Zinc Alloy Electrodeposition for Corrosion Protection

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This paper explores four types of the most widely used commercial zinc alloy electrodeposition systems for application in the automotive and building industries. Process parameters are investigated and optimized conditions determined for each system, using various methods of coating assessment.

It is known that the protective value of zinc is partially a result of its ability to form a protective film when plated on a base metal, such as steel. The zinc is sacrificial and corrodes preferentially to protect the steel. Although pure zinc coating provides some degree of protection for the substrate, in a severe corrosion environment, zinc is consumed rapidly. For this reason, it is usual practice to increase the thickness of the zinc coating. This is not commercially cost effective and the thick coating causes problems during forming and welding of the steel. Consequently, in the last 20 years, most industries, especially the automotive and building industries, began to look for an alternative process. The result was the development of zinc alloy systems, such as zinc-nickel,[1-4] zinc-cobalt,[2,5,6] zinc-iron,[7,8] zinc-manganese,[9,10] and the most current process that includes a combination of zinc-cobalt-chromium alloy[11] and zinc-iron-manganese alloy[12] deposits.

These alloy systems offer superior corrosion resistance and mechanical properties, weldability, paintability and thinner coating. Such coatings are always high in zinc content, have less noble metal to maintain anodic protection of the steel substrate, and remain less active than plated zinc alone.[1,4,13] The zinc in the alloy will still corrode sacrificially to protect steel, but at a much slower rate. The selection of a particular alloy process depends on the application; this may include ease of controlling plating bath composition, the degree of corrosion protection it can provide and, last but not least, the operating cost. For this reason, great attention must be paid to selection of a suitable zinc alloy system. This paper points out some of the advantages and merits of each process and draws attention to their applicability for individual use.

Many zinc electroplating processes are being developed for corrosion protection, and they contain various constituents (in addition to the main ions in solution) to control and increase the life of the electrolyte. This paper reports on the investigation of four types of commercially used zinc alloy processes, namely zinc-nickel, zinc-cobalt, zinc-iron and zinc-manganese. Tables 1 and 2 offer some examples of zinc alloy systems. These form the basis of this study and are a guide to the constituents, operating conditions and some of their industrial applications.

Coating Assessment

Many methods have been used in assessing the corrosion performance of zinc alloy coatings and each test result is a measure of certain criteria of coating performance in appropriate environments. The main objective is always to relate the performance of zinc alloy coatings to that of pure zinc coatings and to be able to predict long-term properties through comparison. The most popular of these tests are as follows:

Salt Spray Test

Most of the corrosion tests employed are to assess the galvanic protection offered by various zinc alloy coatings, based on salt spray test results. For this test, a series of samples is usually scribed diagonally across the coating to expose the steel substrate before testing in a salt-spray chamber. The samples

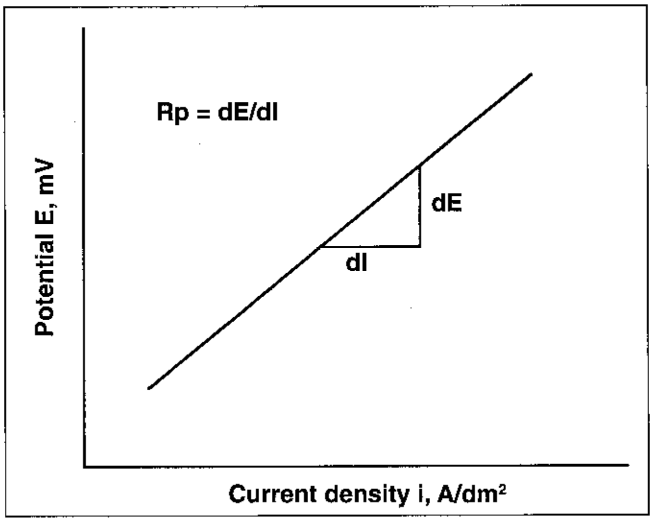

Fig. 1—Potential vs. current density for measurement of polarization resistance.

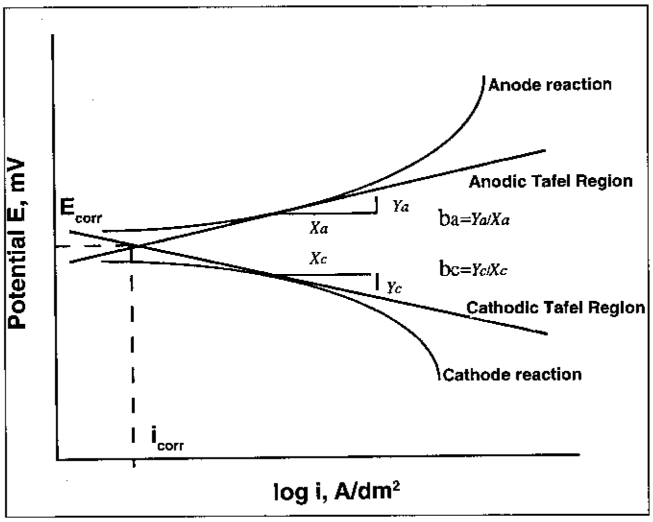

Fig. 2—Potential vs. logarithmic current density for oxidation and reduction of a metal for measurement of corrosion current and Tafel slopes.

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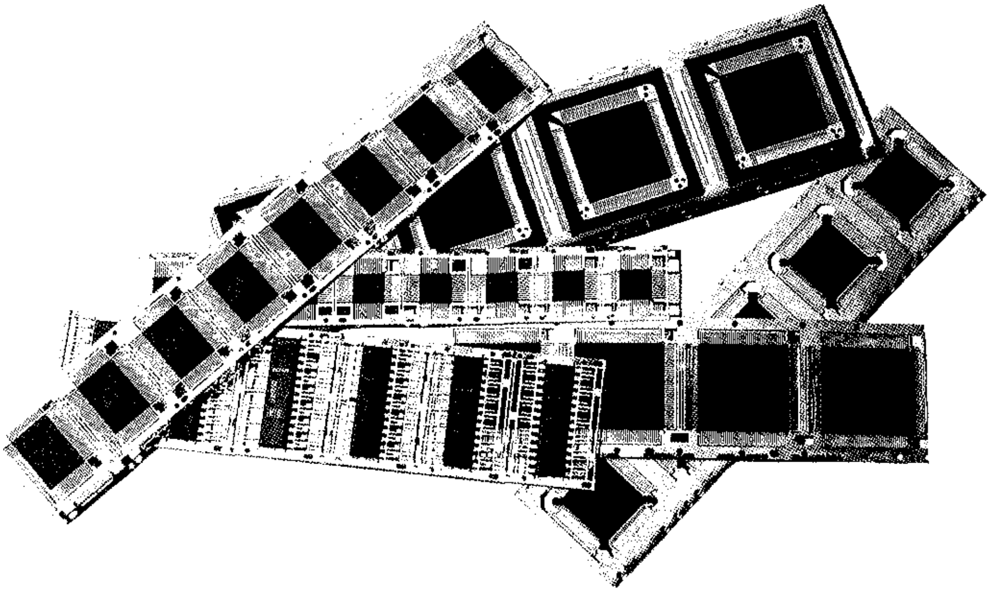

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are then exposed to a spray mist derived from a solution containing 5-percent analytical grade sodium chloride for a specified time. A detailed test procedure is carried out in accordance with BS 5466(1977) or ASTM B 117.

Corrosion of zinc alloys is generally assessed against the time required for the coating to show either white or red rust. White corrosion indicates partial depletion of the zinc in the protective film formed on the steel substrate. Red rust shows complete depletion, plus corrosion of the steel substrate.

Acetic Acid Salt Spray Test

This test consists of continuous exposure to a spray of 5-percent sodium chloride solution with addition of acetic acid to obtain a pH of 3.1 to 3.3 at an operating temperature of 35 °C. The test procedure is carried out according to ASTM B 117. The coating assessment is similar to that of the salt spray test.

Some researchers have also assessed the coatings by measuring weight loss after the salt spray test. Such measurements are carried out before the test and after the scribed area shows red rust.

Table 1
Types of Electrodeposited Zinc Alloy

Coating Systems	Electrolyte		Operating Conditions	Remarks
	Constituents	Conc., g/L		
Zn	$ZnSO_4{\cdot}7H_2O$ H_2SO_4 to adjust pH	249-379	<34 °C, Current density (CD) 2-4 A/dm², pH 3.5-4.5. For barrel plating, pH 5	Acid-type bath. Cheap to operate. Produces white deposit. Suitable for cast iron. Deposits are less subject to hydrogen embrittlement.
Zn	$ZnCl_2$ NH_4Cl + Brighteners	27 174	25 °C, pH 5.8, CD 5 A/dm²	Average coating thickness for rack and barrel platings are 9 and 8 µm, respectively.
Zn	Zinc NaOH	10-12 100-120	Zinc or steel anodes, continuous filtration, anode CD1.5-3 A/dm², cathode CD1-4.5 A/dm², 21-35 °C, agitation; some solutions contain A1 to suppress rapid dissolution of zinc anode	Zinc alkaline plating bath (zincate bath); Main application in rack and barrel plating.
Zn-Ni	$ZnSO_4{\cdot}7H_2O$ $NiCl_2{\cdot}6H_2O$ CH_3COOH	260 240 3%v/v	Nickel strike bath prior to alloy plating 50 °C, pH 1.5-3.5, CD 32 A/dm²	Acid-type bath; Coatings contain 15% nickel. One application is in continuous strip plating.
Zn-Ni	$ZnCl_2$ $NiCl_2{\cdot}6H_2O$ CH_3COOH	104.1 113.5 2.2% v/v	50 °C, pH 4.5, CD 50 A/dm²	Continuous strip plating. Electrolyte produces a ductile Zn-Ni alloy deposit on strip steel. Coating contained 11% nickel.
Zn-Ni	$ZnCl_2$ $NiCl_2{\cdot}6H_2O$ NaCl NH_4Cl +Brightener, stress reliever and wetting agent	50 15-100 200 30	Zn and/or Ni anodes 40 °C, pH 4.5, CD 3 A/dm²	Zn-Ni alloy demonstrated that the optimum corrosion resistance is provided by alloy containing 11-13% nickel. Average coating thicknesses for rack and barrel plating are 9 and 6.5 µm, respectively.
Zn-Ni	$ZnCl_2$ KCl H_3BO_3 $NiCl_2{\cdot}6H_2O$	83.3 210 25 1-40	25 & 30 °C, pH 5.5, CD 1-4 A/dm²	Claim for the optimum corrosion resistance of Zn-Ni alloy is the same as the above. Plating efficiency is around 95%.
Zn-Ni	$ZnCl_2$ $NiCl_2{\cdot}6H_2O$ H_3BO_3 NaCl +B2 unsaturated aromatic compound (brightener) +phenolic derivative, LA aromatic carboxylate (leveling agent)	135 142 30 156	25-60 °C, pH 4.8, CD 3.12 A/dm²	High concentration of additives produced a mirror bright deposit but poor corrosion resistance. Good corrosion property is achieved by optimizing the concentration of additives.
Zn-Ni	Zinc NaOH Nickel Zinc:nickel	6-12 100-120 0.7-1.5 6-7:1	Zinc or steel anodes, continuous filtration, anode CD 1.5-3 A/dm², cathode Cd 1-4.5 A/dm², 21-32 °C	Zinc-nickel alkaline plating bath. Main applications are rack & barrel plating. Not able to plate over cast iron and hardened steel. Plating efficiency ranges from 60-80%.

Polarization Behavior

Because corrosion in a wet environment is usually of an electrochemical nature, electrochemical corrosion test methods have been of particular interest in assessing the corrosion protection of zinc alloy coatings. The recording of polarization curves is of importance in elucidating the mechanism of many corrosion reactions. The environment in which the test is carried out must be similar to the conditions in which the coating is to be exposed. Accordingly, it is possible to determine the kinetics of atmospheric corrosion by electrochemical experiments on the coating in a controlled environment. Such polarization measurement techniques are described as follows:

Polarization Resistance Method

Corrosion current is calculated using the polarization resistance technique, applying the Stern-Geary equation.[14] This is

Table 2
Types of Electrodeposited Zinc Alloy

Coating	Electrolyte			
Systems	**Constituents**	**Conc., g/L**	**Operating Conditions**	**Remarks**
Zn-Co	$ZnCl_2$ KCl H_3BO_3 $CoCl_2 \cdot 6H_2O$	83.3 210 25 1-25	*30, 35&40 °C, pH 5.5,* CD 1-4 A/dm²	The optimum corrosion resistance is provided by alloys containing 1% cobalt. With such a composition *the corrosion resistance is similar to Zn-Ni alloy.*
Zn-Co	ZnO NaOH $CoSO_4 \cdot 7H_2O$ Tetren Additives: pyridine with epichlorohydrin, vanillin/heliotropine added as a brightener	10 117.3 33.7 0.06	Electrodeposition conducted under galvanostatic conditions using a flow cell with a steel cathode and a parallel Pt-coated titanium anode. Reference electrode was Ag/AgCl, 10-50 °C, CD 0.5-10 A/dm²	Zn-Co alloy deposits are highly superior to Zn deposits in the base metal protection but, when chromated, there is little difference between them during the cycles (times) tested. The deposit color is dull without additives.
Zn-Co	Zn chloride Sodium chloride Boric acid Cobalt ions Possible wetting agent or carrier are sodium benzoate, polyethlene glycol, ethoxylated long chain acetylenic alcohols	78 200 20 1-4	Agitation by air or barrel rotation plating 20-32 °C, pH 5-5.5, CD 50 A/dm²	Suitable for most applications. Average coating thicknesses for rack and barrel plating are 9 and 7 µm, respectively. The current density for continuous plating depends on the speed of passage through the plating bath. 0.3-1.2% cobalt in the deposit is recommended. Mild steel can be plated directly, whereas cast iron requires an initial deposit from an alkaline strike[31]; without alkaline strike, it is not possible to deposit over cast iron and hardened steel.
Zn-Fe	$ZnSo_4 \cdot 7H_2O$ $FeSO_4 \cdot 7H_2O$ Na_2SO_4 $CH_3COONa \cdot 3H_2O$ $C_6H_8O_7$	500 30 20 5	Use of insoluble anode is recommended 40° C, pH 3, CD 50 A/dm²	Recommended two layers of deposits, first layer (20 g/m²) containing 15-25% iron suitable for mild corrosion environment. Second layer (3 g/m²) containing 50% iron ensures good corrosion and good paint keying adhesion.
Zn-Fe	$ZnSO_4 \cdot 7H_2O$ $FeSO_4 \cdot 7H_2O$ $(NH_4)_2$ sulfate citric acid KCl Teepol W.A.	9 250 100 0.5 10 0.4 ml/L	50° C, pH 1.7, CD 20 A/dm²	Iron content of the zinc alloy coating is 6%
Zn-Mn	Zn sulfate Mn sulfate Tri sodium-citrate	70 50 200	With/without air agitation 30-50° C, pH 3, CD 1.5-4 A/dm²	It is possible to obtain Zn-Mn alloy deposits containing 40% manganese or above at ambient temperature and at a current density of 1.5 A/dm². Coatings with 60-70% manganese produced at 40-50° C were much better than pure zinc coatings. *Major effect of agitation depending on the current* density. In general, agitation enhanced Mn content.
Zn-Mn	$ZnSO_4 \cdot 7H_2O$ $MnSO_4 \cdot H_2O$ $Na_3C_6H_5O_7 \cdot 2H_2O$ Na thiosulfonate	68.9 30.3 47.6 0.1-0.15	Electrodeposition conducted under potentiostatic or galvanostatic conditions using a flow cell with a steel cathode and a parallel Pt-coated titanium anode; reference electrode was Ag/Ag Cl 50-60° C, pH 3-6, CD up to 50 A/dm²; flow rate 1-2 m/s.	Mn-deposition of Zn-Mn occurred only at high current density (>10 A/dm²), pH 5.4-6 prevented the formation of precipitate. Adding sodium thiosulfate improved cathode current efficiency.

applicable to very small values of polarization (up to 20 mV) from corrosion potential, where there is a linear relationship between the applied current (I) and polarization potential (E). The slope of this straight line, dE/dI (determined experimentally), is a measure of polarization resistance (Rp) of the coating (see Fig. 1).

Therefore, $Rp = dE/dI$

and corrosion current (i_{corr}) is obtained from the Stern-Geary equation which is as follows:

$$i_{corr} = \pm b_a b_c / 2.303(b_a + b_c)Rp$$

where b_a is the anodic slope and b_c is the cathodic slope. The values of b_a and b_c are determined from the Tafel lines (see Fig. 2).

Table 3
Comparison of Corrosion Performance

Comparative corrosion performance results of yellow chromated zinc and zinc alloy

		WCP	RR
CCT	Heated†	Zn<Zn-Co<Zn-Fe<Zn-Ni	Zn<Zn-Fe<Zn-Co<Zn-Ni
CCT	Not Heated	Zn<Zn-Fe<Zn-Co<Zn-Ni	Zn<Zn-Fe<Zn-Co<Zn-Ni
NSS	Heated†	Zn<Zn-Fe<Zn-Co<Zn-Ni	Zn<Zn-Fe<Zn-Co<Zn-Ni
NSS	Not Heated	Zn<Zn-Co<Zn-Ni<Zn-Fe	Zn<Zn-Fe<Zn-Co<Zn-Ni

Comparative corrosion performance results of black chromated zinc and zinc alloy

		WCP	RR
CCT	Heated†	Zn<Zn-Fe<Zn-Ni<Zn-Co	Zn<Zn-Fe<Zn-Co<Zn-Ni
CCT	Not Heated	Zn<Zn-Ni<Zn-Fe<Zn-Co	Zn<Zn-Fe<Zn-Co<Zn-Ni
NSS	Heated†	Zn<Zn-Ni<Zn-Fe<Zn-Co	Zn<Zn-Fe<Zn-Co<Zn-Ni
NSS	Not Heated	Zn<Zn-Ni<Zn-Co<Zn-Fe	Zn<Zn-Fe<Zn-Co<Zn-Ni

†Prior to corrosion testing, the test panels were heated for 1 hr at 120 °C.

Extrapolation of Tafel Lines

Corrosion current is determined directly from the point of intersection by extrapolation of the anodic and cathodic Tafel lines (Fig. 2). Finally, corrosion rate (weight loss) is calculated from Faraday's law,

$$W = ZIt/nF$$

where W is weight loss (g), Z is molecular weight (g/mol), I is current (A), t is time (sec), n is number of electrons transferred (n = 2 for zinc), and F is Faraday's constant (96,500 C/mol). Also,

$$W = pV$$

where p is density (g/m^3), V is volume[thickness x area] (m^3). If A = area (m^2), then by substitution,

$$\text{Corrosion Rate} = V/At \text{ (m/sec)}$$

The values obtained for corrosion current from the polarization resistance method and/or Tafel extrapolation lines are substituted in the equation and the results are usually expressed in millimeters per year (mpy).

Weight Loss Measurement

This is a simple technique of generating data. The weight loss of zinc alloy coated samples are measured after exposure to the acetic acid salt spray test. The results are usually compared with a pure zinc deposit.

Isopotential Contour Mapping

Fairly recently, a microprocessor-controlled scanning reference electrode was developed to produce isopotential contour maps of corroding surfaces, using a Ag/AgCl microelectrode. This technique has now been adapted and used to obtain further information on the galvanic protection of zinc alloy coatings.[1] The measurements are carried out on scribed samples in an appropriate environment, such as sodium chloride or ammonium chloride solution. The samples are scanned in two directions (X and Y) and the signals from the fixed and scanning reference electrodes are fed to a high-impedance differential amplifier and the amplified difference is sampled by a controlling computer system. The computer program includes a control sample movement, data acquisition, treatment conditions and contour plotting package. The scan rate, contour interval, overall scan dimensions, and the increment between sample points is entered by the operator. Once the test is complete, information is plotted and assessed. This technique appears to be very useful in assessing the uniformity of the coatings and pinpointing the activity of localized corrosion sites.

Environmental Corrosion Test

In this test, the samples are exposed to the same type of atmosphere, such as water or soil, occurring where the material is to be used. The results of well-conducted field tests are judged the most reliable. It should be noted that samples on a test site are exposed to conditions somewhat different from those, for example, in the proximity of façade cladding on a building, where drying, rain protection, slope etc., will not necessarily be the same. A detailed explanation of electrochemical and environmental corrosion tests can be found in the publications of Fontana,[15] Crow,[16] and Scully.[17]

Discussion

Zinc-Nickel Alloy

The most common and commercially used zinc alloy electrodeposition is based on the zinc-nickel process. The earliest patent on this process dates from 1947, when Schantz added

Table 4
Industrial Applications by Chromate Color

Zinc Alloy Systems	Color Requirements	Environmental Service Conditions
Zinc-Nickel	Yellow chromate	Hot, humid + marine
Zinc-Cobalt	Yellow chromate	Parts subjected to corrosive and abrasive environment
Zinc-Iron	Black chromate	Humid + marine
Zinc-Cobalt	Black chromate	Hot, humid + industrial

mate at high temperatures (for example, during curing of cathodic electrophoresis and powder coating) have long been known. Experience with chromated zinc-nickel alloy film shows that the coating can withstand high temperatures (300 °C) while maintaining high corrosion resistance.[4] Although such a benefit is achieved using chromate passivation treatment on zinc-nickel alloy deposit, the environmental problem associated with it forces some of the industry to look for new formulations. This may include the use of inorganic polymer-type solutions containing zirconium, fluoride and tannin[27] or lithium and tannin[28] and others.[29,30] Zinc phosphating as an alternative to chromate has long been utilized; the corrosion properties offered are not as good, however. An important consideration in selecting the right post-treatment for zinc-nickel alloy is that it must be compatible with subsequent painting.

The use of additives in the alloy electrolyte has a major effect on the coatings. Albalat *et al.* studied the relationship between additives (brighteners and leveling agents) and deposit properties.[3] They found that high concentration of all additives gave mirror-bright deposits of alloys, but poor corrosion resistance. By altering the concentration of additives in alloy electrolyte baths, however, they obtained bright electroplates that provided good corrosion resistance. This draws attention to the importance of optimizing additive concentrations in the plating bath.

Zinc-Cobalt Alloy

Zinc-cobalt alloy electrolytes can be either acid or alkaline. The source of zinc in electrolytes is either zinc oxide or a zinc salt, such as the sulfate or the chloride. The cobalt supplements the bath in the form of the sulfate or chloride electrolyte. Some acid baths may also contain sodium sulfate and sodium acetate, whereas others contain potassium or sodium chloride and boric acid (Table 2). The operating pH is usually between 5 and 5.5, and electrolyte temperature is between 20 and 35 °C.[2] The alkaline baths are similar to acid baths, but contain either sodium or potassium hydroxide instead of boric acid or acetic acid. An increase in bath temperature from 10 to 50 °C increases the cobalt content in the deposit. The cathode current efficiency increases very slightly from 10 to 30 °C and then falls toward 50 °C. The cathode current efficiency is also affected by additives in the plating bath.[5] As for zinc-nickel electrolyte, the solution may contain additives, such as brighteners, stress relievers and a wetting agent. Care should be taken in optimizing of such additives, because they will influence the corrosion properties of the coating. The major advantages of zinc-cobalt alloy in comparison with zinc-nickel alloy are that it exhibits good throwing power and does not require a high rate of agitation for plating components in conventional shops.[27]

The current density used for zinc-cobalt alloy plating may vary from 2 to 4 A/dm^2 (where 2.5 to 3.5 A/dm^2 are preferred) with uniform air agitation in the bath and around the cathode for rack plating. The same range of current density can also be used for a reciprocating cathode, producing a thickness of about 9 µm, at 0.4 to 0.6 A/dm^2 with good agitation; for barrel plating, yielding a thickness of about 7 µm; for continuous strip plating, much higher current density is required to deposit sufficient alloy coating.

The major corrosion study of zinc-cobalt alloy deposits containing 0.5, 4.6, 7.5, 10.5 and 19.5 percent cobalt from a laboratory-prepared acid bath and zinc-cobalt alloy deposits containing 0.3 and 1 percent cobalt from a commercially produced electrolyte, was carried out by Short, Abibsi and Dennis, using linear polarization technique.[2] They demonstrated that the corrosion potentials for the laboratory-prepared bath for pure zinc and alloy coatings containing up to 5 percent cobalt were all very similar in value and that similar results were obtained also with the subsequent deposits. The alloys containing in excess of 10 percent cobalt, however, exhibited significantly more noble values. The corrosion rates determined by polarization study for alloys containing 0.5, 7.5 and 19.9 percent cobalt were very similar to those of a pure zinc deposit, whereas alloy deposits containing 4.6 and 10.5 percent cobalt showed no real reduction. These authors showed that the time to red rust in 5-percent neutral salt spray for laboratory-prepared zinc-cobalt alloy varied with cobalt and that the maximum corrosion resistance with zinc-cobalt alloy was between 11 and 14 percent cobalt in the deposit, not 4 to 8 percent, as reported when compared with a pure zinc deposit. This makes the real comparison between each test difficult. It can be said, however, that coatings containing sufficient cobalt in the deposit can offer some degree of corrosion protection over zinc alone, but the cobalt contained should be controlled to obtain a less noble deposit with respect to steel substrate. The cobalt content in the deposit has been reported by many authors to vary in composition. Kume used 4.8 percent cobalt in his study of corrosion of zinc-cobalt alloy from an alkaline bath[5] and Smart and Wake used 0.8 to 1 percent cobalt in the deposit,[27] whereas Short, Abibsi and Dennis reported a concentration of 1 percent and more cobalt from an acid bath to give corrosion properties similar to zinc-nickel alloy. The Verberne and Hadley patent uses an even lower content of cobalt (0.15 to 0.35 percent).[32] Geduld reported that a typical solution shows 2184 hours to 10 percent red rust in a 5-percent salt spray test, whereas for plain zinc, the result was 504 hours to 10 percent red rust.[19] The real benefit of cobalt in an alloy system over zinc results from chromate passivation, in which time to red rust in 5-percent neutral salt spray tests for laboratory and commercially produced deposits increased as cobalt content of the deposit increased from 0 to 15 percent. This agrees also with the results obtained from alkaline baths.[5] Hisaaki and Urakawa, in their study of the mechanism of electrodeposition of zinc alloy from an acid bath containing a small amount of cobalt sulfate, explained that electrodeposition of zinc proceeds with initial zinc hydroxide formation, through which the discharge of cobalt ions occurs.[33] Consequently, the nobility of cobalt over zinc is canceled by the resistance of zinc hydroxide, resulting in anomalous codeposition.

Zinc-Iron Alloy

Zinc-iron alloy electrolyte systems are acid-type processes and most of the electrolyte is based on sulfate or chloride salts (see Table 2). The electrolyte[7] may contain ferrous sulfate, zinc sulfate, sodium sulfate, sodium acetate and citric acid and may be operated at 40 to 90 °C, but the preferred temperature is 40 °C and the maximum amount of iron contained in the deposit is obtained at pH 3. The recommended current density for strip plating is 50 A/dm^2, with plating speed of 1 m/sec. For maximum corrosion protection, two layers of coating, one containing 15 to 25 percent iron and a top layer containing 50 percent iron in a zinc-iron alloy deposit. Adaniya *et al.* have developed a bath containing zinc and ferrous sulfate, as well as potassium chloride, ammonium sulfate, citric acid and some additives, such as Teepol W.A.[8] This electrolyte contains ammonium sulfate to improve the quality of the deposit and to widen the plating range. The potassium chloride in electrolyte improves anode corrosion and the citric acid prevents precipitation of ferric hydroxide by complexing ferric iron in the bath.[19] The operating temperature is 50 °C, pH 1.7, and cathode current density, as reported, depends on the concentration of ions in the solution (17.5 to 20 A/dm^2).

The mechanism of zinc-iron alloy plating postulated by Adaniya *et al.* is that any plating condition, such as an increase in temperature or flow rate increases the diffusion of the zinc ions to the cathode.[7] Naturally, such an increase results in an increase in pH, mainly at the electrolyte-cathode interface, causing the formation of zinc hydroxide and suppressing the iron content of the coating. Increasing current density evidently promotes dissolution of the zinc hydroxide and an increase in the iron content.

Probably the major problem with zinc-iron alloy plating is control of the electrolyte, mainly because of formation of ferric hydroxide. The hydroxide is incorporated in the coating, resulting in poor plate adhesion. For this reason, methods have been suggested that prevent this by using electrochemical reduction.[19] The corrosion resistance offered, therefore, may be influenced by hydroxide in the coating. There is controversy,[22] however, regarding the use of this type of zinc alloy system, because the degree of corrosion protection offered by the coating is less than that of zinc-nickel, but more than that of pure zinc deposit alone.[7] To evaluate the various alloys against zinc deposits, a comparative and detailed study of chromate passivation treatment of zinc-iron, zinc-nickel, zinc-cobalt and zinc alone electrodeposited on steel substrate, was carried out by Verberne,[25] using different corrosion conditions. The results of cyclic corrosion (CCT—Japanese automotive manufacturer) and neutral salt spray (NSS-ASTM B 117, or DIN 50021) tests for yellow and black chromated zinc and zinc alloy were found to be as listed in Table 3.

From the results shown in the table, it was concluded that the accelerated tests do not correspond with each other and that they indicate the limitations of such tests. The findings are, however, an indication of performance of the coatings in the particular accelerated corrosion test environment, but are only a tool for prediction of long-term environmental corrosion. The accelerated test results for zinc-iron were found to be good up to white rust, but once the passivated film is pierced, the advent of red rust is rapid, in contrast with zinc-nickel and zinc-cobalt.

Some industries are now selecting zinc alloy/chromated systems for particular color and environmental service conditions. This is perhaps a way to balance cost with good corrosion properties. An example is shown in Table 4.[25]

Zinc-Manganese Alloy

Because of an increase in demand for zinc-alloy systems, some industries are looking for much better corrosion properties than those offered by the above alloying systems, bearing in mind the cost factor. For this reason, many alternative processes have been developed. One that shows some promise is zinc-manganese alloy (see Table 2). The literature cited on this alloy shows that the electrolytes contain zinc sulfate, manganese sulfate and sodium citrate; for this reason it is known as the sulfate-citrate bath. Sodium citrate is added to the electrolyte as a complexant. The bath is known to be very difficult to control. Under optimized conditions, however, it is possible to maintain the bath in good working order for several days.

Govindarajan *et al.*[9] studied the effects of temperature (between 30 and 50 °C), pH (4.4, 5.4 and 6.4) and current density (1.5 to 4 A/dm^2) of zinc-manganese electrolyte. They obtained zinc-manganese alloy deposits of 40 percent manganese and above at 30 °C at a current density of l.5 A/dm^2. Although the corrosion potential of the coating was similar to that of pure zinc, the result of acetic acid salt spray corrosion tests for 5, 5 to 30, and 30 to 80 percent corrosion was 2.5, 1.5 and 1.3 times better than for a pure zinc deposit. This was found to disagree with the results obtained from the weight loss in acetic acid salt spray test, in which, at 40 percent, the weight loss was greater for zinc-manganese in comparison to zinc coating alone. This indicates that the coating was very active in this test. An interesting point is that alloy coatings containing 60 percent manganese produced weight loss similar to that of zinc coating alone, but the acetic acid salt spray test results showed only about 1.5 times better corrosion resistance than zinc alone. Therefore, higher manganese content favors zinc-manganese alloy coating. This was confirmed by the results of acetic acid salt spray tests and weight loss measurements for a deposit containing 60–70 Percent manganese, produced from a zinc-manganese bath at a current density of 1.5 A/dm^2 and temperature of 30 to 50 °C, and showing better corrosion resistance compared to pure zinc.[9] The result of similar types of bath applied on steel strip on a horizontal line, using plating cells equipped with electrolyte-injecting, slit-type nozzles, showed that manganese deposition from a zinc-manganese bath occurred only at high current density (greater than 10 A/dm^2).[10] At a pH of 5.4 to 6, formation of a precipitate is prevented; a decrease in sodium citrate reduced the manganese content in the deposit. Addition of sodium thiosulfate improved cathode current efficiency and maximum manganese content (up to 60 percent) was obtained at 50 °C at a flow rate of 2 m/sec.

The use of other zinc alloys, such as tin-zinc, as a replacement for cadmium plating,[34] or codeposition of chromium,[11] titanium,[35] silica[36] has been reported elsewhere. These alloys are not covered here because they require further detailed study, as some have yet to be developed for commercial application.

Summary

As can be seen from the results of polarization study of various alloy coatings produced under optimized conditions (Table 5), a potential is reached similar to that of zinc coating alone. At this potential, the corrosion property of zinc alloy coating is better than pure zinc coating. If, however, the cost of the metals deposited for each of the above zinc alloy systems is compared to the coatings' weight/thickness (See Table 6) it is apparent that the cost from least to most expensive would be: zinc-iron (reported to have inferior corrosion resistance compared to zinc-nickel), zinc-manganese, zinc-nickel, and zinc-cobalt, respectively. In real terms for selecting zinc alloy systems, however, the cost should be calculated in terms of the electrolyte process (many of them containing additives such as brighteners and stress relievers), degree of corrosion protection, electrolyte efficiency, ease of operation, cost of maintenance and disposal.

Findings

1. Zinc-Nickel Alloy

The results obtained from various corrosion tests for zinc-nickel alloy demonstrated that the optimum corrosion resistance is provided by alloys containing 11 to 13 percent nickel. The best operating temperature is between 25 and 30 °C, with pH 5 to 5.5. The optimum coating thickness for most application is 5 to 8 µm.

2. Zinc-Cobalt Alloy

Zinc cobalt alloy demonstrated that the optimum corrosion resistance is provided by alloys containing one percent cobalt to give similar corrosion test results to those of zinc-nickel alloys. The operating pH is usually between 5 and 5.5 and electrolyte temperature is between 20 and 35 °C. The optimum coating thickness for most application is 5 to 8 µm.

The real benefit of cobalt in alloy systems over zinc is derived from chromate passivation.

3. Zinc-Iron Alloy
For mild corrosion environments, a layer (20 g/m^2) of a deposit containing 15 to 25 percent iron is recommended. To ensure good corrosion resistance and keying adhesion, however, a second layer (3 g/m^2) containing 50 percent iron should be deposited. This process is generally applied in continuous strip plating. The preferred temperature is 40 °C and the maximum iron content of the deposit is obtained at pH 3.

4. Zinc-Manganese Alloy
Maximum corrosion resistance of the coating is obtained with manganese content of 40 percent and above at a current density of 1.5 A/dm^2, at a temperature of 30 °C. This gives double the corrosion protection provided by a zinc deposit alone. A deposit with 60 to 70 percent manganese at 40 to 50 °C at the same current density provides even better corrosion test results. A pH of 5.4 to 6 is preferred. The zinc manganese electrolyte under optimized conditions can last for several days.

5. The operating current density (for all zinc alloy systems) varies with method of application.

6. In general, acid-type baths are used for continuous strip plating; alkaline baths find major application in rack and barrel plating.

7. Chromate passivation is generally used as a post-treatment for small components. In reel-to-reel applications, chromating is often not required.

8. Zinc alloy coatings produced better corrosion resistance than pure zinc coatings.

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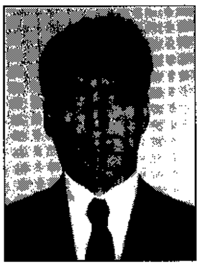

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