

Alkaline Noncyanide Zinc Plating

by Edward Budman,
Dipsol-Gumm Ventures, Kearny, N.J.

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Scarcely 30 years ago, the first commercially available alkaline noncyanide zinc was introduced. The concept hinged on a very valid determination to eliminate cyanide in the plating room. These first baths reflected the most immature stage of development in the learning curve for this new technology.

These early baths offered some very favorable traits, such as excellent throwing power, low zinc metal content, and no need to add cyanide. They typically had high levels of hard chelates that proved troublesome for waste treatment. The addition agents were numerous, and some even contained small amounts of cyanide as an ingredient.

Just imagine, the platers of the day thought they had eliminated cyanide,

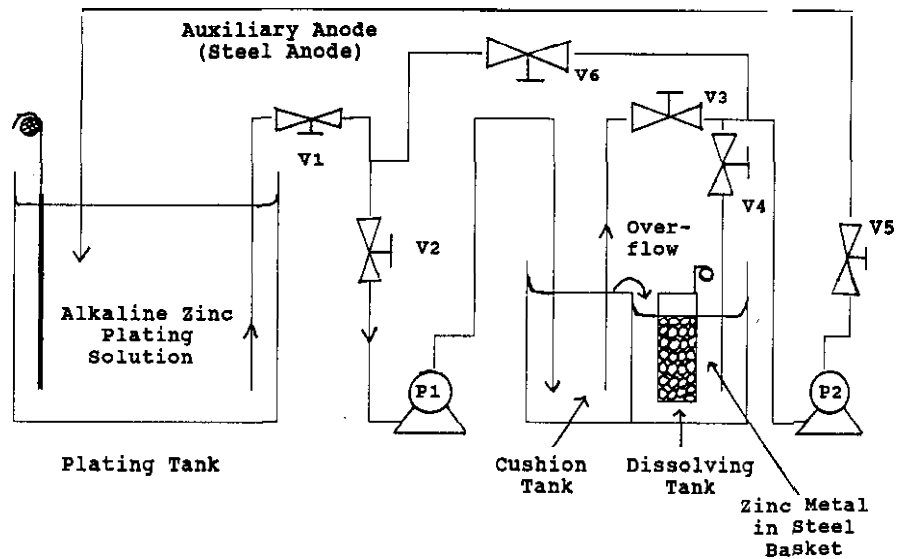


Figure 1. Typical circulation system for alkaline zinc—Style A. (When zinc concentration in the zinc plating solution becomes too high or over range, valves V2 and V3 are closed. Valve V6 is opened and V4 is closed after the solution in the dissolving tank is brought out.)

Table I. Typical Formulations of Alkaline Noncyanide Baths

Zinc	6–20 g/L
Caustic soda	100–200 g/L
Addition agents	Per supplier recommendations

only to have phantom traces continue to be found in their effluent. These early baths also gave deposits that were susceptible to delayed blisters, which could appear hours, days, or weeks after plating. Additionally, the effi-

ciency of the alkaline noncyanide zinc baths at 70–86% is lower than that of other types of systems, such as cyanide (75–93%) and chloride (95+%).

Manufacturers and vendors have done a very creditable job in curing

Table II. Effects of Impurities and Method of Removal

Impurities	Permitted Limit	Phenomena	Method of Removal
Hexavalent chromium	0.1 mg/L	1) Lowering of brightness in whole current density areas. 2) No brightness in high current density areas.	1) Add 0.2 g/L aqueous solution of sodium hydrosulfite and leave it for a night. 2) No suitable method other than diluting solution.
Lead	0.5 mg/L	1) Blackening or nondeposition in low current density areas. 2) Lowering covering power. 3) Lowering throwing power.	1) Zinc dust treatment. 2) Add 0.1–0.3 g/L sodium sulfide and then filter the solution.
Copper	1 mg/L	1) No brightness in low current density areas. 2) Blackening in nitric acid dipping.	Zinc dust treatment.
Iron	1 mg/L 5 mg/L	Discoloration in baking treatment 1) Blackening in low current density areas. 2) Lowering of the bending property after plating 3) Lowering of adhesion.	Zinc dust treatment.
Nickel	10 mg/L	1) Lowering of the bending property after plating 2) Lowering of adhesion.	Plate out at low current density (0.2–0.5 A/dm ²)
Sodium carbonate	80 g/L	1) Lowering of the bending property after plating 2) Lowering of adhesion.	Carry out bath filtration after cooling.
Organic materials, oils, and floating materials		1) Adhesion of oils to plated components. 2) Occurrence of rough surface.	1) Filtration. 2) Filter through filter aid packed in unit. 3) Active carbon treatment.

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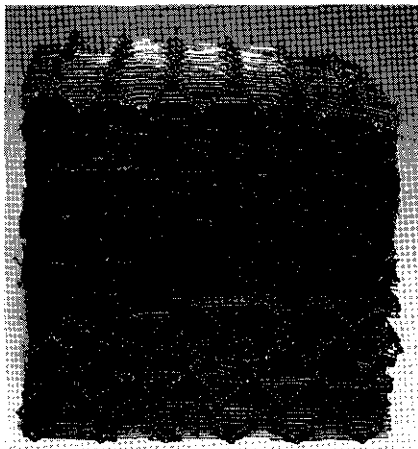
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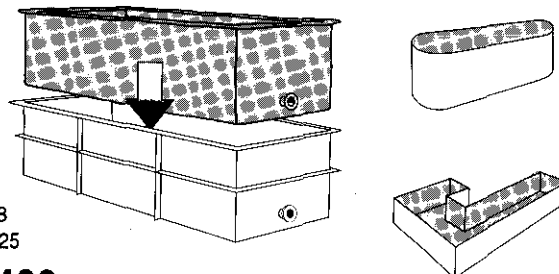
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Table III. Table of Best Application and Corrosion Resistance for Chromates

Chromate	Cyanide Zinc Bath			Noncyanide Alkaline Zinc Bath			Acid Chloride Zinc Bath		
	Application	Color Tone	SST	Application	Color Tone	SST	Application	Color Tone	SST
Blue bright	Good	Light blue	48/192	Good	Blue	72/288	Good	Light blue, little yellow	48/192
Yellow iridescent	Good	Yellow iri- descent	96/360	Good	Yellow iri- descent	96/360	Good	Yellow iri- descent	72/288
Black									
Phosphate type	Good	Deep black	96/360	Good	Deep black	120/480	Good	Deep black	96/360
Acetic acid type	Good	Deep black	72/288	Good	Deep black	96/360	Good	Deep black	72/288
Green									
Rack formula	Best	Light green	168/552	Good	Light green	192/600	Good	Light green	168/552
Barrel formula	Not recommended				Dark green	192/600	Not recommended		

SST, salt spray test hours to corrosion.
Thickness: 8 μm.

many of the objectionable deficiencies of these early baths. The newest generation baths offered by many manufacturers today (see Table I) have neither cyanide nor hard chelates in their formulas. This permits the plater to treat the effluent more easily. It also eliminates the delayed blistering problems of the earlier baths.

Domestic thought leans to reduced organics in the brightener as the reason for blister elimination. Many Pacific Rim platers, however, believe that the culprits are the wetting agents that are formulated into the systems. Eliminate the wetters and you can eliminate the blistering.

Quite often, if the zinc content of the bath keeps dropping, you can use a zinc generator tank to place additional zinc metal in contact with the solution. The diagrams in Figures 1-3 indicate three possible zinc generators that work effectively.

CONTAMINANTS

Alkaline noncyanide zincs are susceptible to metallic and organic contamination, just as are other baths. Table II shows some typical contaminants, their suggested limits, appearance, and removal techniques.

A SINGLE-SAMPLE METHOD FOR ANALYTICAL CONTROL

Alkaline zinc baths typically see up-and-down movement of the metal content. Good analytical control is a very important responsibility of the plater.

There are many good techniques available for analysis, and the following method should be of interest. With this technique, you can analyze both zinc

and caustic soda by using a single pipetted sample.

Required Analytical Reagents

- 0.1% Sulfo-Orange indicator
- 1.0 N Hydrochloric acid

- pH 5 Buffer solution (15% anhydrous sodium acetate solution with pH adjusted by acetic acid to pH 5)
- 0.1% X-O (Xylenol-Orange) indicator
- 0.1 M EDTA standard solution

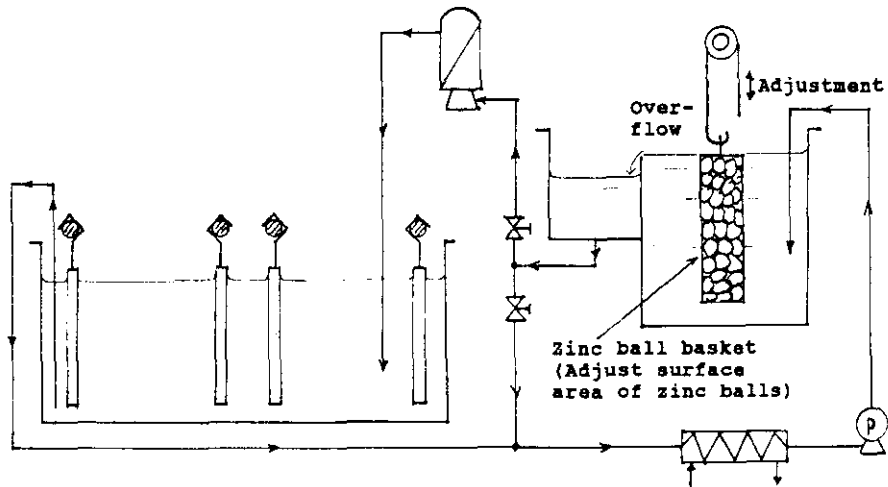


Figure 2. Typical circulation system for alkaline zinc—Style B.

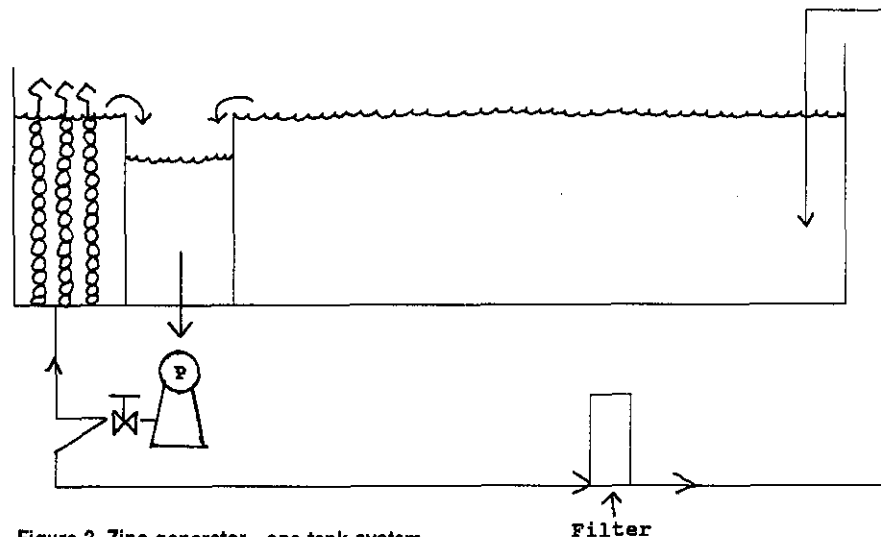


Figure 3. Zinc generator—one tank system.

Zinc and Caustic Soda Procedure

1. Prepare a 300-ml wide-mouth Erlenmeyer flask.
2. Pipette a 5-ml sample of plating solution into the 300-ml Erlenmeyer flask.
3. Add about 100 ml of deionized water.
4. Add 3-5 drops of 0.1% Sulfo-Orange indicator.
5. Dip the glass electrode of a pH meter into the analyzed solution.
6. Titrate with 1 N hydrochloric acid standard solution until the solution pH becomes 11.5. When the solution pH becomes 11.5, the solution color should appear completely yellow.
7. Read this endpoint as "V1" ml of N hydrochloric acid.
8. Add 1 N hydrochloric acid again until the solution pH becomes 5-6.
9. Pull out the pH glass electrode and wash with deionized water.
10. Add 15 ml of pH 5 buffer solution.
11. Add 1-3 drops of 0.1% X-O (Xylenol-Orange) indicator.
12. Titrate with 0.1 M EDTA standard solution until a pink to yellow color endpoint occurs.
13. Read this endpoint as "V2" ml of 0.1 M EDTA standard solution.

Calculation

$$\text{Zn (g/L)} = V2 \times 1.31 \times 0.1$$

$$\text{NaOH (g/L)} = V1 \times 8 \times 1$$

POSTPLATE TREATMENTS

Chromate conversion coatings are used on alkaline noncyanide zinc deposits, just as with other types of baths. Table III shows the number of hours that typically can be expected, by type of chromate, as applied to the three major types of plated zinc.

Table IV. Main Types of Chromate Coatings for Zinc Plating

Coating Type	Color	Comments
Thin	Colorless (bright dip, blue bright)	Polishing type (better appearance) Nonpolishing type (higher corrosion resistance) Yellow or iridescent type
Thick	Colored Dark green Olive drab Black	Acetic acid type (better black color) Phosphate type (higher corrosion resistance)
(Dyeing)		

It should be noted that some of the results appear higher when applied to alkaline noncyanide zinc deposits. One belief is that the extra protection comes from a very small percentage of iron that codeposits with the zinc. In the cyanide baths, iron complexes with cyanide and is blocked from codeposition. The chloride baths employ either peroxide additions and/or air agitation to oxidize and precipitate the iron, causing it to be removed by filtration.

Table III reflects hours to white/red corrosion, using the ASTM B 117 Salt Fog Test.

A general chart of most generic chromates on zinc is shown in Table IV. The chromate conversion coating is formed by a reaction between the chromating solution and the plated zinc deposit. Table V gives the dimensional change in the zinc and the thickness of the actual chromate film.

When the chromate conversion coat-

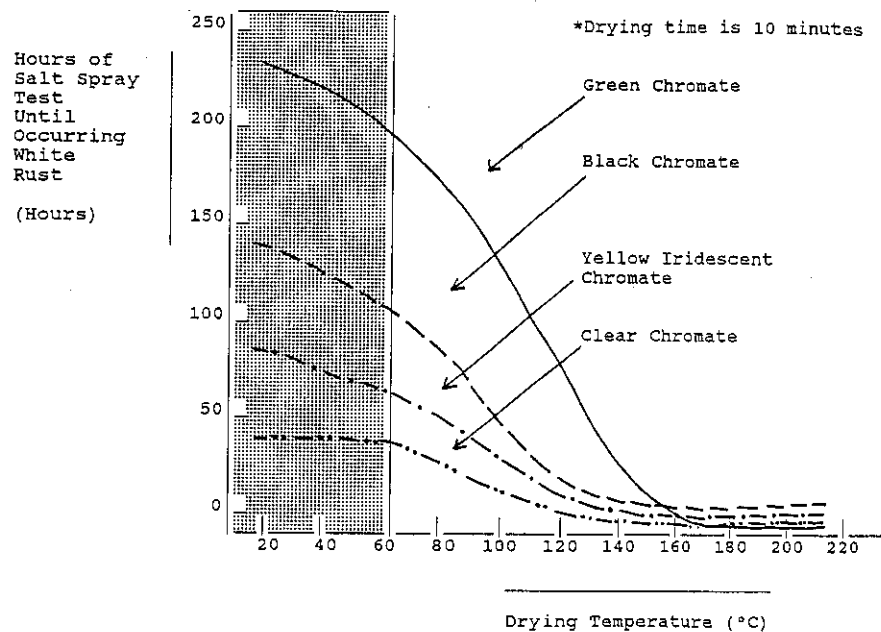


Figure 4. Relation between corrosion resistance and drying temperature after chromating. (Corrosion resistance depends upon the thickness of the chromate film and the quantity of hexavalent chromium in the chromate, which is influenced by the drying temperature.)

Table V. General Information for Chromate Coating on Zinc Plating Corrosion Resistance of Chromate Coating

Types of Chromate Coating	Decrease Thickness of Zinc Plating by Chromate Coating (μm)	Approximate Chromate Coating Thickness (μm)	Corrosion Resistance to White Rust by Salt Spray Test (hr)
Colorless chromate	0.2-0.8	0.02-0.05	Polishing type (24) Nonpolishing type (48-72)
Colored chromate	0.1-0.4	0.02-0.03	72-120
Dark green, olive drab	1-2	1.0-2.0	168-240
Black chromate	2-3	1.5-2.5	72-168

ing is applied to the plated part, you must exercise great care in drying the work. One common error is to dry the parts at too high a temperature. This may desiccate the chromate film, thereby reducing the corrosion resistance. The chromate film cannot be rehydrated, and the product quality is sacrificed. Figure 4 shows the effect of drying temperature on the salt fog test to white corrosion products.

CONCLUSION

Alkaline noncyanide zinc is a very important type of plating system in today's metal-finishing world. Factors such as lower metal content, no cyanide, good chromate receptivity, no hard chelates, and convenient waste treatment should ensure the popularity of this type of system for a long time to come. Deposits plated out of these baths accept all popular chromates offered by vendors in the industry. You can expect this type of zinc plating system to be a viable alternative to cyanide and acid chloride zinc applications.

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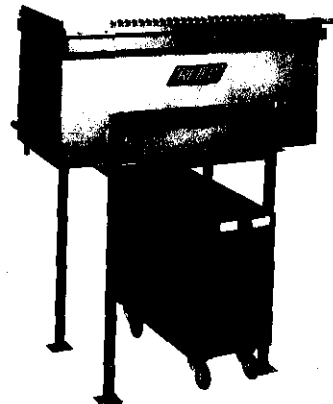
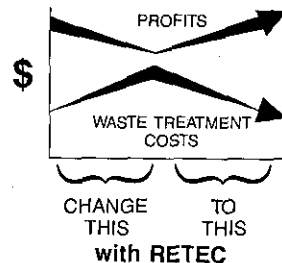
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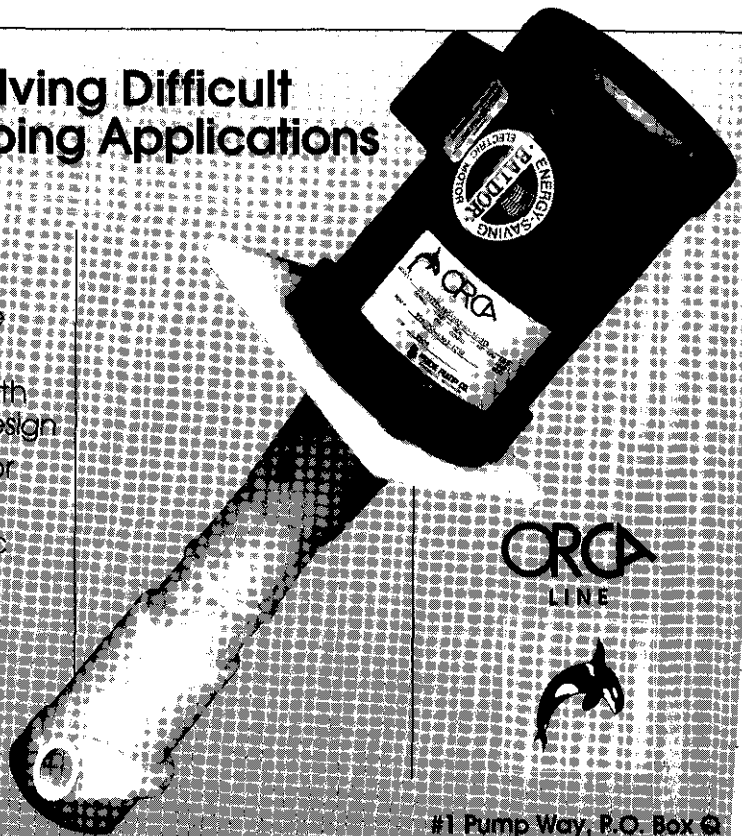
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