

HAVALLOY Z-N allows for uniform deposition across a wide range of current densities and offers the unique advantage of accepting clear, iridescent, and superior black (non-silver) chromate coatings.

HAVALLOY Z-N conforms to many automobile manufacturing specifications, including heat aging requirement.

OPERATING PARAMETERS:

<table>
<thead>
<tr>
<th>Component</th>
<th>Optimum</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Metal</td>
<td>1.3 oz/gal (10.0 g/l)</td>
<td>0.8 - 1.6 oz/gal (6.0-12.0 g/l)</td>
</tr>
<tr>
<td>Nickel Metal</td>
<td>2000 ppm</td>
<td>1200 - 2500 ppm</td>
</tr>
<tr>
<td>Caustic Soda (Sod Hydroxide)</td>
<td>17.4 oz/gal (130 g/l)</td>
<td>14.7-18.7 oz/gal (110-140 g/l)</td>
</tr>
<tr>
<td>Na2CO3 (Sodium Carbonate)</td>
<td>&lt; 10.0 o/gal (75g/l)</td>
<td></td>
</tr>
<tr>
<td>HAVALLOY Z-N MU</td>
<td>12.0 % by/vol</td>
<td>10.0 – 14.0 % by/vol</td>
</tr>
<tr>
<td>HAVALLOY Z-N R</td>
<td>1.5 % by/vol</td>
<td>1.25 – 1.75 % by/vol</td>
</tr>
<tr>
<td>HAVALLOY Z-N Brightener</td>
<td>0.4 % by/vol</td>
<td>0.2 – 0.6 % by/vol</td>
</tr>
<tr>
<td>HAVALLOY Z-N LCD</td>
<td>0.2 % by/vol</td>
<td>0 - 0.4 % by/vol</td>
</tr>
<tr>
<td>Current Density (cathodic)</td>
<td>9.3 ASF (1.0 A/dm²)</td>
<td>7-11 ASF (0.75 – 1.25 A/dm²)</td>
</tr>
<tr>
<td>Current Density (anodic)</td>
<td>9.3 ASF (1.0 A/dm²)</td>
<td>9.3-18.6 ASF (1.0 – 2.0 A/dm²)</td>
</tr>
<tr>
<td>Anode / Cathode Ratio</td>
<td>2:1</td>
<td></td>
</tr>
<tr>
<td>Voltage</td>
<td>12 – 18 V</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>73°F (23°C)</td>
<td>68 – 80°F (20 – 27°C)</td>
</tr>
</tbody>
</table>

BATH MAKE-UP:

<table>
<thead>
<tr>
<th>MAKE-UP COMPONENTS</th>
<th>1000 GALLONS</th>
<th>1000 LITERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAVALLOY Z-N MU</td>
<td>120 Gallons</td>
<td>120 Liters</td>
</tr>
<tr>
<td>HAVALLOY Z-N R</td>
<td>15 Gallons</td>
<td>15 Liters</td>
</tr>
<tr>
<td>HAVALLOY Z-N Brightener</td>
<td>4 Gallon</td>
<td>4 Liter</td>
</tr>
<tr>
<td>HAVALLOY Z-N LCD</td>
<td>2 Gallons</td>
<td>2 Liter</td>
</tr>
</tbody>
</table>

1. Add 25% of final volume to operating tank of DI water.
2. Add 63 gallons / liters of HPC Zinc Sol (22oz/gal zinc metal/72oz/gal Membrane Grade NaOH.)
3. Add 820 lbs NaOH (Caustic Soda / Sodium Hydroxide) Membrane Grade.
4. Dilute tank to within 90% of operating volume with DI water.
5. Continue stirring, and mix the following components-one at a time- IN THE ORDER LISTED:
6. Add water to bring the volume to 1000 gallons and mix thoroughly.
7. Dummy plate at 30 ASF for up to 75 amp/hr per gal.
8. After the color of the solution changes from violet to brownish color, the bath is ready.
EQUIPMENT:

Tanks  Steel covered with Polypropylene or PVC

Heating / Cooling  Cooling coils made of stainless steel, titanium.

Filtration  Continuous recommended, 2 to 4 tank volumes per hour throughput, 10 micrometer mesh filter media.

Electrolyte agitation  2 – 4 m/min
Only use a slight air agitation.

Barrel rotation  4 – 8 rpm

Anodes  It is recommended to use insoluble anodes in the working tank (Nickel anode plates or semi-bright nickel plated steel - DO NOT USE STAINLESS STEEL, DO NOT USE TITANIUM BASKETS!) Have a separate Zinc generator tank connected via bypass to the working tank. THIS IS HIGHLY RECOMMENDED! The Zinc generator should have a volume of approx. 10 – 15% that of the plating tank (see fig. 1 below)

Anode : Cathode ratio  1:1 to 1.5 :1  The area ratio of anode to cathode should not exceed a value of 2:1.

Rectifier  15 – 20 V (for barrel plating)
6 – 12 V (for rack plating)

![Fig. 1](image-url)
PROCESS CONTROL:

<table>
<thead>
<tr>
<th>Product</th>
<th>ml / 1000Amp/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAVALLOY Z-N MU</td>
<td>400</td>
</tr>
<tr>
<td>HAVALLOY Z-N R</td>
<td>600</td>
</tr>
<tr>
<td>HAVALLOY Z-N Brightener</td>
<td>175</td>
</tr>
<tr>
<td>HAVALLOY Z-N LCD</td>
<td>25</td>
</tr>
</tbody>
</table>

HAVALLOY Z-N MU and HAVALLOY Z-N R and HAVALLOY Z-N Brightener and LCD may be pre-mixed together for ease of additions by amp/hr.

Regular additions of HAVALLOY Z-N R are made according to analytical results. 1 ml/l Z-N R will increase the nickel content by 100 ppm. Please add slowly into the plating tank under vigorous agitation. Keep the nickel content always as constant as possible.

Regular additions of HAVALLOY Z-N MU are made along with additions of HAVALLOY Z-N R. For every 600 mls of HAVALLOY Z-N R, add 400 ml HAVALLOY Z-N MU. NOTE: Z-N MU and Z-N R can also be mixed together for added convenience when making additions. Please add slowly into the plating tank under vigorous agitation.

Additional HAVALLOY Z-N Brightener additions are required only if brightness decreases and by utilizing Hull Cell analysis.

Under normal circumstances, HAVALLOY Z-N LCD is added only as a corrector, as impurities that cause LCD haze are carried into the electrolyte by the drag-in from preceding tanks. As rough guideline, use 100 ml HAVALLOY Z-N LCD for every 2.2 lbs / 1 kg NaOH replenished or depending upon Hull Cell results (Attention, always use steel anode for Hull Cell testing).

RECOMMENDED PROCESS CYCLE:

⇒ HAVAKLEAN KP (or equivalent high quality soak cleaner)
⇒ Rinse
⇒ KP ELECTROCLEAN EXP
⇒ Rinse
⇒ Rinse
⇒ Rinse
⇒ HCl pickle
⇒ Rinse
⇒ Rinse
⇒ Pre-Dip/Neutralization (optional) using 25 g/l NaOH
⇒ HAVALLOY Z-N
⇒ Triple Rinse
⇒ Dry
PROCESS NOTES:

NIKEL METAL
The percentage of nickel in the deposit depends upon the nickel concentration in the plating bath. Keep the nickel concentrations within the ranges previously listed. Low nickel concentrations will create deposits with less than 12% nickel, resulting in reduced corrosion protection. High nickel concentrations create deposits with greater than 16% nickel and result in brittleness.

The nickel anodes do not supply nickel metal to the bath. Replenish the nickel using HAVALLOY Z-N R. 1ml/liter ZN-R will raise the nickel content by 100 ppm.

NOTE: X-Ray fluorescence (thickness tester) is required to determine the alloy content of zinc and nickel in the zinc-nickel deposit.

NOTE: MAINTAIN THE ZINC TO NICKEL RATIO AT 5 to 6:1

IMPROVING CONTROL OF ZINC METAL CONCENTRATIONS:
Use a zinc generator (side) tank to supply metal to the plating tank. This will improve control of the zinc concentration and minimize roughness caused by film blow-off and anode passivation.

ZINC GENERATOR REQUIREMENTS:

• Size the generator tank to be 10-15% of the plating tank volume.

• Use zinc balls in steel baskets or zinc slabs in expanded steel trays (promotes faster metal dissolution). Steel baskets must have a blue film (mill/weld scale) and should not be welded to the generator tank.

• Use ventilation to remove sodium hydroxide mist and hydrogen gas

• Install a filter between the zinc generator and plating tank to remove zinc fines and sludge.

• Install a bypass line to filter only the bath when the zinc concentration has reached desired levels.

• Pump the plating solution through the generator tank, and re-circulate to the plating tank (sodium hydroxide concentration will influence the rate of zinc dissolution).

EQUIPMENT & MECHANICAL REQUIREMENTS:

HEATER: Teflon coils or titanium heat exchanger insulated to prevent circuit problems.

CHILLERS: Teflon coils or titanium heat exchanger insulated to prevent circuit problems.

POWER SUPPLIES: For rack applications -12 volts recommended (on smaller installations, 8 volts). For barrel, a variable 15-volt rectifier is required. In rack and barrel, low ripple (<10%) rectification is required.

VENTILATION: Welded or threaded PVC recommended (PVC glued joints may fail).
TANK: Plating tank must be lined. Koroseal, rubber, polyethylene or polypropylene are recommended tank linings. Fiberglass linings are not recommended because of the possible solubility of their bonding resins.

NOTE: PVC glued joints may fail.

PIPING: Clean, welded or threaded PVC, polypropylene, and mild steel (if kept out of the circuit) are suitable. CPVC and glued PVC must be used.

FILTRATION: Continuous filtration through a 5-10 micron siliceous-type filter aid (such as diatomaceous earth) is necessary to maintain the bath. The bath turnover rate should be at least 2-3 times per hour. To remove the buildup of impurities, the filter should be packed with tube carbon filters or fresh carbon every two weeks for a more consistent alloy composition.

AGITATION / CIRCULATION: For optimum results, used a separate pumping system from the filtration setup and return the solution through a series of flo-ductors placed below the cathode. Limited mechanical agitation will improve bath throwing power (1-2 bath turnover per hour)

ANODES: Use nickel slab anodes. Do not use nickel balls in titanium baskets. Titanium’s poor conductivity in alkaline solutions limits the amount of current carried by the solution. Use an anode to cathode surface ration of 2:1 for optimum bath efficiency. Nickel plated steel plates can be used as long as the nickel plate is continuous and 25 microns thick at all times. 

NOTE: Barrel plating example – A 36” X 16” barrel, 7 anodes (4” wide) per anode bar

CARBONATE REMOVAL: A suitable off-line tank, with chilling equipment, is required to cool up to 20% of the total solution volume to at least 32°F (0°C). Steel mesh in the tank will help crystallize the carbonate.

ZINC GENERATOR: Required to maintain the zinc content of the solution (See notes on Zinc metal).

PROCESS NOTES:

PRE-PLATE TREATMENT: The HAVALLOY Z-N PROCESS is an alkaline non-cyanide system and does not have the built-in cleaning ability of a cyanide bath. Good control and maintenance of the cleaners and acid pickle is essential for consistent deposit quality. The HAVALLOY Z-N PROCESS should be preceded by the typical soak and electrocleaners used in alkaline non-cyanide zinc plating.

PREDIP
A reverse current (12v/30 Amp/sq. ft) pre-dip of sodium hydroxide (Membrane Grade) 8-10 oz/gal (60-75 g/L) is optional. The predip removes acid film and prevents flash rusting of the substrate. Do not rinse between the pre-dip and the plating tank.
ANALYTICAL PROCEDURES:

ZINC METAL:

1. Pipette 5 mL of plating solution into a 250 mL Erlenmeyer flask.
2. Add 50 to 75mLs Alkaline Zinc Buffer Solution until solution turns clear
3. Add about 0.2 gram Zylenol Orange Indicator Mix
4. Titrate immediately with 0.1 M EDTA Solution to a yellow/orange endpoint.
5. Record Result

CALCULATION: mls of 0.1M EDTA x 0.174 = oz / gal zinc
                   mls of 0.1M EDTA x 1.3033 = g/L zinc

RANGE: 0.8-1.8 oz/ gal (6-13.5 g/L)  RECOMMENDED: 1.4 oz/gal (10.5 g/L)

NICKEL METAL:

Use standard Atomic Absorption to analyze

RANGE: 0.16-0.33 oz/gal (1.2-2.5 g/L)  RECOMMENDED: 0.27 oz/gal (2.0 g/L)

SODIUM HYDROXIDE:

1. Pipette a 5 mL bath sample into a 125 mL Erlenmeyer flask.
2. Add 25 mL of 10% Barium Chloride Solution and mix well
3. Add 2-3 drops of Phenolphthalein indicator and titrate with a 1.0 N Sulfuric Acid solution until the red color turns to milky white.
4. Record Results.

CALCULATION: mls of 1.0 N H₂SO₄ x 1.07 = oz/gal Sodium Hydroxide
                  mls of 1.0 N H₂SO₄ x 8 = g/L Sodium Hydroxide

RANGE: 14.7 – 18.7 oz/gal (110 to 140 g/L)  RECOMMENDED: 17.4 oz/gal (130 g/L)
TROUBLE SHOOTING GUIDE:

<table>
<thead>
<tr>
<th>Problem</th>
<th>Cause</th>
</tr>
</thead>
</table>
| High Nickel in Deposit | >High nickel in the solution  
|                     | >High zinc content                           
|                     | >High solution temperature                    
|                     | >High NaOH content                           |
| Dullness in LCD areas | >Low HAVALLOY Z-N LCD                        |

SAFETY INFORMATION:

Additives may cause skin irritation. Use chemical goggles and rubber gloves when handling. Always read the Material Safety Data Sheet for any chemical product to ensure familiarity with the methods of safe handling and the health hazards associated with the product.

WASTE DISPOSAL:

Wastes must be tested using methods described in 40 CFR Part 261. It is the generator’s responsibility to determine if the waste meets applicable definitions of hazardous wastes. Dispose of waste material according to Local, State, Federal, and Provincial Environmental Regulations.

When empty, containers may still be hazardous because of product residue. All labeled hazard precautions must be observed.

Consult MSDS for additional safety and waste treatment information.

NON-WARRANTY:

The data contained in this bulletin is believed by Haviland Products Company to be true, accurate and complete. However, since final methods of use for this product are in the hands of the customer and beyond our control, we cannot guarantee that the customer will obtain the results described in this bulletin. Haviland Products Company cannot assume any responsibility for the use of this product by the customer in any process, that may infringe the patents of third parties.

Revised March 23, 2010  Approved: Graham M. Torr, CEF  
Revised February 2, 2010  Approved: Dave White