Effect of Process Variables and Contaminants:

For a given concentration of tin and nickel in a solution, the factor exerting the most profound influence on the deposit is the fluoride content. Since fluoride has complexing action on tin (stannous), an increase in fluoride content will decrease the tin content of the deposit and vice versa.

Free hydrofluoric acid content should be maintained between 6 and 12 g/L to avoid loss of brightness and burning in the high current density areas.

The presence of grease, oil and organic contaminants in the solution will give rise to serious pitting of the deposit. The presence of lead over 25 ppm is very harmful to the solution. Metallic impurities such as copper, antimony, iron, zinc, cadmium, etc, under 200 ppm have no detrimental effect on the deposit but can be removed by dummying.

Troubleshooting:

1. ~~Cloudy deposits are due to lack of nickel content, low temperature or organic contamination.~~
2. ~~Dark deposits in low current density areas are due to metallic contamination, copper in particular if more than 50 ppm.~~
3. ~~Gray deposits in high current density areas are due to high tin (stannous) content, lack of free fluoride content, iron contamination above 750 ppm or chromium contamination over 50 ppm.~~
4. ~~Burnt deposits are due to lack of tin content, low temperature, and pH imbalance.~~
5. ~~Loss coverage is due to excessive iron contamination.~~
6. ~~Poor solderability is due to surface passivation and aging.~~

Plating from Proprietary Baths:

~~Tin-nickel alloy may be electroplated with the use of proprietary additives in fluoride baths. Incorporation of proprietary additives allows the operation of the process at a little lower temperature range (120-130°F) and pH between 4 and 5, resulting in bright and ductile deposits.~~

~~Tin-Nickel Alloy Plating from Pyrophosphate Baths:~~

~~Because of the corrosive and toxic nature of fluorine in fluoride baths, pyrophosphate baths have been developed which operate at lower temperatures and near neutral pH.~~

~~Bright deposits of tin-nickel alloy have been successfully obtained from baths consisting of the following composition and operating parameters:~~

Stannous chloride ($SnCl_2 2H_2O$)	3.8	oz/gal	28.2	g/L
Nickel chloride ($NiCl_2 6H_2O$)	4.2	"	31.3	"
Potassium pyrophosphate ($K_4P_2O_7 3H_2O$)	25.8	"	192.2	"
Glycine	2.7	"	20.0	"
Temperature	122°F		50°C	
pH	7.5–8.5			
Current density	4.8–14	amps/ft²	0.5–1.5	amps/dm²

The composition of the alloy obtained from this solution does not vary with changes in pyrophosphate concentration, but variation in the content of individual metals, tin or nickel, changes the composition of the alloy. pH values below 7.5 or above 8.5 are undesirable.

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ZINC PLATING

by Herb Geduld

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Each of the three general types of bright zinc plating electrolytes in general use today (cyanide zinc systems, alkaline non-cyanide baths, and acid zinc baths), will produce bright, acceptable deposits when operated correctly. To help the electroplater determine which electrolyte would be best for his particular installation, their advantages and disadvantages are given below.

BRIGHT CYANIDE ZINC PLATING ELECTROLYTES

Advantages:

1. Oldest processes in use; familiarity of employees with operation.
2. Most forgiving electrolytes to poor pre-cleaning.
3. Excellent covering power.
4. Analysis and control of bath relatively easy.
5. Good ductility of deposits.
6. Non corrosive electrolyte.

Disadvantages:

1. Highly toxic electrolytes requiring cyanide waste treatment.
2. Will not deposit on most cyanide heat treated and cast iron parts.
3. High temperature operation, above 105°F costly or impractical for bright deposits.
4. Relatively poor bath conductivity.
5. Cathode current efficiencies drop dramatically at higher current densities.

Among the three cyanide systems themselves, the overall ease of operation, control and minimization of rejects is parallel to the cyanide content of the bath. The regular cyanide baths are the most trouble-free to run simply because their higher overall formulation makes them more tolerant to dragged-in organic and metallic impurities and to variations in the bath content due to drag-out. The mid-strength baths, however, perform so closely to the regular bath with substantially less drag-out, that most cyanide plating is now done in these lower cyanide content formulations.

BRIGHT ALKALINE NON-CYANIDE ZINC PLATING ELECTROLYTES

Advantages:

1. Least toxic zinc electrolyte.
2. Waste treatment simplest, requiring only zinc precipitation.
3. Low make-up costs.
4. Good plate distribution.
5. Can be used in steel plating tanks.

Disadvantages:

1. Requires close control of zinc metal content, usually daily analysis.
2. Low tolerance to poor pre-plate cleaning.
3. Efficiency drops rapidly with lower metal contents.
4. Low tolerance to metallic impurities in make-up salts and hard water impurities.
5. Deposits have a greater tendency to brittleness than cyanide baths.

The effectiveness and ease of operation of the alkaline non-cyanide electrolyte is totally dependent on the proprietary additive system used in the bath. Without any additive, an amorphous gray-black deposit is obtained.

Unlike cyanide zinc brighteners, which are based on over 40 years of development and which today tend to contain similar basic ingredients that are usually compatible with each other, non-cyanide brightener systems may be quite different chemically and often one proprietary process may be totally incompatible with another. The quality of deposit, bright plating range and ease of operation may vary extensively in these systems, so the careful plater would be wise to check out a number of proprietary alkaline non-cyanide processes when evaluating this electrolyte.

BRIGHT ACID CHLORIDE ZINC PLATING ELECTROLYTES

Advantages:

1. Produce brilliant, level, nickel-like deposits.
2. Readily plates on carbonitrided, cast iron and malleable iron parts.
3. Operate at much higher current efficiencies than cyanide or alkaline non-cyanide baths.
4. Waste treatment is simple, requiring only precipitation of zinc at high pH.
5. Acid baths have high conductivity, producing substantial energy savings.
6. Produce minimal hydrogen embrittlement compared to alkaline and cyanide baths.
7. Can produce brilliant deposits at higher temperatures than cyanide solutions in barrel baths.

Disadvantages:

1. Solutions are corrosive and require lined tanks and auxiliary equipment.
2. Bleedout of entrapped solution may be an insoluble problem on some spot welded or fabricated parts.
3. Ductility may be a problem on thicker deposits.
4. Filtration and cooling coils or refrigeration is usually required.

The choice among the acid chloride electrolytes will depend upon a number of factors. The ammonium chloride bath operates at higher maximum current densities than the potassium chloride bath, but its use is restricted in many localities which limit the ammonium ion content of wastewaters.

The all-sodium chloride bath has limiting current density problems and its use is generally restricted to barrel operations. Mixed ammonium-potassium and ammonium-sodium baths using 4 oz/gal of ammonium chloride and 16 oz/gal of potassium or sodium chloride have come into increasing use in the past two years as excellent high temperature, work-horse electrolytes, especially for barrel plating.

OTHER ZINC PLATING ELECTROLYTES

Zinc can be plated from a number of other acidic electrolytes including fluoborate, sulfamate, and sulfate baths. During the development of bright acid zinc plating technology, a number of proprietary bright acid sulfate processes were developed and found limited application in the industry. These have been replaced by the acid chloride electrolytes for most decorative applications.

Acid sulfate baths, however, still find wide application in continuous, industrial plating of zinc on electrogalvanized sheet and wire, where bright deposits are not required. A bright zinc pyrophosphate electrolyte saw limited commercial use in the 1960's, but was replaced by other electrolytes due to the high cost of the process.

MAKE-UP OF ZINC PLATING BATHS

CYANIDE ZINC PLATING SOLUTIONS:

Cyanide zinc baths may be prepared using either zinc cyanide or zinc oxide as the zinc metal source. Zinc cyanide contains fewer metallic impurities than zinc oxide and is the preferred make-up salt for this reason. Most platers, however, use USP grades of zinc oxide since the cost savings per gallon of make-up solution are substantial.

When preparing a cyanide zinc plating bath, the following equivalents must be kept in mind:

1 oz/gal of zinc cyanide = 0.56 oz/gal of zinc metal in bath and = 0.84 oz/gal of cyanide in bath. Therefore, to obtain 1 oz/gal of zinc metal requires 1.0/0.56 or 1.8 oz/gal of zinc cyanide which also produces the equivalent of 1.5 oz/gal of sodium cyanide.

1 oz/gal of zinc oxide = 0.80 oz/gal of zinc metal in bath and = 1.0 oz/gal of caustic soda in bath. Therefore to obtain 1 oz/gal of zinc metal requires 1.0/0.8 or 1.25 oz/gal of zinc oxide which also produces the equivalent of 1.25 oz/gal of caustic soda.

To prepare a cyanide zinc bath using zinc cyanide, the chemicals listed in Table I are required.

In addition to the basic components of cyanide zinc baths listed in Table I, two other additives are often added to an initial solution: sodium carbonate and sodium polysulfide. Sodium carbonate invariably builds up in an existing zinc bath; however, many platers find it expedient or, in some cases, essential to add 1 to 2 oz/gal of sodium carbonate to a new bath to "age" the solution to initial trouble-free electrodeposition. Most sources of caustic soda contain measurable amounts of sodium carbonate, but it has been repeatedly demonstrated in the field that extra initial additions of sodium carbonate may be necessary to initiate plating, especially in rack baths for sheet metal parts.

In addition to sodium carbonate, most newly prepared zinc solutions require an addition of between 0.5 and 1.0 g/L of sodium polysulfide to precipitate heavy metal trace contaminants, essentially lead and cadmium, from the solution. Sodium polysulfide, te-

Table I. Chemicals for Preparing a Cyanide Zinc Bath

	Conventional Bath		*Mid Bath*	
	oz/gal	*lbs/100 gal*	*oz/gal*	*lbs/100 gal*
Zinc cyanide	8.1	51	4.0	25
Sodium cyanide	5.6	35	2.9	18
Caustic soda	10.0	63	10.0	63
Operating Temp.		70°-110°F		
Alternatively, the bath may be prepared by using a high purity USP grade of zinc oxide as follows:				
Zinc oxide	5.6	35	2.8	17
Sodium cyanide	12.4	78	6.2	38
Caustic soda	4.4	28	7.2	45
Operating Temp.		70°-110°F		

trasulfide, or sulfide is marketed as a dry powder or liquid additive under a number of names, such as zinc purifier, doctor solution, etc. The liquid additives have the convenience of minimum preparation, and generally do not create as much sludging in the bath as the solid materials.

The exact amount of the initial polysulfide addition required will vary greatly, depending upon the purity of the make-up chemicals. Baths prepared from high purity zinc cyanide require little, if any, polysulfide, while those prepared from normal grades of zinc oxide may require much larger additions. Luckily, no deleterious effects are produced in standard or medium cyanide baths by excess additions, and amounts in excess of those required to precipitate trace metallic impurities will merely precipitate zinc as a milky-white sulfide which slowly redissolves into the body of the bath.

Occasionally, a zinc dust treatment to remove heavy contamination of metallics is necessary for the initial bath make-up, but this is extremely rare and generally is used more as a purification procedure.

A typical procedure for the preparation of a bright cyanide zinc electrolyte is as follows:

1. Fill the plating or, preferably, makeup tank 1/3 full with cold tap water.

2. Dissolve the required amount of sodium hydroxide.

3. Allow the bath to cool, if necessary, to below 130°F.

4. Dissolve the required amount of sodium cyanide.

5. With constant stirring, slowly add the required amount of zinc cyanide or zinc oxide and stir until dissolved. When zinc oxide is used, the minimum amount of water should be employed and the zinc oxide should be added slowly as slurry.

6. When completely dissolved, bring up almost to operating level and add the required amount of sodium polysulfide purifier diluted with 10 parts water.

7. Dilute the required amount of addition agent with water, add to the bath, and bring to operating level.

8. Insert anodes and bring to operating temperature.

The vast majority of zinc cyanide baths will begin plating immediately, with no working-in required. However, occasionally as just noted, an initial sodium carbonate addition may be required.

Many plating supply houses throughout the world sell purified, concentrated, cyanide zinc solutions in varying strengths, which may be diluted with water as required to form a quick, convenient method of initiating zinc plating in new installations.

ALKALINE NON-CYANIDE ZINC BATHS

An alkaline non-cyanide zinc bath may be prepared in two ways: dissolving zinc anodes in caustic soda or from zinc oxide and caustic soda. In either case, the highest purity grade materials available must be used to eliminate metal impurities in initial make-up. USP grade zinc oxide and mercury cell caustic soda are recommended. Baths are prepared as shown in Table II.

1. Slurry zinc oxide by slowly adding to minimal amount of water in plating tank, or preferably separate make-up tank.

Table II. Preparation of Alkaline Non-Cyanide Zinc Baths

	oz/gal	lbs/100 gal
Zinc oxide	1.5	9.5
Caustic soda	10	62
Addition agents	As specified	
Operating Temp.	70°-115°F	

2. Slowly add caustic soda and water up to approximately one third of final volume.
3. Stir continually until all zinc oxide is dissolved.
4. Add 6 lbs/100 gallons of zinc dust to bath and stir for 30 to 60 minutes.*
5. Allow to settle and filter or decant into plating tank.
6. Place zinc anodes in bath and electrolyze on dummy cathodes overnight at low current density.

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*Zinc dust treatment and dummying are optional and are required only if metallic impurities are present in the make-up salts.

When preparing an alkaline zinc bath using zinc anodes, a makeup tank or a series of 55-gallon steel drums should be filled with liquid caustic soda and zinc anode balls in steel baskets. The solution will rapidly build up in zinc metal and, after standing for 36 to 48 hours, should be analyzed for zinc metal and caustic soda content and diluted to produce a bath containing 1 oz/gal of zinc metal. Additional caustic soda will usually be required.

ACID CHLORIDE ZINC BATHS

Acid chloride zinc baths are prepared from mixtures of zinc chloride, and ammonium, potassium or sodium chloride. The all-potassium bath requires boric acid. The highest purity technical grade materials available are recommended for these baths. It is especially important to specify grades of ammonium chloride which are *not* formulated for zinc galvanizing, as these often contain anti-caking agents or flux additives which are contaminants in bright acid chloride baths.

The following equivalents should be noted when maintaining the chloride content of a bath:

Ammonium chloride is 66% chloride
Potassium chloride is 48% chloride
Sodium chloride is 61% chloride
Zinc chloride is 52% chloride and 48% zinc.

Therefore, to raise chloride content 1.0 oz/gal. requires:

1.52 oz/gal ammonium chloride
2.08 oz/gal potassium chloride
1.66 oz/gal sodium chloride

To raise zinc metal content 1.0 oz/gal requires 1.92 oz/gal zinc chloride. Zinc metal content is normally maintained by dissolution of the anodes as the baths exhibit 100% anode efficiency.

To prepare typical acid chloride bright zinc baths, the chemicals listed in Table III are required.

All bright acid chloride zinc baths are based on patented proprietary formulas and the exact specifications for a particular bath make-up should be followed. In addition to

Table III. Preparation of Acid Chloride Bright Zinc Baths

	Potassium Chloride Bath oz/gal	*Ammonium Chloride Bath oz/gal*	*Mixed Chloride Bath oz/gal*
Zinc chloride	9.0-12.0	4.5-6.7	4.5-6.7
Potassium chloride	25-32.0	–	25.0-29.0
Ammonium chloride	–	20.0-25.0	4.0-6.0
Sodium chloride	–	–	or 4.0-6.0
Boric acid	3.5-5.5	–	–
Operating Temp.	65°-115°F	65°-125°F	65°-130°F

the make-up salts, the baths will require 3% to 5% by volume of a make-up or carrier brightener and 0.1% to 0.25% of a maintenance brightening agent.

A typical bath preparation is as follows:

1. Fill make-up tank half full of warm (115 to 135 °F) water.
2. Add boric acid if required and stir in until completely dissolved.
3. Add zinc chloride and mix until dissolved.
4. Add potassium, ammonium or sodium chloride as required and mix until dissolved.
5. Bring the bath to approximately 95% of operating volume with water.
6. Dilute and dissolve in make-up or carrier brightener followed by maintenance brightener.
7. Check and adjust pH to recommended value.
8. Dilute up to final volume and bring to operating temperature.