

Zinc Electroplating

CHOOSING THE BEST PROCESS FOR YOUR OPERATION

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Zinc and its alloys have been used for over a hundred years as protective and decorative coatings over a variety of metal substrates, primarily steel. Over the years there have been a number of processes developed for applying zinc coatings depending on the substrate, coating requirements and cost. Of these, electroplating is the most prevalent for functional and decorative applications.

When choosing a zinc plating process, it is important to know what processes are available and each of their particular advantages and disadvantages. Table 1 compares some of the more important factors related to these processes.

FACTORS TO CONSIDER

Listed below, in order of importance, are the primary factors that must be considered when choosing a zinc plating process:

- Does the plating specification for the part require a zinc or a zinc alloy deposit?
- Substrate(s) to be plated?
- Required corrosion protection?
- Required deposit thickness uniformity?

Considering these questions should somewhat reduce the number of usable plating processes. The next step is to consider the secondary factors. These factors are listed below in no particular order because their importance will vary from shop to shop:

- Deposit characteristics (appearance, ductility, adhesion, etc.)
- Make-up and operating costs
- Operating factors (efficiency, pre-plate requirements, corrosivity, etc.)
- Environmental restrictions (air quality, heavy metal removal, ammonia, etc.)

After fully evaluating how these factors affect your circumstances and referring to Table 1, the choice of the most applicable process should be considerably narrowed down. The following sections present more specific information for each of the different basic zinc plating processes.

ALKALINE CYANIDE ZINC PLATING

Cyanide zinc plating was for a long time the workhorse of the industry. Its popularity has significantly decreased over the years in the U.S. and other countries. The cyanide processes are presented here because there is still a fair amount of cyanide zinc plating done in a number of countries and cyanide processes are still considered by many to be the benchmark to which all other processes are compared.

Operating requirements for a cyanide zinc plating process are really minimal when compared to the other zinc plating processes. Bath analysis, Hull cell testing, and other plating tests should be done on a weekly basis. Cleaning and pickling requirements are not very stringent but should be corrected if an obvious preparation problem exists.

Bath makeup. Two options are available for bath makeup: Using caustic, sodium cyanide and zinc oxide; or using caustic, sodium cyanide and zinc cyanide. Option A is labor-intensive, but material costs are low. Caution must be exercised with this option as the reaction is highly exothermic (more than 250°F).

Option B has higher material costs, but is less labor-intensive and faster.

Process steps. Soak alkaline cleaning followed by electro-cleaning is preferred to

TABLE I— Attributes of Zinc Electroplating Processes

5 = Excellent 3 = Good 1 = Poor	Alkaline Zinc				Acid Zinc			
	CN		NCN		CHLORIDE			SO ₄
	LC	HC	LC	HC ⁺	NAm	LAm	Am	
Substrate ¹	2	3	3	4	5	5	5	4
Ecological Concerns ²	2	1	5	5	5	4	4	5
Make-up Cost	5	3	5	4 ⁺	3	4	4	3
Operating Cost ³	3	2	4	4 ⁺	3	3	3	3
Pre-Plate ⁴	5	5	2	3	3	3	3	3
Soln. Corrosivity	4	4	4	4	3	2	2	1
Soln. Conductivity	2	3	2	3	4	4	4	3
Soln. Rinsability	2	2	4	3 ⁺	3	3	3	3
Ease of Operation	4	5	4	3	3	3	4	4
Plating Speed	2	3	2	4	5	5	5	5
Throwing Power	4	4	3	5	3	3	3	2
Covering Power	2	2	3	3	4	4	5	3
Deposit Ductility	4	5	4	4	3	3	3	3
Deposit Adhesion	5	5	3	3	4	4	4	4
Appearance	3	3	3	4	5	5	5	2
Chromate Receptivity	5	5	4	5	4	4	4	4
Corrosion Protection	2	2	2	3	2	2	2	2

- 1) Ability to plate a wide variety of substrates i.e. hardened steels, cast iron or low carbon stampings
- 2) Toxicity, waste-treatability, etc.
- 3) Direct bath operating cost including waste treatment, not pre or post plating costs or equipment costs.
- 4) Bath's ability to tolerate or compensate for poor preparation.

*Sodium and potassium baths are available. Using a potassium based bath can affect the values shown below. The superscript (+ or -) indicates the effect of using a potassium based bath over a sodium based bath.

PLATING/ANODIZING

avoid contamination of the plating bath. If parts are not completely cleaned, however, the plating bath itself will clean them so cleaner maintenance is not quite as critical as with other plating processes. Cleaning should be followed by pickling in hydrochloric acid (20–30%) at room temperature or sulfuric acid (5–15%) at 105–120°F (40–50°C) to activate, descale, etc. steel parts prior to plating. Stripping rejected parts off-

line is preferred to avoid the introduction of chromium contamination and to extend the life of the acid. Parts can, however be stripped on-line if necessary. Proprietary acid additives and/or fluoride salts may be beneficial in cleaning and activating parts, as well as increasing acid longevity.

Chromate and passivate coatings and lacquers are the usual post plate treatments for any zinc deposit. Chromate conversion

coatings that can provide up to 500 hr to white salt formation are available, as are a wide variety of passivates in colors from clear to black.

Equipment and operating parameters.

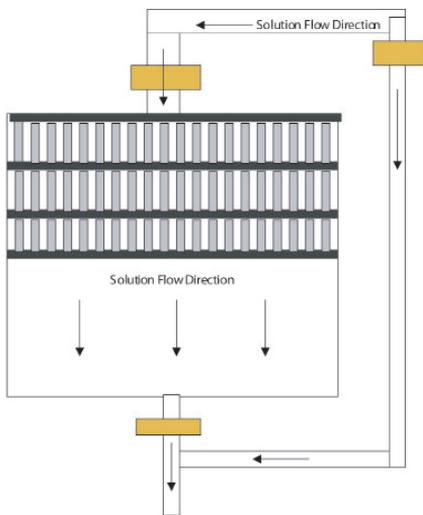
Tanks for zinc cyanide plating can be made of either low-carbon steel, polypropylene, PVC or rubber-lined steel. Low-carbon steel tanks should be insulated from the electrical circuit to avoid stray current. For barrel plating, rectifiers operating at 6–15 V, 5–10 asf are recommended. Operating range for rack operations is 3–9 V, 10–40 asf.

Most baths operate at a range of temperatures, but cooling equipment is recommended and heating equipment may be desirable in colder climates. Steel is the material of choice for any equipment in contact with the plating solution. Agitation is optional for zinc rack operations.

Special high-grade zinc anodes are preferred, but lower grades have been used with moderate success by some platers. If anode bags are used to avoid roughness be sure that the tops of the bags remain above the plating solution.

Covering power, throwing power and bath efficiency. Covering power is the ability of a plating bath to deposit metal in a deeply recessed area. Throwing power is the ability of a plating bath to deposit a uniform thickness of metal on areas of high and low current density. The throwing power of a cyanide bath is significantly better than that of a chloride zinc bath. Plating efficiency of cyanide zinc baths varies greatly depending on the bath chemistry, plating temperature and the plating current. The efficiency can vary anywhere from 40–85%.

Deposit properties. Zinc deposit ductility, uniformity, and chromate receptivity from a cyanide zinc bath is better than that achieved by chloride zinc baths and in some cases better than an alkaline non-cyanide baths. The deposit exhibits no chipping or star-dusting. The brighter the zinc deposit, the higher the organic level in the deposit,



Zinc generation tank—overhead view.

thus making the deposit less ductile and more stressed. Thus brighter parts may look better but their performance in other areas may suffer. This observation is true for all of the zinc plating systems.

ALKALINE NON-CYANIDE ZINC

In early cyanide-free alkaline zinc plating systems, cyanide was replaced by complexing or chelating agents such as sodium gluconate, triethanolamine, or polymeric amines. The resulting baths presented problems with both waste treatment and co-deposition of iron. A second generation of organic addition agents eliminated chelating agents, but had other drawbacks.

Most of the currently available processes have eliminated these problems with the use of an entirely new family of organic reaction products. Platers have a choice of low-chemistry alkaline non-cyanide zinc (low-metal bath) or high-chemistry alkaline non-cyanide (high-metal bath). In addition, potassium-based baths have been introduced that offer faster plating speeds and higher efficiencies.

Operating requirements for alkaline non-cyanide zinc plating processes are as follows:

- Perform bath analysis, Hull cell testing, and other plating tests daily.
- Analyze, maintain and dump cleaners and acids on a regular basis.
- Perform preventive maintenance to reduce production problems and minimize costs.
- Install automatic feeders for liquid components to eliminate human error.
- For troubleshooting, follow the supplier's recommendations carefully.

Bath makeup. Three options are available for bath makeup: using caustic and zinc oxide; using ready-made zinc concentrate; and using zinc anodes and caustic. Option A is labor-intensive. Material costs are moderate. Caution must be exercised because the reaction is highly exothermic; however, these high temperatures cannot be avoided because they are required to dissolve the zinc oxide. Option B has higher material costs, but is the least labor-intensive and the fastest. Option C is the least expensive overall, but requires a delay for zinc dissolution, as well as possible low-current-density electrolysis to remove unwanted metallic impurities.

Process steps. Cleaning and pickling as described above for alkaline cyanide zinc processes activates and prepares steel parts for plating. After plating, chromate conversion coatings that can provide up to 1,000 hrs to white salt formation per ASTM B 117 are available and may provide a cost-effective alternative to alloy plating. A wide variety of trivalent passivates ranging in colors from clear to black are now available. These passivates are normally used by themselves or with topcoats or sealers and provide from 12 to 200+ hr of protection to white salt corrosion.

Equipment. The plating tank can be made of either low-carbon steel, polypropylene, PVC or rubber-lined steel. Low-carbon steel

tanks are preferred but should be insulated from the electrical circuit. For barrel operations, power of 6–15 V at density of 5–10 asf is recommended; for rack operations, 3–9 V and 10–40 asf. Most baths operate at a broad range of temperatures, but cooling equipment is essential and heating equipment may be needed in colder climates. Steel is the material of choice for any equipment in contact with the plating solution.

Filters are essential for an alkaline non-cyanide zinc process. One to two turnovers of the plating solution per hour are practical in most installations using polypropylene cartridges and 10–15 μm screens. Paper or cellulose-type filter screens can be attacked by the alkalinity of the system and should be avoided. Use of a filtration system that can be carbon-packed is recommended. Mechanical agitation is optional for alkaline zinc rack operations. Air agitation is not generally recommended.

Anodes are ideally made of low-carbon steel, perforated, and with a thickness of 0.125–0.375 inch. Thicker steel has a higher current carrying capacity than thinner steel. Titanium baskets are not recommended due to their high resistivity. Make sure that low-carbon steel baskets are filled appropriately as per supplier's suggestion when zinc anodes are used. Knife-edge anode hooks make better contact than other designs. Polypropylene material is recommended for anode bags. Cotton bags will be attacked by high alkalinity and dissolve in the plating bath. Ensure that the tops of the bags remain above the plating solution to avoid roughness. Anode-to-cathode ratio should be about 1:1; zinc metal consumption is 2.7 lb/1,000 A/hr at 100% plating efficiency.

An off-line zinc generation tank that is 10-20 % of the volume of the plating tank makes control of zinc concentration easy. The zinc generation tank is a low-carbon steel tank with steel and zinc in contact. The zinc anodes are galvanically dissolved

in the steel tank (low-carbon steel anodes are recommended in the plating tank). New technology is available that may reduce the size of or eliminate auxiliary tanks. Figure 1 shows an overview of the galvanic generator setup.

Covering power, throwing power and efficiency. The alkaline bath's throwing power is approximately 40-65% (Haring cell), depending on the bath chemistry and/or type of additives used. Nearly any part plated in an alkaline plating bath will have thicker deposits in the low-current-density areas when compared to chloride zinc. The bath efficiency of alkaline non-cyanide zinc decreases with current density. Higher efficiency can be achieved with higher zinc concentrations and higher temperatures.

Deposit properties. Zinc deposit ductility, uniformity, and chromate receptivity in an alkaline non-cyanide bath is better than that achieved by chloride zinc baths. Unlike chloride zinc, the alkaline bath does not exhibit chipping or star-dusting when operated properly. The brighter the zinc deposit, the higher the occlusion of organics in the deposit. This makes the deposit less ductile and highly stressed.

CHLORIDE ZINC PLATING

Chloride zinc plating processes have been available for more than 40 years and have changed considerably over this period. They have evolved from processes that were very sensitive to bath chemistry, temperature, current density, etc. to processes that can be operated over a wide range of conditions. Over the last five or so years, however, there have not been any really significant changes in the available systems.

Advantages. The chloride processes offer three important advantages over the alkaline systems:

- Superior brilliance and leveling, rivaling that of nickel-chrome.
- Plating efficiencies of 95–100%.
- Ability to plate substrates such as cast

iron and, more importantly, steels that have been hardened using any number of different methods.

Disadvantages. Unfortunately, associated with these advantages are two major disadvantages:

- The solutions are corrosive, and therefore more expensive, due to the need for corrosion-resistant equipment.
- Throwing power of the systems is only fair, resulting in poor plate distribution.

In some instances, one just has to live with these disadvantages or work around them in order to make use of the advantages.

The three most commonly used chloride zinc plating bath chemistries are shown in Table II.

Operating requirements. Suggested requirements for trouble-free operation of a chloride zinc plating operation include monitoring and adjustment of pH as frequently as possible, at least every two hours. The bath should be analyzed once per shift or at least once a day, and cleaners and acids must be analyzed, maintained, and dumped on a regular basis. Preventive maintenance can reduce production problems and minimize costs, while automatic feeders for liquid components eliminate human error and smooth out operating performance.

Bath makeup. No matter which bath chemistry is chosen, zinc chloride is the source of the zinc in the bath and is available as either a liquid or a solid. Zinc chloride is normally only used for bath make-up unless an unforeseen problem should occur. It is very important that the zinc chloride be lead-free or as lead-free as possible; the presence of lead in the bath will result in a very dull, dark and unrefined deposit and requires "dummying" the bath to remove the lead.

Potassium chloride provides solution conductivity. The untreated form of potassium chloride is preferred. Ammonium chloride

serves a number of purposes: It provides conductivity, acts as a buffer and as a complexor for the zinc. Baths using ammonium chloride in general have a wider window of operation and are therefore easier to control. Ammonium chloride-based baths also pose a potential waste treatment problem. If nickel or copper waste streams are not segregated, the ammonia could make removal of the nickel or copper difficult. In some areas, the discharge of ammonia is also restricted.

Other possible bath constituents include boric acid, used only in non-ammonia systems to provide some buffering action; proprietary grain-refining and brightening additives; hydrogen peroxide to treat the bath for iron and some contaminants; and potassium permanganate, which is used in

much the same way as hydrogen peroxide. For rack operations, this material should only be added during down time.

Process steps. Parts should be cleaned and pickled using the steps outlined for the alkaline zinc processes above. After plating, chromate conversion coatings and lacquers are available in a wide variety of colors to provide white salt corrosion protection of anywhere from 12–500 hr. For additional corrosion protection or lubricity control, organic, inorganic or blended topcoats or sealers are available.

Equipment and operating parameters. Tanks for zinc chloride plating can be made of polypropylene, PVC, fiberglass or lined steel. All should be leached before use. For barrel operations, 4–12 V at density of 3–10

TABLE II—Common Chloride Zinc Bath Chemistries

Chloride Zinc Bath Type	All Potassium	Low Ammonium	All Ammonium
Zinc (oz/gal)/(g/L)	3–5 / 22.5–37.5	2.5–4.5 / 18.7–33.7	2.0–4.5 / 15–33.7
Ammonium Chloride (oz/gal)/(g/L)		4–8 / 30–60	18–22 / 135–165
Potassium Chloride (oz/gal)/(g/L)	25–30 / 187–225	16–20 / 120–150	
Boric Acid (oz/gal)/(g/L)	3–5 / 22.5–37.5		
Proprietary Additives	As recommended	As recommended	As recommended
pH	4.5–5.2	5.5–6.0	5.5–6.0
Temperature, °F (°C)	70–130 (21–55)	80–140 (27–60)	85–140 (29–60)
Agitation	Recommended	Recommended for rack	Recommended for rack
Filtration	Yes	Yes	Yes
Type of Operation	Rack or barrel	Rack or barrel	Rack or barrel
Voltage (V)	2–13	2–12	2–12
Current Density, asf	1–25	1–30	1–35
Plating Efficiency, %	95–100	95–100	95–100
Plate Distribution	Fair	Fair	Fair

asf is recommended; for rack operations, 3–9 V at 10–40 asf. Most baths operate over a broad range of temperatures, but cooling is essential and heating equipment may be needed in colder climates. Any equipment coming into contact with the plating solution must be constructed of corrosion-resistant materials.

Filters are also essential, operated at one to two turnovers of plating solution per hour using polypropylene cartridges with 10–25 μm filter screens. Some form of agitation is required for rack operations. Special high-grade zinc anodes must be used, and titanium baskets with slab or ball anodes can be used as can slabs hung from hooks. Polypropylene or cotton material is recommended for anode bags; napped polypropylene is preferred. The bag weave should not be too tight since this could result in the bags plugging prematurely. Be sure that the tops of the bags remain above the plating solution to avoid roughness. At 100% efficiency, zinc metal consumption in a chloride zinc bath is 2.7 lbs/1,000 A/hr.

Covering power, throwing power and efficiency. Chloride zinc deposits have excellent covering power but poor throwing power. A chloride plating bath can plate deeper into the inside of a tube than an alkaline non-cyanide bath. Deposit thickness distribution, however, is poorer. In past editions of this article, the deposit distribution was rated in the tables for chloride zinc as a 2 out of 5 and called fair. New technology has allowed the chloride zinc systems to plate with much improved distribution, better conversion coating receptivity, and no star-dusting, while maintaining all the deposit properties of chloride zinc, including its laminar deposition.

Deposit properties. Chloride zinc deposits from baths run under normal conditions are full bright with very good leveling and acceptable ductility, uniformity, and chromate receptivity. The deposits particularly from barrel plating processes or where there

is a lot of making and breaking of contact will exhibit chipping or star-dusting. High brightener or organic levels can also make the deposit less receptive to chromates which will result in unacceptable appearance and poor corrosion performance.

ZINC ALLOY PLATING

Zinc alloy plating, not including brass, did not receive meaningful recognition until the early 1980s. Since then, the range of alloys has increased and the production processes have been refined considerably. However, it was within the last ten years that these processes gained any commercial acceptance. This delay was the result of several factors:

- No compelling need had developed for the advantages offered by the alloy deposits.
- The processes were difficult to operate consistently.
- The cost of operating the alloy baths was too high.
- No general consensus on which alloy was most suited for any specific application.

These factors were either overcome or at least became acceptable because of two developments in the automotive and electronics industries. The first was the push for an environmentally acceptable method to obtain increased corrosion protection. The second was the pursuit of an acceptable replacement for cadmium deposits. The zinc alloy baths available today are capable of satisfying both of these needs, producing deposits that provide enhanced corrosion protection and increased lubricity, ductility and hardness.

Available processes. There are a number of commercially available zinc alloy processes, including zinc/nickel (Zn/Ni), zinc/nickel/iron (Zn/Ni/Fe), zinc/cobalt (Zn/Co), zinc/cobalt/iron (Zn/Co/Fe), zinc/iron (Zn/Fe), tin/zinc (Sn/Zn) and zinc/manganese (Zn/Mn). Of these, the

nickel, cobalt, tin and iron alloys are currently the only ones of any real commercial prominence. The Zn/Mn alloys will not be presented here. Table III lists the different alloy compositions and their associated processes.

The plating processes for the iron and cobalt alloys are operated and have additive systems similar to their non-alloy counterparts. The Zn/Ni systems, however, require processes that are quite different from their non-alloy counterparts.

Zinc/nickel alloy deposits can be produced using either an alkaline or chloride process. Regardless of process, the zinc/nickel alloy is by far the most expensive to operate of any of the alloys discussed here. But, it provides the best corrosion protection, maintains a majority of its corrosion protection at elevated temperatures and provides greater wear resistance.

The alkaline plating process gives good plate distribution but has very low efficiency. The complexors used can adversely affect waste treatment. It is because of these complexors that a zinc/nickel/iron tri-alloy is the usual result. This co-deposition of iron, however, seems to have no effect on deposit performance. The zinc and nickel are replenished using either zinc anodes or a galvanic zinc generator and nickel salts. If a zinc generator is used, the anodes are nickel, but nickel salts are still normally required.

New technology has developed chloride zinc-nickel alloy systems that have alloy distribution properties almost as uniform as alkaline zinc-nickel. The metal replenishment of chloride zinc-nickel baths can be from one of four methods: 1) zinc and nickel anode on the same anode bar; 2) inert anodes with zinc generation and nickel salts; 3) zinc anodes and nickel salts, and; 3) zinc and nickel anodes on separate rectifiers.

Tin zinc is more of a tin alloy than a zinc alloy, since the tin is present in the deposit at 70–75% while the zinc is present at 25–30%. While the tin-zinc alloy bath is plated in acidic as well as alkaline bath formulations, the most user-friendly are generally plated at a near neutral pH range of 6.0–7.0. The anodes used are usually 75/25 tin/zinc. Cathode agitation is mandatory, and "no-air" agitation is specified.

Zinc/cobalt. Alkaline systems for plating zinc/cobalt alloys are easy and economical to operate and produce a deposit with exceptional alloy and thickness uniformity. Like the alkaline nickel alloy process it is not unusual to actually plate a tri-alloy of zinc/cobalt/iron because of the presence of complexors. The alkaline plating process is preferred, but the chloride system can be used where it is necessary to plate hardened or cast metal parts.

Zinc/iron deposits are currently produced using only an alkaline non-cyanide process; chloride processes to produce Zn/Fe alloys

TABLE III—Zinc Alloy Processes

Alloy Type	Alloy Composition	Plating Processes
Zn/Ni	5–10% nickel (low)	Alkaline non-cyanide or acid chloride
Zn/Ni	10–16% nickel (high)	Alkaline non-cyanide or acid chloride
Zn/Co	0.2–1.2%	Alkaline non-cyanide or acid chloride
Zn/Fe	0.2–1.2%	Alkaline non-cyanide
Sn/Zn	70–80% tin	Neutral non-cyanide

are not yet widely used commercially. The Zn/Fe baths are the most economical and easiest of the zinc alloy systems to operate. The deposit has very good corrosion resistance, ductility and weldability. Iron alloy deposits have only one real negative: they lose substantial corrosion protection when exposed to elevated temperatures. Thus they are not recommended for use at temperatures greater than 200°F.

Choosing the right zinc alloy process.

There are only two choices to be made. The first is the type of alloy required. The second, in the case of nickel and cobalt alloys, is whether to use an alkaline or chloride plating bath. The first choice is easy, since this is usually spelled out in the customer's specifications. The choice of bath types can be a little more involved. There are several considerations:

- Some substrates, such as cast iron, hardened or carbonitrided parts, require chloride type baths to plate correctly.
- Chloride baths necessitate the use of corrosion-resistant equipment. The alkaline alloy baths contain complexors of one kind or another that can also be corrosive to equipment. Depending on the alloy bath and the complexors used, it may be necessary to use more corrosion resistant equipment than would be required for a normal alkaline zinc plating bath.
- In the case of nickel alloys, waste treatment modifications may be needed to handle nickel and (in alkaline baths) high levels of strong complexors.

Topcoats and sealers. Because of the alloy content of the deposit, special chromate or passivate formulations are required for each of the different alloy deposits. There are currently both hexavalent and trivalent chromates available in a range of colors for most of the zinc alloys. Without a chromate or passivate conversion

coating, the corrosion characteristics of the iron and cobalt alloys are not significantly different than those of pure zinc. In the case of nickel alloys, with no chromate or passivate, the onset of white salt corrosion is about the same as for pure zinc but the progression of the corrosion is slowed depending on the nickel content. ■

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Plating for Growth

This article provides the fundamentals on zinc plating processes. Follow the link to learn how one zinc barrel plating shop expanded by installing a rack line:

pfonline.com/articles/110401.html.