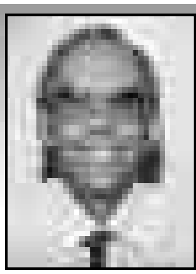

Finishers' Think Tank

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2001: A Plating & Surface Finishing Odyssey The Journey Continues, Part 3

As the *P&SF* Express pulled out of Orlando in February, we reviewed some of the features and applications of zinc plating in this column's travel brochure. With great anticipation, the Express sped along the orange groves to our first stop.

Welcome to Zincmalia. This is perhaps the most densely packed land of zinc plating. Its geographical boundaries include these industrious states: Acid, Alkaline, Cyanide, Alloy, and Galvanize. Our initial border crossover into Zincmalia enlightened us as to the region's continued strength and prosperity: cheapest metal to electroplate and excellent sacrificial corrosion protection. There is no indication that zinc's position in our industry will change. Barrel, rack, continuous strip, and hot dip process lines all provide a large variety of finished parts. Worldwide markets include: consumer, commercial, engineering, functional, military, aerospace, and automotive. No wonder Zincmalia operates on a nonstop universal schedule. Let's visit our first state, updating its maintenance, control, and individual contributions to zinc finishing.

Cyanide

This state contributed much of the technology development and experience related to zinc plating. For several decades, cyanide zinc plating was a major backbone of zinc finishing. Ecological considerations, waste treatment upgrades, and newer process developments have increased the applications of acid, alkaline, and alloy zincs. These states eagerly await the *P&SF* Express. Our present trip itinerary has our train pulling into Port Cyanide station, to review cyanide zinc plating. We make a quick exit to Technology Blvd., confirming the chemistry that makes it work.

Bath Constituents—Low-Cyanide Bath

Constituent	Range oz/gal	Opt. oz/gal	Range g/L	Opt. g/L
Zinc metal	1.0-2.0	1.3	7.0-15.0	10.0
* Zinc oxide	1.2-2.5	1.7	9.0-19.0	12.5
* Zinc cyanide	1.8-3.6	2.3	13.5-27.0	20.2
Sodium cyanide	1.5-4.0	2.4	11.0-30.0	18.0
Sodium carbonate	8.5-12.0	10.2	63.8-90.0	76.5
Caustic soda	10.7-12.0	11.3	80.0-90.0	85.0

* Optional to add either zinc oxide or zinc cyanide
Ratio of sodium cyanide to zinc metal: Range (1.5-2.2) optimum = 1.8

Bath Constituents—Medium-Cyanide Bath

Constituent	Range oz/gal	Opt. oz/gal	Range g/L	Opt. g/L
Zinc metal	2.0-3.35	2.7	15.0-25.0	20.0
* Zinc oxide	2.5-4.0	3.4	19.0-31.0	25.0
* Zinc cyanide	3.6-6.0	4.9	27.0-45.0	36.0
Sodium cyanide	4.0-8.7	6.7	30.0-65.0	50.0
Sodium carbonate	9.0-12.6	10.7	67.5-94.5	81.0
Caustic soda	8.0-10.7	9.3	60.0-80.0	70.0

* Optional to add either zinc oxide or zinc cyanide
Ratio of sodium cyanide to zinc metal: Range (2.0-3.0) optimum = 2.5

Bath Constituents—High-Cyanide Bath

Constituent	Range oz/gal	Opt. oz/gal	Range g/L	Opt. g/L
Zinc metal	4.0-5.4	4.7	30.0-40.0	35.0
* Zinc oxide	5.0-6.7	5.9	37.0-50.0	44.0
* Zinc cyanide	7.2-9.7	8.4	54.0-72.8	63.4
Sodium cyanide	10.0-14.7	12.3	75.0-100.0	87.5
Sodium carbonate	8.0-12.6	11.0	60.0-94.5	77.2
Caustic soda	10.0-12.0	11.0	75.0-90.0	82.5

* Optional to add either zinc oxide or zinc cyanide
Ratio of sodium cyanide to zinc metal: Range (2.5-3.5) optimum = 3.0

Three distinct cyanide level baths: low, medium, and high comprise the working electrolytes.

Safety Caution

Cyanide additives and the plating solution formulas listed are poisonous and corrosive. Always read the appropriate MSDS sheets to understand the risks and health hazards. Use the recommended safety clothing and related equipment when handling these additives and the plating solutions. Consult with responsible plant personnel, vendors, and safety engineers.

Each of the plating solutions, when correctly mixed and prepared, chemically form two distinct electrolytes:

Sodium zinc cyanide .... $Zn(CN) + 2NaCN = Na_4Zn(CN)_4$
Sodium zincate .... $Zn + 4NaOH = Na_2Zn(OH)_4$

In preparing the solution, about 75-90 percent of the zinc metal forms the Sodium Zincate complex, with the remainder in the form of sodium zinc cyanide. Each bath constituent contributes specifically to the plating operation.

- Zinc Complexes—A secondary source of metal, complementing the anodes.
- Cyanide—Functions as a "carrier" for metal deposition. Additional properties include: enhancing effectiveness of the organic brightener agents, promoting satisfactory deposit adhesion, promotes anode corrosion & cathode efficiency, and "last stop" cleaning and descaling.
- Caustic Soda—Helps prevent anode polarization, contributes to zinc deposition rate & speed, and improves coverage of complex shaped parts.
- Sodium Carbonate—Promotes deposit fine grain structure.

Analysis

The plating process depletes active concentrations of the bath salts. Solution drag out also affects their concentrations. All of these bath components can be readily analyzed by simple, very accurate titration procedures. Addition agents (brighteners) such as: aldehydes, long chain alcohols, inner transition metals, and complexing agents in specific ratios, produce a modified deposit grain structure. The resulting deposit exhibits good brightness and leveling throughout the operating current densities. Concentration of a polysulfide additive (purifier) is maintained to precipitate metallic bath contaminants, such as copper. After confirming concentration of bath salts with appropriate additions, the hull cell method is used to monitor desired level of the brightener. Polysulfide test papers are normally sufficient for semi-quantitative determination of the purifier.

Equipment

The bath doesn't require lined tanks or special corrosion-resistant equipment. Related cost savings are realized.

Tank—Mild steel, reinforced polypro, or fiberglass.

Operating Parameters
Low - Medium - High Cyanide Baths

Parameter	Rack	Barrel
Cathode Current Density	1-20 ASF	3-6
Voltage	3-6	9-18
Temperature	65-120°F (18-49°C)	65-120°F (18-49°C)
Anodes	*High purity grade only	*High purity grade only
Current Efficiency	60-90%	60-90%
Anode/Cathode ratio	1.5:1.0 or 2.0:1.0	1.5:1.0 or 2.0:1.0

* >99.99% pure zinc. This is very important to avoid cadmium contamination. Steel may also be used to help control desired zinc metal concentration.

Under the Hood Troubleshooting Guide

Defect	Probable Cause
Poor adhesion	Poor surface prep. Hex-chrome contamination. Delayed blistering due to hydrogen absorption. Bath out of balance.
Burnt deposit	Low cyanide and or caustic levels. Excess current.
Hazy, deposit stains	Organic/metallic contamination. Solution/brightener out of balance.
Dark deposit	Organic/metallic contamination. Solution/brightener out of balance.
Low conductivity	Low temp. Low: zinc, caustic, cyanide or combination
Poor throw	High conc.: zinc, caustic, cyanide or combination.
Shelf roughness	Suspended solids in bath.
Polarized anodes	Improper anode area. Low: cyanide, caustic or combination.
Zinc conc. rises	Excessive anode area.
Cold bath crystallizes	High carbonates. Contributes to anode polarization & low cond.

Cooling—Coil or chiller recommended to maintain below upper temperature limit.
Ventilation—*Mechanical to maintain levels below permissible exposure limits.
Anode Baskets—Steel
Agitation—Not essential. Non air-agitated solution movement is preferred.
Filtration—Not essential. Good for particulate removal.

*Organic wetting agents do form a stable, thin foam blanket during plating. This significantly reduces corrosive mist and spray. Care should be taken to prevent thick, stable foam blankets, that may result in hydrogen gas explosions.

Owners Manual

The majority of commercial zinc platers have some exposure to cyanide zinc plating. The deposit typically meets the finish applications for a wide variety of industry parts. Bright cyanide zinc deposits develop aesthetically "chrome white" deposits and with application of a chromate conversion coating, provide excellent corrosion protection. Baths are easy to operate and maintain. By optimizing the basic operating parameters (plating current density, time, temperature, concentrations of salts & addition agents, surface preparation), exceptional throwing power and coverage are realized. Solution temperature and bath chemical composition especially affect plating speed and current efficiency. A minimum of 0.0002-in. zinc thickness is required for sufficient chromating. Most commercial applications require at least 0.00025-in. zinc, readily meeting most thickness requirements. Steel parts such as: stampings, welded frames, fasteners, washers, nuts, bolts, and nails are easily cyanide zinc plated. In this system, iron is not a contaminant.

Troubleshooting Tips

- High zinc metal concentration reduces throwing power and increases the burning limit. Low zinc metal contributes to deposit burning.
- High sodium cyanide level reduces brightness, contributing to increased additive brightener con-

sumption. Low cyanide produces a brittle zinc layer. Maintaining a sufficient cyanide concentration reduces bath sensitivity to impurities.

- Higher caustic concentration increases the rate of anode dissolution (increasing solution zinc metal). Low caustic reduces the burning limit.
- Excess carbonate reduces brightness thereby increasing the brightener consumption. It can also passivate anodes resulting in poor current distribution and a lower anode dissolution rate. Chilling the solution below 50°F (10°C) or passing the solution through an appropriate chiller unit is recommended to precipitate excess carbonate.
- Metallic contaminants such as cadmium, copper, nickel, lead, and tin, reduce brightness and overall appearance of the zinc deposit. Additions of the polysulfide purifier, minimizes these contaminants by forming their insoluble sulfide precipitants.
- Hexavalent chromium contamination reduces the low current density coverage, current efficiency, contributes to dull and blistered deposits, and affects chromating. Additions of sodium hydrosulfite effectively reduce hexavalent chromium (Cr +VI) to it's insoluble trivalent chromium (Cr +3) hydroxide.

The Good, the Bad & the Ugly

Cyanide zinc has and still does provide a functional, bright sacrificial corrosion layer that can be post finished with chromate, paint, or lacquer. It's a popular finish application, specified in some requirements.

Unlike the plot of those old spaghetti westerns, we don't aim to lynch a good working process. But, weak points of the cyanide zinc process helped concerted R&D efforts to formulate, test, develop, and fine-tune the next set of states that our *P&SF* Express will visit. Some of the cyanide zinc associated problems include:

- Waste treatment technology. Specific methods are well documented and effective. However, more stringent effluent discharge levels have become a problem. Closed looping is a good procedure.
- Waste disposal of the solution may be at least three times greater than chemical maintenance of the bath.
- Toxicity of cyanide enhances the switch to cyanide-free zinc plating systems.
- Cyanide zinc is less conductive than acid zinc, resulting in greater power costs.
- Efficiency of the cyanide bath is more dependent on cyanide concentration and solution temperature. >90% cathode efficiency is not experienced.
- Although cyanide zinc deposits are bright, they do not provide the leveling of the acid zinc system.

We now bid a hearty "cyanato" to our hard working associates in the Cyanide state. Their system is dependable, easy to maintain, and helps tremendously in the never-ending battle against corrosion. Our shuttle bus traverses Andreas Marggraf Blvd., on the way to Zn Tube #1, where our *P&SF* Express is ready to depart. Join us next month, as we visit the Alkaline state in Zincmalia. Incidentally, baseball fans in Michigan think it's great that a hall-of-famer is well represented in our next visit. ***P&SF***