Zinc-Nickel Alloy Plating
By
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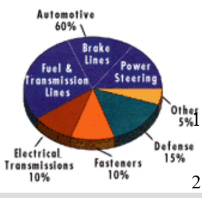
Electrochemically, alloys can be designed to produce different corrosion potentials than their alloying elements. It is possible, therefore, to maintain the sacrificial protection of zinc coating over steel, but at a different potential, closer to steel, by alloying it with another metal, preferably more noble than zinc. As a result, the alloy corrodes at a much slower rate than zinc alone, affording better corrosion protection. Some of these alloys have been found to be excellent replacements for cadmium plating in many applications.

Zinc alloy plating technologies were introduced in the mid 1980's in the U.S. Although started in Japan and Europe some 10 years earlier, it was only recently that their acceptance and use on a commercial basis was felt in the U.S. and Canada.



1. Industries using alkaline zinc-nickel

Several factors may have delayed the adoption of these technologies by U.S. industry, despite their documented success in Japan and Europe:

1. Our regulatory agencies have only recently restricted the use of cadmium as a protective coating. Finding a good substitute, therefore, became urgent.
2. The desire for improved quality and product reliability surpassing that of zinc plating.
3. The simultaneous introduction of several zinc alloys and processes required time to evaluate in order to sort out the best ones before new specifications were drawn.

The various technologies offered to the metal product finisher today include: zinc-iron, alkaline or acid zinc-nickel, zinc-cobalt, and tin zinc.

Zinc-Nickel

There are two types of zinc-nickel plating systems available commercially:

- Alkaline-type (non-cyanide) bath
- Acid-type bath

The nickel content in this alloy ranges from 5-15% by weight of the deposit; the balance is zinc. Corrosion resistance studies have shown a peak performance after chromating in alloys containing 10-15% nickel. At nickel levels higher than 25-30%, the deposit ceases to be sacrificial to steel.

The alkaline-type bath plates at 20-40% efficiency, and has the advantage of producing uniform thickness and nickel distribution in the deposit across low- and high- current density areas. The deposit has good ductility and has been successfully used on parts requiring post plate forming. The inherent alkalinity of the bath reduces corrosion tendency of unplated surfaces such as internal areas of tubular parts.


2. Automotive components plated with alkaline zinc-nickel and bronze or iridescent chromated.

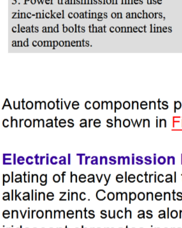
The acid type bath plates faster at twice the efficiency and has been used to produce 10-15% nickel alloys. However, due to its higher efficiency, plate distribution varies across CD range, and nickel content in the deposit may be higher in low-CD areas.

Proper care must be exercised with zinc-nickel alloy baths to not substantially exceed 15% nickel in the deposit in order to maintain optimum corrosion resistance. As the nickel content increases beyond 15%, chromate passivation becomes exceedingly difficult, and eventually impossible to obtain resulting in reduced corrosion resistance.

Several years of pilot lab and field tests have showed the zinc-nickel process to be superior to all other zinc alloys in terms of corrosion resistance, and range of applications, including cadmium replacement.

Subsequently, various industries adopted zinc-nickel into their finishing specifications. This prompted several plating facilities, captive and contract shops, to install the process to accommodate the new finishing requirements. These plating installations vary in size from 200 to 5,000 gal, for rack and barrel. Fig. 1 shows the use of zinc-nickel by various industries.

Automotive Industry. This industry continues so far to be the prime beneficiary of this technology. A combination of substantial upgrading of warranties on performance, and the need to replace cadmium plating were behind the decision to specify zinc-nickel coatings.

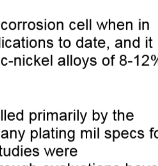

3. Power transmission lines use zinc-nickel coatings on anchors, cleats and bolts that connect lines and components.

Most Japanese and European car manufacturers adopted zinc-nickel specifications in the early 1980's. U.S. car manufacturers incorporated zinc-nickel as well as other zinc alloys in the early 1990's to replace cadmium and improve corrosion resistance of conventional zinc coatings, mostly for under-the-hood components. Ford Motor Co issued its engineering code in 1990 to replace cadmium with zinc-nickel after considerable lab and proving ground testing. The end product goes into passenger car and light truck power steering, air conditioning and hydraulic brake components. New salt spray test requirements on some of these components now stand at 768 hrs to red rust, for 8 microns ofzinc-nickel with iridescent chromate. Other automotive requirements for zinc-nickel with bronze chromates are currently being produced and regularly achieve 1,000-1,200 hrs to red rust in NSS testing. These new technologies allowed plating shops the removal of cadmium baths, and remain in environmental regulatory compliance, while supplying a superior alternative to the industry.

Automotive components plated with alkaline zinc-nickel and chromated with iridescent or bronze chromates are shown in Fig. 2.

Electrical Transmission Industry. Several zinc alloy processes were thoroughly evaluated for the plating of heavy electrical transmission components. Alkaline zinc-nickel was selected to replace alkaline zinc. Components such as anchors, cleats and bolts are exposed to the elements and harsh environments such as along highways and near seashore areas. (Fig. 3) Zinc-nickel coatings with iridescent chromates increased the corrosion resistance of these components from 250 hrs to more than 1000 hrs in salt spray testing. The new coating may be applied directly over steel or pre-galvanized steel for the required additional protection.

Another growing application is the plating of coaxial TV cable connectors, assembled to painted aluminum housings. These connectors are traditionally cadmium plated for maximum corrosion protection both indoors and outdoors. Alkaline zinc-nickel has replaced cadmium as an environmentally safer substitute.


4. Alkaline zinc-nickel-plated fasteners. Right is as plated; left after 136 hrs salt spray and one hr heat treatment at 250F.

Fastener Industry. This is another in-dustry that depended heavily on cadmium plating. Zinc-nickel has out performed plain zinc or cadmium in corrosion resistance before and after crimping and baking for hydrogen embrittlement relief. Like cadmium, zinc-nickel-plated parts can be easily chromated after baking or heat treating with minimum activation. Another advantage of chromated zinc-nickel over cadmium and zinc is its ability to maintain a high corrosion resistance following heat treatment (Fig. 4). Since it is an alloy-rich chromate, the thermal degradation is not as critical as with conventional chromated zinc or cadmium. Fig. 5 shows how heat treatment breaks down the corrosion resistance of zinc-cobalt and zinc-iron plating.

Other tests conducted by Boeing some years ago, and later by other industries, confirmed that zinc-nickel-plated fasteners did not set up a detrimental galvanic corrosion cell when in contact with aluminum. This is the closest performance to cadmium in such applications to date, and it opens the door for industries involving aluminum bodies. Plating fasteners in zinc-nickel alloys of 8-12% nickel is now a growing industry.

Defense Industry. A wide range of activities are taking place in this area, propelled primarily by the desire to replace cadmium. Since cadmium coatings have been at the core of many plating mil specs for many years, its replacement in such a critical industry must proceed carefully. Studies were commissioned to research labs such as Battelle and Ocean City Research. Thorough evaluations have been conducted at several plating shops.

TABLE I—Zinc-Nickel Bath Parameters	
Caustic	15-19 oz/gal
Zinc	0.8-1.6 oz/gal
Nickel	0.18-0.24 oz/gal
Temperature	74-86F
Anode CD	5-9 A/sq dm
Cathode CD	1-5 A/sq dm
Alloy composition	5-8 pct Ni; Balance Zn

Army. In 1990, FMC a prime supplier of tanks and armored personnel carriers to the army adopted zinc-nickel plating as replacement for cadmium at it's previous Loma Pieta, California plant. Since then, various army branches such as maintenance depots, showed an increasing interest in these new cadmium alternatives.

Ocean City Research Center, under government contract, undertook a comprehensive study of available environmentally acceptable plating technologies. Its initial findings show the zinc-nickel at the forefront of candidates for cadmium replacement. Additional work is being done in this area to arrive at a complete range of options.

Alkaline Zinc-Nickel Bath. The bath is quite simple to operate, and is similar to the alkaline non-cyanide zinc bath. The alloying nickel metal is added in a liquid form on an ampere-hour basis along with grain refiner brightening agents.

TABLE II—Bath Compositions — Acid Zinc-Nickel		
	Types	
	Potassium Chloride	**Ammonium Chloride**
Zinc Chloride	130 g/liter	120 g/liter
Nickel Chloride	130 g/liter	110 g/liter
Potassium Chloride	230 g/liter	
Ammonium Chloride		150 g/liter
pH	5-6	5-6
Cathode CD	0.1-4.0 A/sq dm	0.5-3.0 A/sq dm
Current Dist. (Zn)	80 pct	60 pct
Current Dist. (Ni)	20 pct	40 pct
Temperature	24-30C	35-40C
Anodes	Zinc, or Zinc and Nickel, connected to two separate rectifiers	
Alloy Composition	8-15 pct Ni; Balance Zn	

Conventional zinc anodes are used to supply the zinc metal. The main electrolyte is caustic soda, containing the dissolved zincate.

The bath parameters for zinc-nickel are listed in Table I. Newer alkaline bath formulations are capable of producing higher alloys of 8-12% nickel.

Acid Zinc-Nickel Bath

This bath operates in a similar manner as many acid chloride zinc processes, and use the same basic electrolytes. Earlier systems required the use of separate anodes of zinc and nickel connected to separate rectifiers. Newer technologies use a single rectifier and zinc anodes, while supplying nickel to the bath in the form of an additive on an ampere-hour basis. A typical bath composition is shown in Table II.

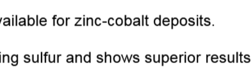
Zinc-Iron

This process produces alloy deposits containing 15-25 pct iron. Electroplated strip steel adapted this process initially to improve its corrosion resistance. The deposit has good weldability and ductility that are needed in subsequent manufacturing steps. This alloy can be adjusted to improve adhesion of electropainting of formed steel components. Black chromating is the most suitable for this type of alloy.

Although zinc-iron offers good corrosion resistance as plated and chromated, exposure to heat deteriorates this resistance rapidly. This makes it unsuitable as a coating for under-the-hood automotive components.

The typical bath formulation for zinc-iron, acid-type, used in strip line plating is shown in Table III.

Zinc-Cobalt


5. Zinc-cobalt-plated sleeve and zinc-iron-plated fastener were salt spray tested 136 hrs. Left is as plated; right after one hr heat treatment at 250F.

Zinc-cobalt alloy plating is becoming more popular because of its relatively lower cost of operation compared to zinc-nickel. It offers lower corrosion resistance; however, the level is still adequate for certain applications and an improvement over plain zinc of the same thickness. The fasteners industry has adopted this technology in many of its applications.

Commercially available processes are similar to low-ammonia or ammonia-free acid chloride zinc baths. Some newer baths operate on the alkaline side. The deposit contains up to one pct cobalt. The acid-type bath has a higher cathode efficiency, and reduced hydrogen embrittlement, but its plating thickness distribution varies substantially between low- and high-current-density areas.

Chromate conversion coatings in iridescent black and yellow are available for zinc-cobalt deposits.

Zinc-cobalt has good corrosion resis-tance to atmospheres containing sulfur and shows superior results in Kesterich (S02) tests.

The compositions of a typical zinc-cobalt bath are shown in Table IV.

TABLE III—Typical Zinc-Iron Bath Composition (Strip Line Plating)	
Ferric Sulfate	200-300 g/liter
Zinc Sulfate	200-300 g/liter
Sodium Sulfate	30 g/liter
Sodium Acetate	20 g/liter
Organic Additive	5 g/liter

Tin-Zinc alloys contain 70-90% tin with the balance being zinc. Tin-zinc alloy plating has been known for sometime, applied mainly from cyanide-based electrolytes. New technologies offer baths that are neutral and cyanide free. The deposit is ductile and maintains good solderability even after aging. Corrosion resistance equals or exceeds that of zinc-nickel alloys. Chromating is usually limited to clear or yellow. Applications of the neutral tin-zinc process are growing in the electronic industry, glass to metal seals and fasteners industry as a direct replacement for cadmium (Table V).

Passivation and Post Plate Treatment

There are several hexavalent chromate passivation treatments for the zinc alloys, which are necessary to produce the enhanced corrosion resistance of these alloys. Recent developments have introduced trivalent chromate formulations as well as chromate free passivates in various finishes ranging from clear to iridescent and black. Inorganic and organic topcoats are also available to further enhance overall corrosion resistance and provide other properties such as lubricity and torque and tension.

As more industries worldwide respond to local bans on cadmium plating, and demands for improved functional coatings, zinc alloys offer the industry a viable alternative to conventional zinc and cadmium plating. The last few years have seen large scale installations of these technologies. The trend is continuing. Corrosion resistance of the various zinc alloy deposits is compared in Table VI. Zinc-nickel alloys maintain the highest corrosion resistance even after heat treatment.

ASTM specifications are available for zinc alloys. They are as follows:

Zinc Cobalt	B840
Zinc Iron	B842
Zinc Nickel	B841

TABLE IV—Bath Compositions—Zinc-Cobalt		
	Types	
Typical Acid Baths	**Boric Acid**	**Ammonium Chloride**
Zinc Chloride	80-90 g/liter	80-90 g/liter
Potassium Chloride	150-200 g/liter	50-150 g/liter
Ammonium Chloride		50-70 g/liter
Boric Acid	20-30 g/liter	
Cobalt Chloride	1-20 g/liter	1-20 g/liter
pH	5-6	
Temperature	24-40C	
Cathode CD	1.0 - 4.0 A/sq dm	
Anodes	Zinc	
Alkaline-Type Baths		
Zinc Oxide	10-20 g/liter	
Sodium Hydroxide	80-150 g/liter	
Cobalt (additive)	1.0-2.0 g/liter	
Organic Additives	as specified	
Temperature	25-40C	
Cathode CD	0.1-4.0 A/sq dm	
Anodes	Zinc	

TABLE V—Bath Composition Neutral Tin - Zinc	
Tin as Sn+2	7.5 - 22.5 g/liter
Zinc	5.25 - 15 g/liter
Temperature	18 - 25 C
Cathode CD	0.5 - 2.0 amps/sq dm
Anodes	Tin-zinc cast alloy

TABLE VI—Corrosion Resistance of Zinc Alloys vs. Zinc			
	Hrs to Red Rust		
	Before Heat Treat	After Heat Treat	
		120C, 4 Hrs	200C, 4 Hrs
Zinc-Nickel	1,500+	800-900	800+
(6-9 pct Ni)	1,000+	200-250	600-700
Zinc-Cobalt	500	300-350	180-240
Zinc-Iron	1000	200-250	180-240
Zinc	300-350		150-200