Electrodeposition of Zinc-Cobalt Alloy From Cyanide-Free Alkaline Plating Bath

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Zinc-cobalt alloy coating having 0.3 to 1.0 percent cobalt has been deposited from a conventional non-cyanide alkaline zinc plating bath containing zinc, NaOH, and proprietary addition agents. The alloying element, cobalt, is added to the bath together with a complexing agent. The influence of plating bath and process variables, such as temperature, agitation and current density on alloy deposition was studied in detail. The deposit characteristics and corrosion resistance of the Zn-Co coating were evaluated and compared with conventional alkaline zinc. The Zn-Co alloy accepts all usual chromate conversion coatings with a modification in composition, pH and time of immersion.

Electrodeposited zinc coatings containing small amounts of other alloying elements, such as Ni, Fe, Co, Cr, Cd, etc.,[1] offer a way to improve considerably the corrosion resistance of plated parts. A major development in this area is the introduction of a zinc-cobalt alloy coating containing 0.3 to 1.0 percent cobalt.[2] This alloy is reported to be two to three times more corrosion resistant than pure zinc and three times that of cadmium on steel.

Zinc-cobalt alloy can be electrodeposited either from acid[3,4] or alkaline baths.[5] The acid bath consists of zinc and cobalt salts, electrolytes, buffers and optional addition agents. It operates at a pH range of 4 to 6. Alkaline zinc-cobalt is basically the same as an alkaline zinc plating bath, but eliminates the limitations of the acid bath. It contains a very low cobalt concentration (1 to 3 g/L) and deposits containing a uniform percentage of Co are obtained over a wide range of current densities: 1 to 10 A/dm^2. The system is ammonia-free and cyanide-free, using 100 to 140 g/L of NaOH. A conventional zinc anode is used and cobalt is added as a liquid concentrate, pre-mixed with a complexer and replenished on the basis of amp-hr consumption.

This paper reports the possibility of converting an existing alkaline cyanide-free zinc plating bath to an alloy bath by introduction of cobalt in the form of a complex. Details of bath constituents and operating conditions are described.

Experimental Procedure

Hull Cell experiments were carried out in a 267-mL cell for five min at various currents to optimize bath composition. Clear Blue, Iridescent Yellow and Olive Green chromate conversion coatings were applied in solutions prepared by modifying the conventional zinc chromating pre-mix concentrates. The chromating process was optimized with respect to the color and adhesion of the chromate film.

The percentages of zinc and cobalt in the deposits were determined by atomic absorbance spectrometry (AAS). After a series of experiments, a standard bath was chosen for further studies, with the composition shown in Table 1.

Corrosion Tests

Corrosion resistance of the alloy deposit was evaluated by conventional neutral salt spray test and by Tafel polarization test. The electrochemical behavior of the alloy was determined in an unstirred 5-percent NaCl solution. A Tafel plot was obtained for a given sample by polarizing it to ±200 mV from the corrosion potential. The resulting current was plotted on a logarithmic scale and the corrosion current, i_{corr}, obtained by extrapolating the linear portion of the curve back to the corrosion potential. Salt spray tests were carried out using a neutral 5-percent solution of NaCl. The specimens were arranged in a salt spray cabinet and exposed in accordance with ASTM B-117.

Surface Examination & Analysis

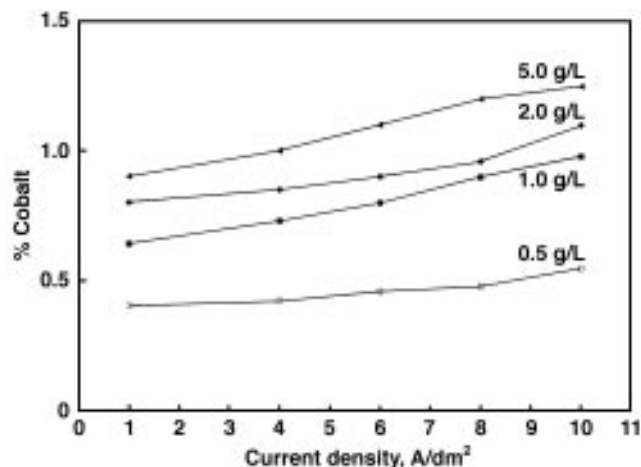The cross-sectional microstructure of the Zn-Co deposit was examined by optical microscope. The surface appearance

Fig. 1—Influence of concentration of cobalt on deposition of Zn-Co alloy.
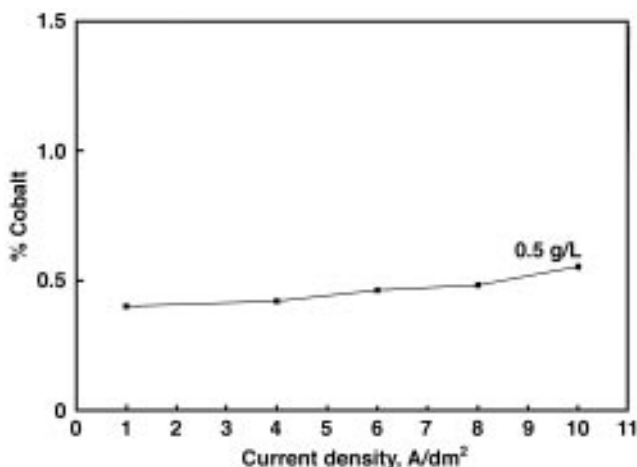

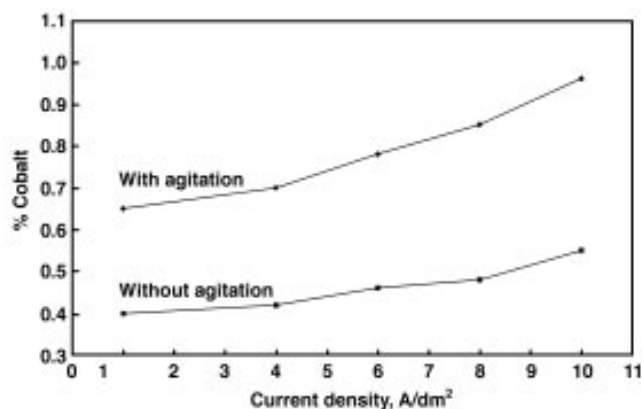*Fig. 2—Influence of current density on composition of Zn-Co alloy.*

Fig. 3—Influence of agitation on composition of Zn-Co alloy.

and topography were studied by scanning electron microscope (SEM). Surface characterization was done by ESCA together with X-ray diffraction.

Results & Discussion

A conventional cyanide-free, alkaline zinc plating bath, as shown in Table 1, having zinc and NaOH with a proprietary brightener in the concentration recommended by the supplier was chosen for this study. The concentrations of cobalt and its complexer were optimized by Hull Cell experiments.

Figure 1 shows the influence of the cobalt concentration on the percentage of cobalt in the deposit. As the cobalt concentration in the bath increases, so does the Co content of the alloy deposit. For example, 0.5 g/L of Co in the bath results in 0.4-0.55 percent Co in the deposit, while 5 g/L produces more than one percent.

Cobalt content in the range of 0.3 to 0.8 percent is quite suitable for best corrosion resistance. This can be obtained from 0.5 to 1.0 g/L of Co in the solution and was chosen as the optimum range.

Influence of Complexing Agent

A complexing agent is required to stabilize the Co^{+2} under alkaline conditions. In the absence of a stabilizer/complexer, the Co would be precipitated as oxides/hydroxides. The amount of complexer required is a function of the cobalt concentration. Of the complexing agents tried, the alkanolamine series, such as diethanolamine (DEA) triethanolamine (TEA), N-methylethanolamine, 2-aminopropanolamine were found to give the best results.
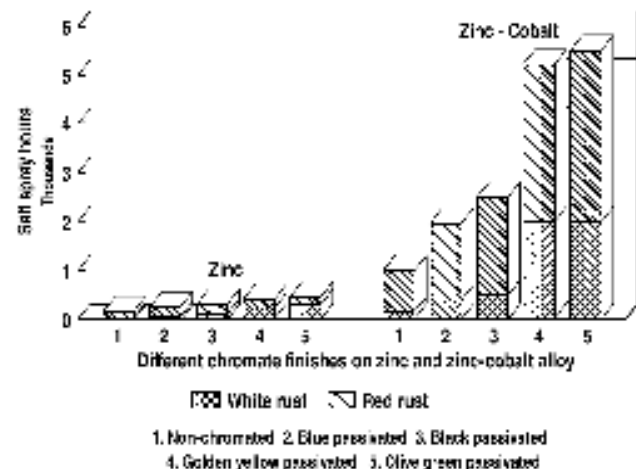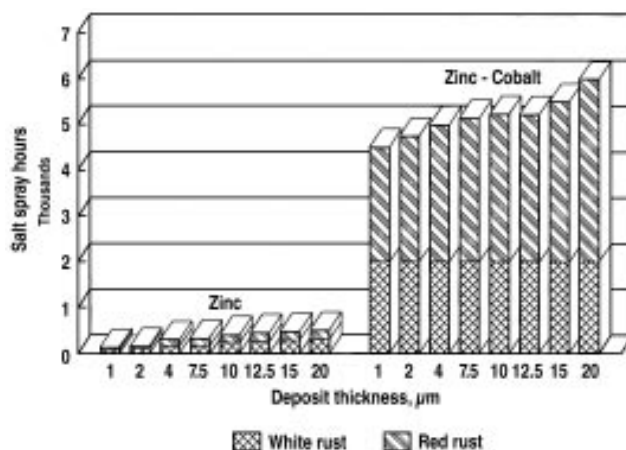

Fig. 4—Comparison of salt spray corrosion resistance of Yellow-chromated zinc and Zn-Co alloy.

Hull Cell experiments were carried out to optimize the concentration of these weak complexing agents, with the objective of obtaining a stable bath and bright and uniform alloy deposits over a wide range of current densities. Concentrations of alkanolamines lower than 10 mL/L produce instability of cobalt under high pH conditions, resulting in precipitates of cobalt oxides/hydroxides. Additional complexer produces a stable bath and increases the bright region 10 A/dm². Addition of more than 30 mL/L produces a thin, bright alloy deposit having a high percentage (>5%) that is not desirable. A range of 10 to 30 mL/L, therefore, was chosen as the operating concentration.

Influence of Current Density

Hull Cell experiments at differing cell currents were employed to optimize the current density range. The Zn-Co bath produces very bright deposits for current densities up to 10 A/dm², whereas a zinc plating bath produces bright deposits only up to 4 A/dm².

Figure 2 shows the influence of current density on the composition of the deposit. As can be seen, there is no significant effect on the cobalt content and uniform alloy composition is obtained over the entire working range of 1 to 10 A/dm².
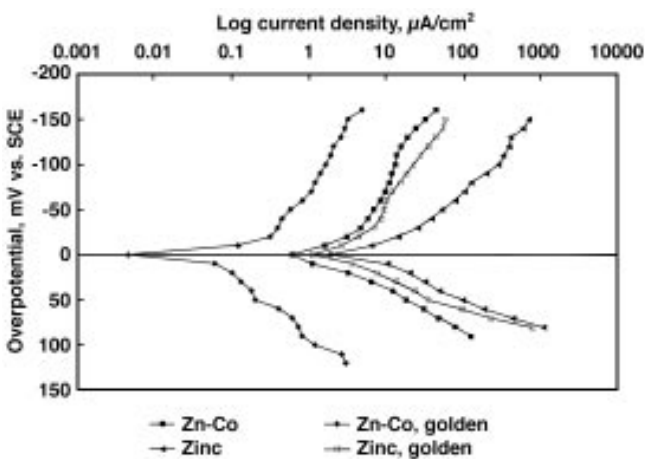

Fig. 5—Salt spray corrosion resistance of zinc and Zn-Co alloy passivated with different chromate conversion coatings.

Fig. 6—Tafel polarization plots of non-chromated and Yellow-chromated zinc and Zn-Co alloy.

Table 1
Typical Bath Composition
For Alkaline Zinc & Zinc-Cobalt Alloy

Parameter	Alkaline Non-cyanide Zinc	Alkaline Non-cyanide Zn-Co Alloy
NaOH, g/L	80-140	80-140
Zinc, g/L	8-14	8-14
Cobalt, g/L	—	0.5-1.0
Fe complexer (TEA, DEA, etc.)		10-30 mL/L
Brightener	As recommended by supplier	As recommended by supplier
Current density, A/dm^2	1-4	1-10
Temp, °C	20-35	20-35

Influence of Agitation
Figure 3 shows the influence of agitation on alloy composition. Air agitation increases the cobalt concentration of the deposit throughout the range of working current densities.

Chromating
The alloy deposits can be chromated just as can normal zinc deposits. The conventional chromating solution cannot be used, however, because it produces gray and black patches. After changes in composition and pH, passivation of the alloy was successful.

Detailed experiments were carried out to optimize conventional zinc chromating solutions with respect to color and adhesion of the chromate film. Table 2 shows the effects of chromating bath composition, pH and time of immersion on Clear Blue, Iridescent Yellow and Olive Green chromate conversion coatings on zinc-cobalt alloy deposits.

Bath Characteristics
The results of the throwing power, cathode efficiency and plating rate measurements for both zinc and zinc-cobalt

Table 3
Bath Characteristics

Parameter	Zinc	Zinc-Cobalt
Oper. current density	1-4 A/dm^2	1-10 A/dm^2
Cathodic current efficiency at 2 A/dm^2	78.85%	84.25%
Throwing power, % at 2 A/dm^2	42.20	44.35
Plating rate at 2 A/dm^2	24.50 μm/hr	27.50 μm/hr

Table 4
Cupping Test for Ductility

Sample	Plating	Cupping Value at 10 kN Load	Drawing Force kN
1	Steel (0.8 mm)	10.6 mm	13.0
2	Zinc - 4.0 μm	10.7 mm	13.0
3	Zinc - 10 μm	10.7 mm	13.0
4	Zn-Co - 4 μm	10.8 mm	13.0
5	Zn-Co - 10 μm	10.8 mm	13.0

plating systems are listed in Table 3. It can be seen that alkaline zinc-cobalt parameters are essentially identical to those of the alkaline zinc plating bath.

Control of the plating solution is simple, as with alkaline zinc. Standard methods will suffice. Regular analysis of cobalt, either by atomic absorbance spectroscopy or other spectroscopy is considered mandatory.

Deposit Characteristics
Ductility & Adhesion
Qualitative examination by bending, scrubbing and heat/quench tests do not result in separation of the zinc-cobalt coating from the base metal. The results of the Ehrichson cupping test for ductility are given in Table 4. They reveal that Zn-Co alloy is a very ductile coating, comparable to zinc on steel.

Hardness
Hardness values for zinc and Zn-Co alloy deposits on steel are listed in Table 5. The hardness of a zinc deposit increases

Table 2
Typical Composition of Chromating Solutions

Bath Type	Operating Parameters			
	Conc. Cr^{+6}, g/L	pH	Time, sec	Finish & Observations
Conventional Clear-Blue	10-15	2-2.5	5-10	Gray lines & patches
Modified bath	100-200	1.6-1.8	5-10	Uniform light blue color
Conventional Iridescent Yellow	25-30	1.6-2.0	30-45	Gray lines & black patches
Modified bath	500-600	1.4-1.6	10-15	Uniform iridescent yellow
Conventional Olive Green	40-60	1.0-1.2	30-45	Black & bleached
Modified bath	500-600	0.8-1.0	10-15	Uniform green color

in the presence of cobalt. A pure zinc coating has recorded hardness of 70 HV$_{50 g}$ (microhardness), while the Zn-Co coating (0.5% Co) exhibits 120 to 130 HV$_{50 g}$.

Corrosion Resistance
Figure 4 shows the corrosion resistance of Golden Yellow-chromated zinc and zinc-cobalt alloy coatings of various thicknesses. The first appearance of white corrosion on the alloy coating was after 2,000 hr, but within 200 hr for pure zinc. The limited variation in corrosion times for the alloy indicates the efficiency of the conversion coating rather than the specific thickness of the alloy coating.

Red rust appeared on a 5-μm alloy coating after 5,000 hr. With increase in plating thickness, red rust is delayed by 100 to 200 hr. Maximum corrosion resistance of 6,000 hr with the alloy coating was obtained with 20 μm
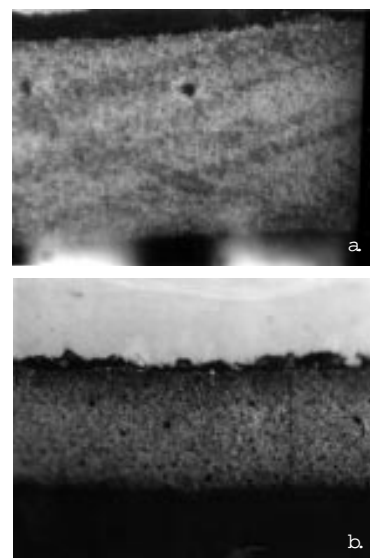

Fig. 7—Cross-sectional optical photomicrographs of (a) zinc and (b) zinc-cobalt alloy. 1000X.
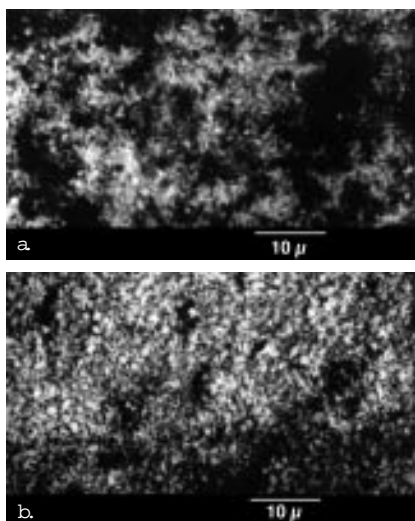
Fig. 8—SEM photomicrograph of (a) zinc and (b) zinc-cobalt alloy surfaces. 2000X.

thickness, a result twice the values reported so far from the same alkaline bath.

Figure 5 shows the salt spray corrosion resistance of different chromate coatings on 10-μm-thick alloy deposits. Non-chromated Zn-Co shows red rust within 1,000 hr. Clear Blue chromated Zn-Co showed red rust within 2,000 hr, while Yellow and Olive Green chromated alloy coatings showed red rust only after 5,225 hr. In all cases, the values obtained are two to three times those reported so far in the literature. When compared with conventional zinc, the corrosion resistance of the alloy is better by about a factor of 10.

A typical Tafel polarization plot of zinc and Zn-Co plating (10 μm thick) is shown with and without Yellow chromate conversion coatings. The corrosion potential of Zn-Co is generally very similar to that of pure zinc and remains at low active values around -1,000 to -1,100 mV vs. SCE. The corrosion current, i_{corr}, or the rate of corrosion varies considerably with the coating. Table 6 shows the Tafel extrapolated corrosion results calculated from the curves of Fig. 6. Lower corrosion rates of about 1.35 to 1.53 mil/yr are obtained for an alloy coating of 10 μm thickness, whereas for zinc alone it is 7.488 mil/yr. Chromate conversion coating can further reduce the corrosion rate to 0.23 mil/yr.

Surface Analysis of Zn-Co Coating

Optical cross-sectional photomicrographs obtained for both zinc and zinc-cobalt coatings deposited from the same alkaline baths are shown in Fig. 7. The amorphous structure of Fig. 7a is typical for pure zinc, while Fig. 7b shows the fine-grained uniform crystalline structure typically obtained for Zn-Co coatings. This difference is considered the explanation of the better corrosion characteristics of the Zn-Co deposit.

The SEM photomicrographs of Figs. 8a and 8b compare the zinc and zinc-cobalt deposits from the cyanide-free alkaline plating baths. Figures 9a and 9b show the X-ray diffraction patterns of the zinc and zinc-cobalt alloy deposits. The spectra agree well with the reported data, revealing the presence or absence of cobalt in the deposits.
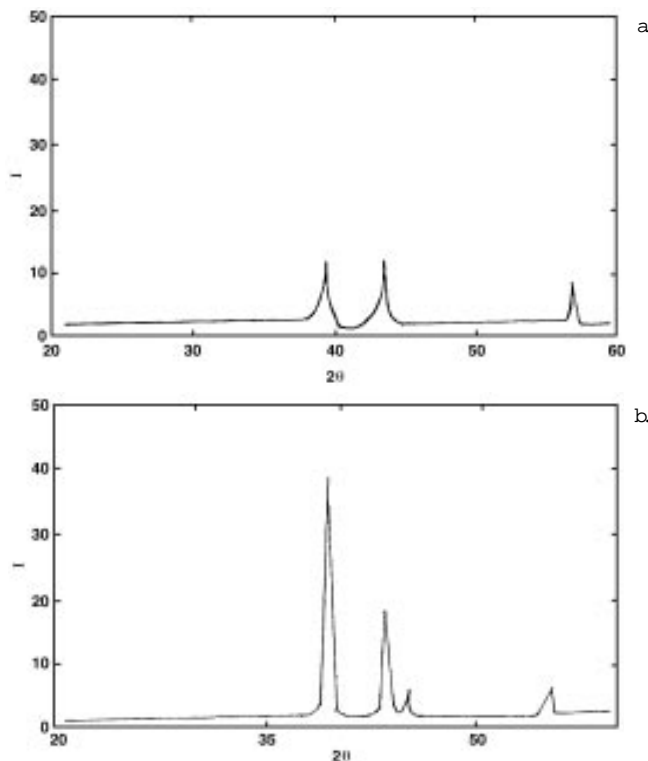

Fig. 9—X-ray diffraction patterns of deposits: (a) zinc; (b) zinc-cobalt alloy.

Findings

Zinc-cobalt alloy deposits from an alkaline, cyanide-free solution can be produced, using existing alkaline zinc plating baths having proprietary brighteners. The deposits obtained contain 0.3 to 1.0 percent Co over a wide range of operating current densities: 1 to 10 A/dm².

Physical properties, such as adhesion and ductility of the alloy deposits are similar to those of conventional alkaline zinc. The alloy offers superior corrosion resistance compared to conventional alkaline zinc.

The alloy accepts all conventional chromate conversion coatings with a modification in composition and pH, consequently exhibiting further improvement in corrosion resistance.

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Table 5
Microhardness

Specimen	Microhardness (HV) at 50-g Load
Mild steel	120-153
Zinc	70-85
Zn-Co (0.5% Co)	120-130

Table 6
Tafel Polarization Corrosion Results

Plating/Finish	E_{corr} V vs. SCE	Ba mV/decade	Bc mV/decade	I_{corr} μA/cm²	C.R. mil/yr
Zinc non-chromated	-1.1510	52.42	110.70	11.590	6.8330
Zinc golden yellow	-1.0270	58.85	101.40	3.872	2.2830
Zinc-cobalt non-chromated	-1.0420	37.74	137.10	2.595	1.5300
Zinc-cobalt	-1.0250	100.00	100.00	0.198	0.1514

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