



Finishers' Think Tank

Stephen F. Rudy, CEF • Enequist Chemical Co.

100 Varick Avenue • Brooklyn, NY 11237 • 718/497-1200 • E-mail: sfrudy@aol.com

2001: A Plating & Surface Finishing Odyssey The Journey Continues, Part 4

Departing our shuttle bus at the Central Zincway Depot, we learn there will be a one-hour delay before continuing our tour of Zincmalia. A routine inspection of ZN Tube #1 found a few loose rail spikes at milepost 48. These will be replaced with a fresh set of hot-dipped, zinc-galvanized spikes. Our tour leader informs us of lingering water collection after heavy rains in that area. He tells us that a hill overlooking the tracks is concentrated with salt deposits. Saline run-off mixes with water drainage flowing down the hill. This solution collects at milepost 48. It's been 30 years since the spikes required changing. We agreed, a quality zinc finish is a great corrosion fighter. Just knowing that zinc "paves the way of our trip," fueled our eagerness to get going.

After a refreshing pint of local ale at the Valence 2 Pub, we board the *P&SF* express, departing from track 65.4. Speeding along, we cross Sacrificial Bay, snapping pictures of the beautiful scenery. Over land, our train approaches Mt. Zinco, with its majestic, bright, leveled peak.

Soon the landscape opens, revealing Chromate Park, a spacious preserve, splashed with colors of blue, yellow, iridescent, green, and black. Right on schedule, the express pulls into the *Alkaline Zinc* state. Our shuttle departs, making its way on the Cyanide-Free Expressway. After a short commute, we exit on to Zincate Boulevard, pulling up to the visitor's bureau. Our tour guide reviews the itinerary before we enter the *Alkaline Zinc* technical grounds.

Alkaline Zinc

This state was incorporated approximately 40 years ago, based on applied, electroplating process development. Its call to fruition grew out of envi-

ronmental concerns and tightening waste treatment restrictions in western Europe. The basic solution, rack and barrel, may consist of the two separate formulations (see chart).

Of major concern was substituting the complexing effectiveness of cyanide. This was initially achieved by incorporating substituted amines, EDTA derivatives, and gluconates. However, two major problems arose:

- Complexation of iron, resulting in detrimental zinc - iron alloy deposits. This significantly altered the preferred aesthetic deposit appearance, and greatly reduced corrosion protection after chromating.
- New waste treatment problems. Metals such as copper and nickel were being strongly complexed by additives in the alkaline zinc solution effluent.

These problems occurred immediately. Two other conditions that had to be addressed were:

- Deposit hazes, streaks, and blistering.
- Delayed blistering.

At first, the incorporation of very small amounts of cyanide (less than 0.1 oz/gal or 0.75 g/L) in the brightener was helpful. But this did not make the system cyanide-free. Returning to the drawing boards, a series of specialized organic compounds were developed that actually provided the necessary process corrections. These compounds are non-chelating and non-

Formula 1		
Component	Conc., oz/gal	Conc., g/L
Zinc metal	1-1.5	7.5-11.25
Sodium hydroxide	10-16	75-120
Formula 2		
Component	Conc., oz/gal	Conc., g/L
Zinc metal	1.5-3.5	11.25-26.25
Sodium hydroxide	15.5-20.5	116.2-153.8

Note: Sometimes the addition of 2-4 oz/gal (15-30 g/L) of sodium carbonate (soda ash) to a new plating solution benefits deposit characteristics. The ratio of sodium hydroxide to zinc metal—approx. 10:1. Recommended purities: zinc metal (<99.9%), sodium hydroxide (<99.5%).

complexing. Iron is not chemically bound, and no additional burden is placed on the waste treatment system. This is a tremendous benefit. Discharge effluent, upon confirmation of actual analysis and bench testing, can be simply pH adjusted to separate precipitated zinc. Dedicated R&D and process refinements improved the organic additives, resulting in these typical alkaline zinc deposit characteristics:

- Superior deposit distribution, due to improved coverage and throwing power.
- Uniform, bright deposits over the entire typical plating range.
- Low internal stress. Avoidance of deposit blistering (post and after baking).
- Good receptivity to chromates.

Similar to several other plating solution chemistries, the organic addition agents are synthesized and refined to a very high purity. Minimizing the co-deposition with zinc of carbon from the organic additives essentially corrected the problem of delayed blister-

ing of alkaline zinc-plated parts. Without the magic of these materials, the alkaline deposit would be a flat, powdery, loosely adherent film.

Deposit streaks, haze, and blistering predominantly occurred as a result of insufficient surface preparation (cleaning, rinsing, pickling, and activation). Without cyanide in the zinc solution, the pre-plate cycle became more of a challenge. Attention to detail readily eliminated these problems.

Under The Hood

The important, critical contributions of the bath components are described as follows:

- **Zinc.** The metal concentration is the heart and pulse of the system. Its level strongly influences plating speed (rate of deposition) and cathode efficiency.
- **Sodium Hydroxide.** Maintains the zincate complex (prevents zinc precipitation), provides solution conductivity, and anode corrosion. The conductivity of Formula 2 is much better than Formula 1.
- **Brightener(s).** Many commercial processes are maintained with two such distinctly functioning materials. They may be referred to as brightener and carrier. Each cannot function effectively without the other complement. By co-depositing, the optimum deposit characteristics are achieved.
- **Purifier.** Sulfide-free, organic type. Minimizes detrimental affects of heavy metal contaminants.
- **Wetting Agent.** The alkaline zinc solution produces corrosive mist and spray when it's being electrolyzed. This organic additive produces a stable, thin foam blanket, typically eliminating over 90% mist & spray.

The Owner's Manual

- Cathode efficiency ranges from 50-80% (Formula 1) to 65-95% (Formula 2).
- Rectification should produce below 10% ripple.
- Deposition rate. In ten minutes at 10 ASF, considering 80% efficiency, thickness is approx. 0.08 mils. Under the equivalent conditions at 1.1 A/dm², the average thickness is 2 microns.
- The ease of chromating and chroming

Troubleshooting Guide: What's Wrong/Making it Right

Defect	Probable Cause	Correction
dull deposit	brightener/carrier low	adjust concentration
dull deposit	high temperature	cool to operating range
blistering	high brightener/carrier	adjust concentrations
blistering	poor surface preparation	correct as required
burnt deposit	high current/cold bath	adjust as required
burnt deposit	low zinc/high caustic	adjust as required
thin deposit	wrong current density	adjust as required
thin deposit	low zinc/anodes polarized	increase anode area, lower current
poor throw	high zinc/high temperature	adjust as required
roughness	suspended particles	filter to remove
bad chromate	post-plate rinsing	dump, refresh, improve rinsing
bad chromate	zinc bath metal contaminant	add purifier, dummy, zinc dust treat
bad chromate	chromate aged, out of spec	replace chromate
no plating	electrical	check buss, cable, connections

Horsepower & Specifications

Parameter	Range	Optimum
Bbl cathode current density	5-15 ASF (0.5-1.6 A/dm ²)	10 ASF (1.1 A/dm ²)
Rack cathode current density	5-50 ASF (0.5-5.4 A/dm ²)	25 ASF (2.7 A/dm ²)
Barrel voltage	12-15	13.5
Rack voltage	3-8	5.5
Ratio anode:cathode	1:1 - 2:1	1.5:1
Temperature	65-125°F (18-52°C)	80-90°F (27-32°C)

Note: Heavy demand production plating will warm the bath. Outdoor/indoor summer-like conditions also contribute to higher solution operating temperatures. Industrial chillers are recommended to maintain operating temperature range.

mate receptivity is better on deposits plated from Formula 2.

- High-current-density ductility of Formula 2 deposits are better than Formula 1 deposits.
- Filtration may range from 1-2 solution turnovers/hour. 5 micron or less sized filter cartridge or a horizontal plate filter may be used.
- Agitation using the eductor type of solution movement is strongly recommended. Air is not recommended.
- Zinc generator. Some of the larger plating baths draw replenishment solution from a "farm bath" or "milk cow." This solution is a modified alkaline zinc bath. The dissolution of zinc is controlled by the zinc surface area corroded in the caustic bath.

Anode baskets Mild steel
Anode bags Dynel or polypropylene (thoroughly leached & rinsed)

Steel equipment, compatible with cyanide zinc, can also be used in alkaline zinc.

Tune Up

The plating process depletes active concentrations of the bath components (this includes organic addition agents). Solution drag-out also affects their concentrations. Analysis of zinc metal and sodium hydroxide are rapidly and accurately determined by titration procedures. The Hull cell is used to evaluate the overall deposit characteristics and requirements for the organic additives.

Most suppliers of zinc plating technologies provide wet analytical and Hull cell methods, with appropriate corrective actions. Their proprietary additives are very compatible with automatic additions on an ampere hour basis.

For those who desire more in-depth, related information, log on the AESF website (www.aesf.org). It opens a

Equipment

Equipment	Description
Tanks, liners	Koroseal-lined steel, polypropylene, CPVC
Pumps	Steel/stainless steel
Heaters	Stainless steel, PTFE
Filters	Polypropylene
Anode hooks	Stainless steel, mild steel, or monel

treasure chest of technical and practical information, from technical articles and committees to training courses, conferences and the bookstore.

Probably the most critical problems that occur are those related to poor surface preparation. Essentially, the cleaning and activation before alkaline zinc should be as good as the levels achieved prior to acid zinc, acid copper, and bright nickel plating. Pre-dips immediately preceding the alkaline zinc bath are very helpful. Typical solutions consist of 2-5 oz/gal (15-37.5 g/L) of sodium hydroxide, with optional add of a hard water conditioner (an organic acid salt). Post-dips, containing approximately 0.25 percent v/v nitric acid, neutralize the surface and condition the deposit before chromating. In some blue chromate (clear) applications, additional fluoride in the chromate enhances development of the desired film.

Meeting at the tour conclusion, we all gained a new perspective for alkaline zinc plating. The ability to plate bright, ductile deposits from rack and barrel solutions is noteworthy. Aged deposits retain a white appearance. Improvements in technology, maintenance, and applications have lowered the overall alkaline zinc operating costs.

We noted a positive, upbeat attitude and very knowledgeable hosts during our tours and meetings in the *Alkaline* state. Our freshly washed and waxed shuttle bus pulled up. To everyone's surprise, our hosts affixed a pennant alongside our bus, reading "Alkaline as Detroit's MVP Outfielder." With a firm grip on the wheel, our driver guided the bus back on to Zincate Boulevard, for the ride to the Alkaline Zinc Depot. Our train awaits us for departure to *Alloy Zinc* state. There are many districts to visit in this state. Our first stop should be to the oldest and most honored state—*Brass*. *P&SF*