Comparison of Alkaline Zn-Ni & Acid Zn-Ni As a Replacement Coating for Cadmium

By James A. Bates

P-04475
28151
PDF

Cadmium plating has been used as a corrosion-resistant coating for many years, providing good corrosion resistance with excellent self-lubricating properties. Because of concern regarding cadmium's toxicity, alternative coatings are pursued. Zinc alloy processes are suitable candidates as substitutes for cadmium for corrosion resistance. Even pure zinc is a suitable substitute, but its effectiveness is short-lived. This article, which is an edited version of a paper that was presented at the 15th AESF/EPA Pollution Prevention and Control Conference (January 24–27, 1994), documents the testing and investigation undertaken to compare acid and alkaline Zn-Ni processes.

Restrictions on exposure to cadmium continue in the United States, and bans already exist or are proposed in Europe, Japan and elsewhere. As of June 30, 1995, cadmium-plated products will be prohibited in equipment and machinery for the production of textiles and clothing, household building materials, agriculture-related equipment/products and vehicles throughout Europe. Applications in aerospace, mining, nuclear industries, safety devices, electrical contacts, and offshore (maritime) industries are exempt from the ban, but only until a substitute material is identified. The zinc alloy processes offer the potential for eliminating two environmental hazards: cadmium and cyanide. Regulatory compliance will be easier to achieve for acid and alkaline Zn-Ni, because zinc and the alloying metal have higher allowable discharge concentrations than those imposed on the cadmium process.

Alkaline Zinc-Nickel

Alkaline Zn-Ni is a cyanide-free plating process. The deposit consists of a zinc alloy containing 5–9 percent nickel, regardless of plating current density. The deposit is characterized by adequate thermal and corrosion resistance, far superior to that of conventional zinc plating processes. Chromate conversion coatings can be easily applied to further enhance corrosion resistance and appearance. The coating provides more than three times the corrosion resistance to salt spray than conventional zinc finishes. The process is maintained at a temperature range of 70–80 °F, using a heat exchanger designed for alkaline solutions. A wide range of current densities can be used, from 20-90 A/ft^2 (45 A/ft^2 is typical).

Proprietary Acid Zinc-Nickel

The proprietary Zn-Ni process (Process 1) was developed and patented by Boeing. It is a Zn-Ni alloy that provides the corrosion protection of cadmium plating without the environmental hazards and without hydrogen embrittlement. The deposit typically contains 10–18 percent nickel, with the balance zinc. The application process normally includes chromate conversion coating after plating. The non-cyanide chloride bath utilized with Process 1 produces deposits that are superior to cadmium in terms of corrosion protection and low hydrogen-embrittling characteristics. The structure is open-grained but smooth, and the porosity is optimized with this particular process to permit hydrogen bake-out and minimize post-plating embrittlement under service conditions. The low hydrogen-embrittling characteristics make it an excellent choice for both low- and high-strength steels.

Hydrogen atoms are easily absorbed by metals, both during processing and when the finished products are in use. Because hydrogen adversely affects ductility, sufficiently high levels of hydrogen can cause brittle failure in metals subjected to sustained stress. Hydrogen embrittlement is a critical concern in aerospace and other industries.

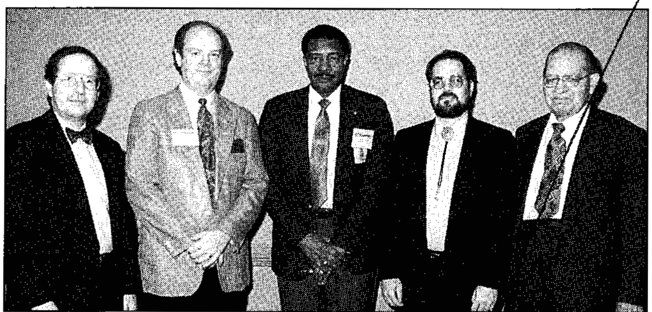
Table 1
Corrosion Testing Results

Plating	Chromate	Hr—96	Hr—500	Hr—1500
Cd	no	no corrosion	n/a	light, white corrosion
	yes	no corrosion	n/a	light, white corrosion
Proc. 1	no	no corrosion	med., white corrosion	med., white corrosion
	yes, immersion	no corrosion	light, white corrosion	light, white corrosion
	yes, immersion & heat-treat	no corrosion	light, white corrosion	light, white corrosion
Proc. 2	no	no corrosion	heavy, white corrosion	heavy, white & light red corrosion
	yes	no corrosion	light, white corrosion	med., white & slight red corrosion
Proc. 3	no	no corrosion	heavy, white, red; Hr-240	n/a
	yes	no corrosion	light, white corrosion	light, white corrosion

NOMINATING—(Front, L-R) Ted Kodama; Ed Budman; Myron Browning, CEF; Jim Tharp; and Dan Leonhardt. (Standing, L-R) Dr. Ken Newby; Steve Schachameyer; Bob McIntyre; Chairman Richard Watson, CEF; John Peck; and Timothy Baublitz.

MEMBERSHIP—(Front, L-R) Sue Watcher, Board of Directors; Sharon Drake, AESF membership services coordinator; and Betsy Kraft-Lieberman. (Standing, L-R) Ted Witt, CEF; Milton Stevenson, Sr., AESF Board of Directors; Chairman Charles Remied; and Charles Reichert.

OSHA—(Front, L-R) Vicki Sherwood; Peter Moleux, P.E.; and Ed Page Jr. Standing (L-R) Dr. John Lott; Michael Kerr; Larry Clark; Martha Martin, CEF; and Tom Martin, CEF.



PRINTED CIRCUIT—(L-R) Mike Faulman; Chairman Bob Audette, CEF; Charles Remied; Dr. Harvey Trop; and Robert Walton.

PULSED ELECTRODEPOSITION—(L-R) Bob Mikkola, CEF; Myron Browning, CEF; Chairman Bob Kappler; Ned Mandich, CEF; and George Carney.

You Can Be A Leader

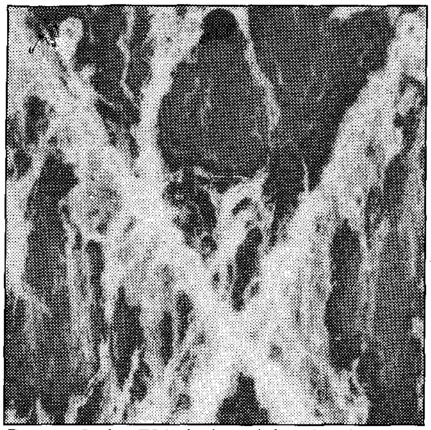
AESF and its president are asking you to lend your voice and skills by volunteering for appointment to one or more of the Society's seven Boards, eight Sections and nearly 40 administrative and technical Committees. They provide leadership and ideas for our vital industry.

Attendance is required at a minimum of two meetings each year (usually at SUR/FIN® and AESF Week). There is no financial compensation for your services, time or travel expenses, but you will be rewarded with great satisfaction, plus:

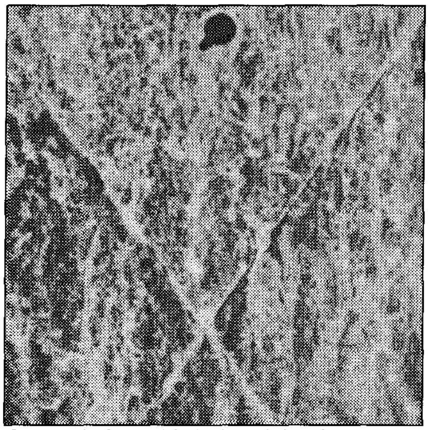
- Idea-Sharing
- Inter-Industry Contacts
- Up-to-the-Minute Info

For information, contact W. Joan Harrison, assistant executive director, AESF. Phone 407/281-6441.

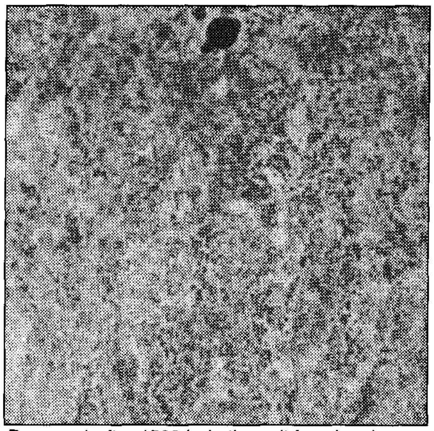
REGIONALS—(Front, L-R) Milt Stevenson, Sr., Empire State Regional; Sue Watcher, Golden West Regional; Chairman Mike Murphy (Mid-Atlantic Regional). (Standing, L-R) Dick Phillips Jr., Piedmont Regional; Jerry Schmidt, Eastern Canada Regional; Kenneth Gatchel, Great Lakes Regional; Jim Tharp, Dixie Regional; Richard Going, CEF, Northeast Regional; Tom Martin, CEF, Tri-State Regional; David Montgomery, CEF; and Jim Mayer, Mid-East Regional.



Process 3 after 72 hr in the salt fog chamber.



Process 2 after 672 hr in the salt fog chamber.



Process 1 after 1500 hr in the salt fog chamber.

Standard acid Zn-Ni baths are more efficient than alkaline processes, releasing less hydrogen during the plating. Alkaline baths are only 40–65 percent efficient, while acid baths are 85–95 percent efficient. Alkaline baths provide 5–9 percent nickel. While protection is similar to cadmium, peak protection occurs at 10–18 percent (typical range for acid Zn-Ni).

Test Program

A test program to examine and compare Boeing's acid Zn-Ni process (Process 1) and two widely used alkaline Zn-Ni processes (Processes 2 & 3) versus cadmium plating was initiated. The investigation included physical properties of the coatings, corrosion resistance, hydrogen embrittlement, paint adhesion, and microscopic and macroscopic examination.

Testing was performed on 4x6-in. panels of SAE 1010. Hydrogen embrittlement specimens were annealed AISI 4340, and tested according to ASTM F 519, using Type 1a notched specimens. (Specimens and testing services were provided by Metals Engineering and Testing of Phoenix, AZ.)

The specimens were plated as follows:

- 4 panels and 5 notched specimens without plating
- 4 panels and 5 notched specimens with cadmium and no chromate
- 4 panels and 5 notched specimens with cadmium plus chromate conversion
- 4 panels and 5 notched specimens with Process 1 (acid Zn-Ni) and no chromate
- 4 panels and 5 notched specimens with Process 1 (acid Zn-Ni) plus chromate conversion
- 4 panels and 5 notched specimens with Processes 2 & 3 (alkaline Zn-Ni) and no chromate
- 4 panels and 5 notched specimens with Processes 2 & 3 (alkaline Zn-Ni) plus chromate conversion
- 1 panel from each group was additionally coated with an epoxy amine paint.

The corrosion resistance test consisted of spraying the specimens with a 5-percent sodium chloride solution in a closed cabinet in accordance with ASTM B 117. (This testing was performed by QC Metallurgical Labs in Ft. Lauderdale, FL.) All panels were plated 0.30-0.45 mil and salt-spray-tested for up to 1500 hr or until the appearance of red rust. Observations were recorded at 96, 500 and 1500 hr.

Galvanic properties were obtained by scribing one panel from each process with an "X" to expose the base material. The samples were then salt-spray-tested in accordance with ASTM B 117.

Painted panels were evaluated by the following criteria:

- Acceptable appearance—Free from runs, scratches, voids and other irregularities
- Acceptable smoothness—No specks, bumps or roughness
- Wet adhesion, 24-hr soak and tape test—No lifting, cracking or damage to the paint
- Chemical resistance—After rubbing the surface with a MEK-saturated cloth, did not remove the paint to the base metal

Metallographic evaluation of the plated specimens included the following tests/evaluation:

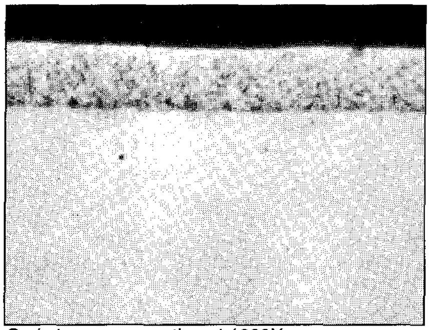
- Hardness—The resistance of a metal to plastic deformation measured by indentation testing technique
- Hydrogen embrittlement—The condition of low ductility, resulting from the absorption of hydrogen measured by tensile testing technique
- Macro photos—Macroscopic evaluation, requiring a high-quality camera with up to 50 magnification
- Micro photos—Microscopic evaluation, including EDX (energy dispersive analyzer) and dot-mapping

Test Results

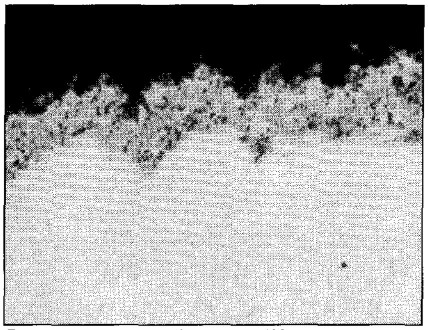
Test data are shown in Tables 1–5. Corrosion cannot be avoided, but the rate at which it occurs can be deterred by use of a coating. The conductivity of the coating results in another property—that of "sacrificiality," which, in coatings, is defined as the preferential corrosion of an active coating layer and the corresponding protection of a less-active metal. Zinc, cadmium and aluminum are common sacrificial metals with respect to ferrous alloys.[1]

Table 2
Hydrogen Embrittlement Testing Results

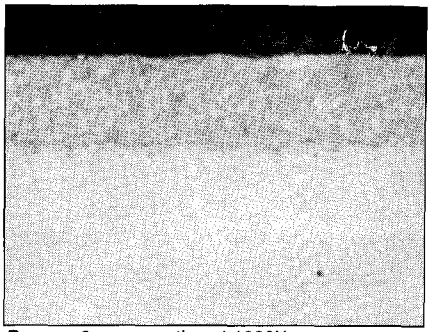
Sample	Chromate	Hr	Results
Cd	no	2	unsatisfactory
	yes	2	unsatisfactory
Proc. 1	no	200	satisfactory
	yes	200	satisfactory
Proc. 2	no	200	satisfactory
	yes	200	satisfactory



Cadmium cross-section at 1280X.



Process 1 cross-section at 1280X.



Process 2 cross-section at 1280X.

Many texts state that cadmium is more resistant to marine environments and alkaline conditions than zinc. Although both metals are sacrificial to steel, cadmium produces smaller amounts of continuous corrosion products. In addition, cadmium performs well as a fastener coating because it has a fine-grained structure that offers excellent torque tension properties. Cadmium metal is toxic, so mold and fungus will not grow on surfaces plated with it.

From this investigation, it was noted that zinc alloy deposits are open-grained and generally harder than cadmium or pure zinc. Zinc-nickel alloys are characterized by high plasticity and good adhesion to base. Corrosion products of cadmium tend to readily break apart, while zinc and zinc alloy corrosion products tend to hold fast. The microcracking of acid Zn-Ni is the very feature that lengthens the time to red rust in corrosion tests. Microcracked ZN-Ni alters the electromotive potential of the deposit. It spreads out the corrosion cells so that there are many weak ones, but few strong cells that help corrosives to burrow down to basis metal, causing red rust.

The Zn-Ni-plated coupons demonstrated less thickness loss than cadmium. The oxidation of zinc is slowed by the presence of nickel, and as oxidation progresses, the nickel remains as a barrier against further corrosion. Initially, therefore, the corrosion protection is sacrificial, but as corrosion occurs, a gradual switch to barrier protection takes place.

The Process 1 (acid Zn-Ni) coating appears homogeneous. No defects or inclusions are present. It shows a columnar and pyramidal structure of crystal grains that appear more rounded after the chromate treatment. Moreover, after chromate treatment, some narrow and deep cracks are visible. As stated previously, this improves the corrosion resistance.

Because the range of nickel concentrations for maximum corrosion is relatively narrow, it is essential that small changes in operating conditions do not lead to substantial changes in nickel concentration from the optimum. A reduction in pH gives a reduction in nickel content of the deposit. A wide variety of variables must be controlled to obtain the "right" alloy composition, often including pH, temperature, chemistry and agitation level. As has been noted in other literature, the nickel content of the Zn-Ni deposit increased with the increase in the concentration of nickel in the plating solution, temperature, pH and solution agitation, but decreased with increase in current density. Chromate receptivity decreases when the nickel content of the alloy deposits is increased to more than 15 percent, resulting in a poor chromate film.

Below a nickel content of about 15 percent, the Zn-Ni alloy gives sacrificial protection to steel, the same mechanism as conventional zinc. Above 15 percent, the potential difference crosses over, resulting in cathodic protection as would be experienced with a nickel deposit. In the latter case, should the deposit be scratched, the base metal becomes sacrificial to the plated deposit.

A dot-mapping of the coating was also undertaken. In this procedure, a field of view is scanned and a modulating X-ray detector is set to be sensitive to a particular element. The resultant image is composed of discrete dots, and the concentration of the dots give a rough indication of the local concentration of the selected element. The Process 1 coating was shown to be the more uniform of the alloy coatings, with greater concentration of nickel.

Table 3
Paint Testing Results

Sample	Chromate	Acceptable Appearance	Acceptable Smoothness	Gloss	Acceptable Adhesion	Acceptable Chem. Resistance	Thickness
Cd	no	yes	yes	87.1	yes	yes	0.0022
	yes	yes	yes	93.3	yes	yes	0.0028
Proc. 1	no	yes	yes	89.1	yes	yes	0.0023
	yes	yes	yes	86.2	yes	yes	0.0022
Proc. 2	no	yes	yes	91.9	yes	yes	0.002
	yes	yes	yes	94.1	yes	yes	0.0023
Control	no	yes	yes	94.7	yes	yes	0.002

Use of cadmium plating on high-strength steel has been a problem for 75 years because of the baking cycles needed to eliminate the likelihood of hydrogen embrittlement. Each application's procedure has certain limitations and problems. Any aqueous electroplating process retains the statistical possibility of embrittlement. Hydrogen can enter into a metal, then diffuse rapidly throughout the material. This will cause delayed fracture under a sustaining load. Fracture occurs with little evidence of ductility and the fracture surface is bright. It is usually intergranular, but sometimes various amounts of cleavage fracture may be present. The release of hydrogen after plating is difficult because the plated coating constitutes a barrier to the outlet of the hydrogen. The Lawrence hydrogen gage is available for measuring uptake of hydrogen. Fatigue properties are measured by standard metallurgical techniques. Some coatings are deposited with a structure that allows the elimination of absorbed hydrogen. Process 1 is an example of one of these coatings. The open-grain structure allows for easy escape of any hydrogen entrapped during processing.

In some applications, engineers have to seek ways of keeping even the sacrificial corrosion from forming for periods of time. One method of doing this is to seal off the surface from the environment by coating it with paint. Paint is effective as long as it remains adherent, continuous, and impervious to moisture. The primers used in this investigation were formulated to be fluid-resistant, and to prevent or retard general exfoliation and dissimilar metal corrosion on interior and detail parts. They feature very good adhesion, fast adhesion, fast dry, easy application and low cost. The primers are also relatively forgiving of difficult application conditions and marginal surfaces. Epoxy amine topcoats are high-gloss, tough, chemical and hydraulic-fluid-resistant closed coatings for use in utility areas.

Eliminating Hazards Without Sacrificing Service

Barrier films of cathodic metals, such as nickel, are effective for corrosion control as long as the films are not damaged. Corrosion of the base metal accelerates after film damage. A coating to replace cadmium must have the same, or better, properties.

The zinc alloy processes offer the potential for eliminating the environmental hazards of cadmium and cyanide. Waste treatment is normally accomplished simply by adjusting pH, thereby eliminating the need for cyanide oxidation. Regulatory compliance would be easier to achieve than with cadmium, because zinc and the alloying metal would have higher allowable discharge concentrations than those imposed on the cadmium process. Deposits resulting from Process 1 are strictly functional. The process is intended to provide a highly functional finish that can be heat-treated, deformed or otherwise handled, while still providing effective corrosion protection. The zinc alloy process exhibits more than five times the corrosion protection of conventional zinc, and three times that of cadmium. The Process 1 solution will not attack the unplated interior surfaces of tubular and other parts.

Process 1 is highly efficient, with little free hydrogen released during plating. Its unique structure facilitates migration of any hydrogen that may become trapped. In other tests conducted by Boeing, Process 1 also showed excellent resistance to re-embrittlement after plating.

Table 4
Hardness Testing Results

Sample	Chromate	Reading	DIM	HK 300	HK 5
Control	no	1	116	317	
	no	2	118	307	
	no	3	116	317	
Cd	no				
	yes	1	51		27.4
	yes	2	50		28.4
	yes	3	50		28.4
Proc. 1	no	1	25		114
	no	2	36		58
	no	3	19		197
Proc. 1	yes	1	17		246
	yes	2	18		220
	yes	3	18		220
Proc. 2	no	1	27		97.6
	no	2	19		197
	no	3	40		44.5
Proc. 2	yes	1	21		162
	yes	2	16		278
	yes	3	18		220

Table 5
Galvanic Corrosion Testing Results

Sample	Chromate	Hr	Results
Cd	no	672	light, white corrosion
	yes	672	light, white corrosion
Proc. 1	no	216	red corrosion
	immersion	600	red corrosion
	immersion, heat-treat	528	red corrosion
Proc. 2	no	192	red corrosion
	yes	672	heavy, white corrosion
Proc. 3	no	72	red corrosion
	yes	960	light, white corrosion

All Zn-Ni-plated specimens passed hydrogen embrittlement tests in this investigation. The sample size, however, was very small and not statistically significant. Hydrogen embrittlement testing is not quantitative. Additional testing to determine actual hydrogen pick-up from the plating procedure is recommended to quantify the process differences and susceptibility of hydrogen embrittlement.

Processing procedures for alkaline Zn-Ni and acid Zn-Ni were similar, but the results of the process were different. The greatest differences were in the concentration of zinc and nickel in the deposits. As stated before, this is determined by the control of the plating process. Process 1 can be maintained with consistent deposition, thereby providing a consistent concentration of nickel and zinc. ❑

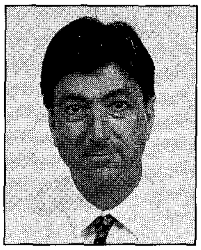
Acknowledgments

Thanks is expressed to Courtaulds Aerospace Coatings for paint application and testing, and to METL Laboratories for investigation assistance. Special thanks is given to Carol Waddel of Pure Coatings and Cheryl Smith of Allied Signal Fluid Systems for designing and coordinating the testing.

Reference

Technical Bulletin, "An Improved Coating Process for Steel Compressor Components—SermeTel Process 5380 DP," Mark F. Mosser, SAE880879, Limerick, PA 19468.

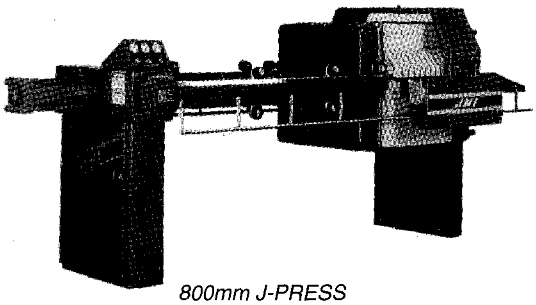
Editor's note: The full text of this paper, including additional figures, EDX test results, electron images and dot-mapping photos, is available in the proceedings of the 15th AESF/EPA Pollution Prevention and Control Conference. Price, excluding shipping, to AESF members is $50; $70 to non-members. Call AESF Publications Sales (1-800/334-2052) to order by credit card.



About the Author

James A. Bates, 13756 Ishnala Circle, West Palm Beach, FL 33414, holds a BS in mechanical engineering from Marquette University. He has been involved with engineered materials throughout his 20-year career, most recently as vice president, Sales and Marketing, for Pure Coatings, Inc. in West Palm Beach, FL. Bates is a member of the AESF South Florida Branch and the Aerospace Materials Section of the Society of Automotive Engineers.

(see pages 20, 41–43)



800mm J-PRESS