Environmentally Friendly Conversion Treatment for Electro-deposited Zinc Coatings

M El-Sharif

Department of Energy & Environmental Technology
Glasgow Caledonian University
City Campus
Cowcaddens Road
Glasgow G4 OBA

Chromate conversion coatings are used widely for further protection of zinc plated parts. Unfortunately, this involves the highly toxic, carcinogenic and environmentally undesirable chromium (VI) solutions. Thus economic consideration coupled with an increase in environmental awareness, have accelerated efforts to find non-toxic alternatives to chromate. Molybdate and tungstates have been examined as possible replacements but chromate treatment was found to be superior to these treatments. This paper involves a detailed study of a novel method that retain chromium species in conversion coating whilst eliminating the highly toxic hexavalent chromium from the treatment solution. This method involves the electro-deposition of zinc-chromium alloy coatings and then oxidising the alloy coating surface by immersion in a simple oxidant solution, such as permanganate.

This paper presents and compares the results of electrochemical and salt-spray measurements of the conversion films formed on zinc-chromium and zinc-choromium-nickel alloy coatings to those found for a selected range of commercially produced deposits. Preliminary investigation into the composition and chemical states of the conversion films using Auger electronspectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) has been conducted.

Introduction

Zinc coating has been successfully employed for protecting steel from corrosive attack in a variety of fields over a long period of time. The principle reason for this has been the low cost of metal zinc. This, allied to the technical suitability, makes zinc coating a popular choice. the protection offered by zinc coating to underlying steel substrate against corrosion is considered to be two fold. Firstly, zinc acts as a physical barrier to corrosive attack in most atmospheric condition. Secondly, due to the fact that zinc is more electronegative to iron it provides an electrochemically sacrificial protection, in which zinc tends to dissolve preferentially when the two metals are in contact in an electrolyte, leaving iron intact.

A disadvantage of zinc coating is that it quickly develops an initial white powdery corrosion product known as 'white rust' in some corrosive environments particularly those contain chlorine. One of the most effective approaches to delay the formation of such a corrosion product is to convert the surface of zinc into a layer of chromate conversion coating by a passivation treatment [1,2] Many types of chromate conversion coatings have been commercially available for decades, some of which such as the colour conversion chromate coating are widely used because their excellent corrosion resistance. It is believed that a colour conversion coating contains Cr(III) species in the form of chromates.[3] The Cr(III) portion is insoluble in aqueous solutions and contributes to the construction of a framework of protective barrier, whilst the Cr(VI) portion, containing chemical compounds which are recognised as effective corrosion inhibiting agents, is soluble in aqueous solutions and contributes to the construction of a framework of protective barrier, whilst the Cr(VI) portion, containing chemical compounds which are recognised as effective corrosion inhibiting agents, is soluble in aqueous solutions and absorbed in the framework. In a humid environment the Cr(VI) species can leach out and react with the exposed zinc, which is a result of corrosion damage, to convert to Cr(III) species which consequently re-heals the broken part of the barrier.[4]

Since the early 1980's there had been much interest and notable development in electrodeposited zinc alloy coatings for the similar end use as zinc coating and for the replacement of electrodeposited cadmium coating. The driving force behind this is the automotive industry as a response to the demand for a longer warranty life of virtually all parts in vehicles, when salt had been increasingly used on the roads as de-icing agent. Some of the zinc alloy coatings such as Zn-Ni with 12~15%Ni and Zn-Co with 0.2~1.2%Co have been widely viewed as more resistant to corrosion in comparison with single metal zinc coating.[5] On the other hand, studies on these zinc alloys have also suggested that although these alloys achieve corrosion resistance superior to single metal zinc the difference between chromated zinc alloys and unchromated zinc alloys is larger.[6,7] This means that chromate conversion coating could be a primary choice to the zinc alloy coatings once greater corrosion resistance is desired.

Therefore, chromate conversion coating appears to have a high potential application once again on zinc alloy coatings. Chromate conversion treatment, unfortunately, suffers from solutions which contain highly toxic, carcinogenic and environmentally undesirable Cr(VI) compounds.[8,9] As a result of this, the concentration levels of Cr(VI) allowed in the workplace and effluent are becoming regulated by government agencies.[10,11] Thus the economic consideration, coupled with an increase in environmental awareness, have accelerated efforts to seek non-toxic alternatives to chromate conversion treatment. In fact, the trend of this development has already indicated the beginning of the end of using chromate treatment in the metal finishing industry.[12, 13] Phosphating treatment[14] and the more recently developed Cr(III) type treatment based on 'Chrometan' [15] give a certain degree of corrosion protection. Also ,over the last decade, some non-chromates-based conversion coatings, such as those obtained from solutions containing other group VIA oxy-anions like molybdates and tungstates, have been proposed to replace the chromates-based conversion coatings.[16,17] The analogy of molybdates and tungstates to chromates has been recognised in the sense of being a corrosion inhibitor, many experimental comparison, however, have shown that chromates-based conversion coatings still possess corrosion resistance superior to molybdates or tungstates-based conversion coatings.[18,19] Therefore, in the present study an alternative approach, which was aimed at retaining the effectiveness in corrosion inhibition of chromates within a conversion coating whilst eliminating the toxic Cr(VI) compounds in solution for conversion treatment, was investigated.

The objective of this study was to develop such a novel alternative to chromate treatment that it should be more environmentally acceptable than chromating treatment and able to generate a conversion coating, with a comparable or superior corrosion resistance to a chromate coating, on the surface of electrodeposited zinc and zinc alloy coatings.

The practical approach was to introduce chromium into zinc and zinc-nickel coatings by means of electrodeposition and to oxidise the surface of the alloys in suitable medium which contain no chromates but a simple oxidising agent. This subsequently yielded a layer of conversion coating containing chromates and other chromium oxide species on the surface of the alloy coating. The chromium content needed to contribute to the chromate-based conversion film comes from within the alloy deposits and the toxic chromate treatment is therefore eliminated.

The investigations presented here are concerned with assessment of conversion coatings formed on Zn-Cr and Zn-Ni-Cr alloy electrodeposits by immersion into a simple acidic solution that contained permanganate.

Experimental

The zinc-chromium electrodeposits were prepared form the bath shown in Table I. In the case of zinc-nickel-chromium deposits, the electrolyte was adjusted so as to achieve a desired composition of 14% nickel, which is believed to give optimum corrosion performance for zinc-nickel alloy deposits.[20]

Mild steel cathodes were used as substrates for deposition of the alloy. The cathodes were polished with silicon carbide paper grade 500, degreased in acetone, and coated with the lacquer to leave a working area of $4x4cm^2$. They were then treated cathodically in a solution containing 50-70 g/l alkaline cleaning agent with a current density of 50 mA/cm^2 at 80°C for one minute, followed by a rinse in deionised water. High density graphite was used as an anode. Electrodeposition was carried out under potentiostatic mode, with circulated electrolyte to ensure a sustained deposition. Cathode vertical movement was employed to minimise the destructive effect of gas bubbles thus improving the quality of the deposits. The composition of the alloys was determined by X-ray fluorescence in a JXA-50A Electromicroscope attached with a Link electromicroprobe analysis unit.

In the formation of conversion films electrodeposited alloys were pre-treated in a 3% (v/v) nitric acid solution for 10 seconds and then rinsed in de-ionised water. This was followed by the immersion of the coatings into a solution containing 5g/l $KMnO_4$,20ml/l H_2SO_4 and 10ml/l HNO_3 for a period of 60 secondsat a temperature of 30C and a pH of 1.5.The chromate solution consisted of a solution cotaining 200g/l $K_2Cr_2O_7{\cdot}2H_2O$,10ml/l H_2SO_4 and 5ml/l HNO_3. After treatment the coatings were rinsed again in de-ionised water, and dried in hot air or idled for a certain period of time.

Poteniodynamic polarisation measurements were carried out for the alloy coatings in a non-deareated 1.0 M NaCl solution pH 6.0 and at 30°C, using an EG & G-352 corrosion measurement system. The anodic and cathodic polarisation curve in the Tafel or linear region were obtained with a typical potentiodynamic scan rate of 10mV/min. The corrosion currents, *I corr*, can be calculated from Tafel Constants (βa and βc) which were obtained from Tafel plots, and from the Polarisation Resistance, *R*p, which was determined from the slope at the origin of polarisation curve, using the Stern-Geary equation[21].

$$I_{corr} = (\beta a \times \beta c)/[2.303 \times Rp \times (\beta a + \beta c)] \qquad (I)$$

In the present case where dissolved oxygen exists in the solution it was assumed that the cathodic reaction was diffusion controlled and $\beta c >> \beta a$. Thus the corrosion currents can be calculated from a simple form of equation (I) as

$$I_{corr} = \beta a/(2.303 \times Rp) \qquad (II)$$

A Perkin-Elmer PHI 550 ESCA/SAM electron spectrometer with an Mg ka X-ray (1253.6eV) anode was used for XPS and AES analysis of the conversion film formed on the coatings. Survey and high-resolution XPS spectra were obtained with the energy analyser operating in a constant transmission energy mode at pass energies of 100 and 50eV. The pressure in the analyser chamber was maintained at less than 10^{-7}Pa during analysis. The voltage and current of electron beam for the AES depth profile were 3KeV and 1μA respectively. An argon ion gun with voltage 3kV and emission current of 100$\mu A/cm^2$ was used for depth profiling studies, the sputtring area was 1 x 1 mm^2. Binding energies were corrected for charging effects by reference to C1s peak (284.6eV) and their estimated error was IO.1eV.

Results and Discussion

Electrodeposition of zinc-chromium and zinc-chromium-nickel

Table 1 shows the bath used to deposit-Zn-Cr and Zn-Ni-Cr alloy coatings. It has been found that the deposition of Zn-Cr alloy reveals characteristics of anomalous codeposition with zinc as a less noble metal being preferentially deposited. Concentrations of zinc and chromium in electrolytes are both critical for the quality and chromium content of Zn-Cr deposits. From a low zinc bath (<0.1mol/l zinc sulphate) thin deposits containing up to 40% Cr could be obtained only when the zinc concentration was maintained at near 0.2mol/l and chromium concentration above 0.8mol/l. Current efficiency was found to be up to 45% in the optimum range of cathode potential. Vertical cathode movement was found to be effective in minimising the negative influence of the hydrogen gas bubbles on deposit quality. The results of the bath operation parameters are previously reported.[22]

Fig. 1a: Optical micrograph of the surface topography of Zn-4% Cr alloy deposit (x400)

Table - Composition of Bath used in Zn-Cr alloy deposition

Component	**Concentration (g/l)**	
	Zn-Cr Electrolyte	**Zn-Cr-Ni. Electrolyte**
$ZnSO_4.7H_2O$	57	57
$CrCl_3.6H_2O$	215	215
$NiCl_2.6H_2O$		240
Urea	240	48
Sec'ry Complexant	38	38
H_3BO_3	9	9
NH_4Cl	27	27
NaCl	29	29
Bulk pH	2.0-3.0	2.5-3.0
Temperature °C	20-25	25
Agitation	Cathode movement	Cathode movement

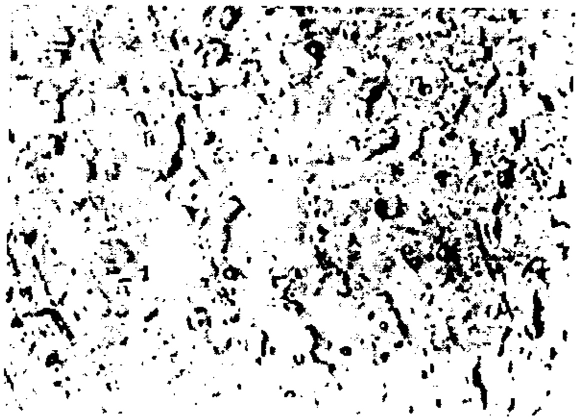

Fig 1b. Optical micrograph of the surface topography of Zn-4%Cr-14%Ni alloy deposit (x400)

Zinc-nickel-chromium alloy coatings were also deposited from a similar electrolyte with an optimum alloy composition of 12~14% nickel and up to 10% chromium. The results of the bath operation parameters are previously published.[23] The surface morphologies were primarily studied by scanning electron microscopy. The surface of the electrodeposited Zn-Cr and Zn-Cr-Ni alloys (Figure 1a and Figure 1b) were very smooth uniform coatings following the topography of the underlying substrate, there was no evidence of any microcracking. Figure 1c shows a typical feature cross-section of Zn-Cr alloy coating after etching.

Fig 1c: Optical micrograph of the cross-sectional structure of Zn-4% Cr alloy deposit (x400)

Conversion Coatings Morphology

Effect of chromium content in base alloy

During the treatment process the chromium necessary of the formation of conversion film comes from within the base alloy and as a result the chromium content of the alloy became significantly important in influencing the content and chemical state of chromium in the conversion film

The effect of chromium percentage in base alloys on conversion coating was investigated in a potassium permanganate solution. A range of Zn-Cr and Zn-Ni-Cr alloy coatings containing up to 6% Cr (containing12% - 14% for Zn-Ni-Cr alloy coatings) were used to form conversion coatings. Table 2 shows some of the typical results, obtained from alloy coatings containing 2%, 6%, 10% Cr respectively. In the table, apart from the effect of chromium content on visual surface appearance of conversion coatings, the effect of immersion time is also presented.

For Zn-Cr alloys, when the duration of immersion was up to 20 second, light yellow conversion films were obtained on the alloys of 2% Cr, whilst iridescent films were obtained on the alloys of 6% and 10% Cr. A similar pattern of variation in film appearance can also be seen for Zn-Ni-Cr alloys, although these films appeared more blue than those formed on Zn-Cr alloys. When immersion times increased, higher chromium content frequently led to darker films, and the difference in appearance between different type of alloys became large. With higher chromium content and longer immersion time, Zn-Cr alloy tended to yield brown iridescent films whilst Zn-Ni-Cr produced dark-blue films. The experimental results have also shown that immersion times beyond 60 seconds usually produced films with micro-cracking although the films were somewhat thicker.

Fig 2a: Typical pattern of microcracks of chromate conversion coating on Zn (x400)

The permanganate passivation treatment generally produced coatings with microcracks not too dissimilar to chromate coating (Figure 2a and Figure 2b). Films of this type are considered to have a gel-like structure when formed, but upon drying they crack.[24]

Fig 2b: Typical pattern of microcracks of permanganate conversion coating on Zn-Cr alloy deposit. (x400)

Composition of conversion film and it's relationship with colour

Information on the composition and chemical states of the present conversion coatings are important for a fundamental understanding of properties of the coatings. Composition of conversion coating has been found to be largely related to its colour, as it was studied by some authors in the cases of chromate conversion coatings.[24] The suggestions have been that the green-blue colour distribution on the film is related to Cr(III) oxide species and the orange-red is related to Cr(VI) oxide species. Certainly another factor that influences film colour is the. thickness of the film and it can be explained by photo-diffraction phenomenon.

Surface examinations of the formed conversion coatings in the present investigation have shown that there was a good correlation between the chromium percentage of alloy and the distribution ratio of green-blue to orange-red area of the film surface, namely, the higher the chromium content of the alloys the higher the ratio of the orange-red colour was found, provided the solutions and operating conditions were identical. This would indicate the existence of both Cr(III) and Cr(VI) oxide species in the films, and it would also indicate that the portion of chromium from the alloy being converted into hexavalent chromium is proportional to the chromium percentage of the alloys. Figure 3a shows a typical surface of conversion coating obtained on Zn-Cr alloy of 6%Cr from permanganate solution. It is compared with a typical surface of chromate conversion coating on zinc in Figure 3b. The permanganate treatment generally produced conversion coatings with a characteristic colour distribution similar to a chromate conversion coatings.

Fig 3a: Typical surface of conversion coating on Zn-Cr alloy deposit obtained from permanganate passivation treatment. (x400)

Fig 3b: Typical surface of conversion coating on Zinc obtained from chromate treatment. (x400)

Examination of the surface of the conversion film formed on the Zn-4%Cr and Zn-Ni-Cr (14% Ni and 4% Cr) alloy deposits, treated in 5 g/l $KMnO_4$ solution, by Auger electron spectroscopy (AES) revealed that the film formed on Zn-Cr contained Cr, C, O, Zn and Mn. Figure 4a shows the distribution of the above five elements in the film as a function of sputtring time. The conversion layer was about 500A^0 thick and was probably a mixture of zinc oxides, chromium oxides and the surface carbon and oxygen were very high presumably due to environmental impurities. The sharp rise in chromium peak intensity between 0-5 min sputtring time supports the mechanism proposed in that the chromium content near alloy surface become enriched when the zinc from the alloy is preferentially dissolved. Again, referring to the AES depth profile of conversion coating formed on Zn-Ni-Cr alloy coatings (Figure 4b). From Figure 4a and Figure 4b, it is found that the contents of the above elements are nearly constant after 5 min of argon sputtering, which suggests the alloy deposits are homogeneous.

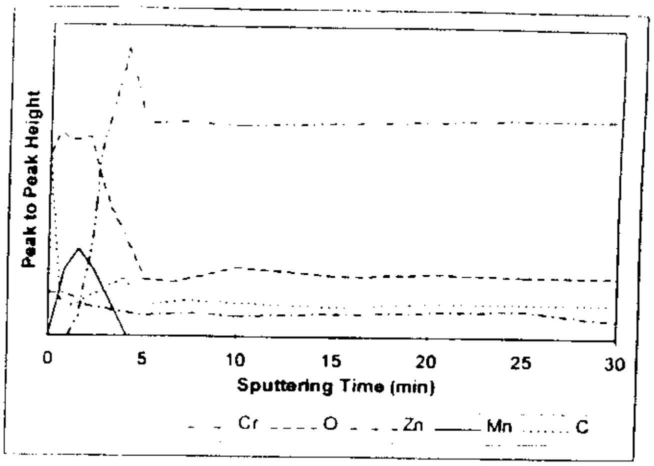

Fig 4a: Depth profile of composition determined by AES for conversion film formed on Zn-Cr coating treated in 5g/l $KMnO_4$ solution.

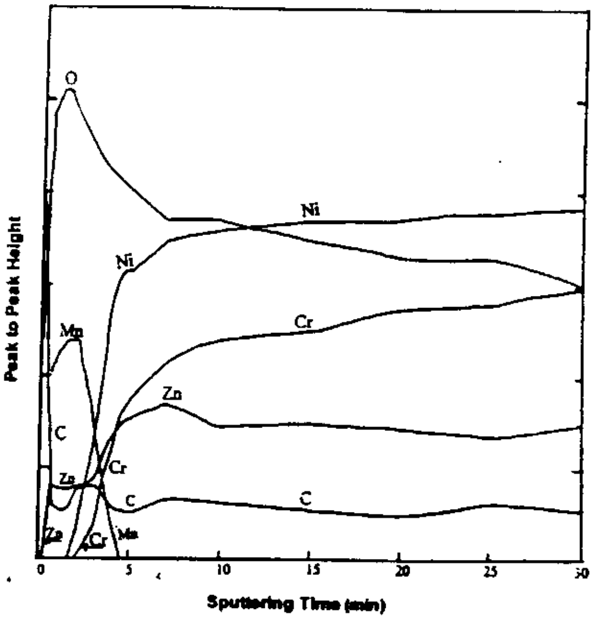

Fig 4b: Depth profile of composition determined by AES for conversion film formed on Zn-Cr-Ni coating treated in 5g/l $KMnO_4$ solution.

X-ray photoelectron spectroscopy (XPS) was used to a understand the valence and type of bonding in the conversion film obtained. A peak correspond to $Cr2P_{3/2}$ at 577.0 eV resulted from chromium oxides, Cr_2O_3 (576.6eV), or CrOOH (576.8eV). Oxygen in the Cr-O bond revealed a peak at 531.3eV. Accordingly, the O1s peak at 531.5eV can be assigned to oxygen in CrO_3 bonds. These values show that there are both Cr(III) and Cr(VI) values show that there are both Cr(III) and Cr(VI) in the film. The existence of Cr(III) and Cr(VI) in the film supports the mechanism proposed for the formation of conversion film on Zn-Cr alloys. The binding energy peak for Zn is 1022.4eV which can be assigned to that of ZnO alloys. The XPS spectra of $Mn_2P_{2/3}$ at 642.0eV can be assigned to Mn_3O_4 (641.1eV), MnOOH (641.5), Mn_2O_3 (641.6eV) or MnO_2 (642.4eV).

Mechanism of Formation of Conversion Coating

The present process of conversion treatment is a chemical immersion process, simply involving a base alloy, either Zn-Cr or Zn-Ni-Cr, and a solution which contains an oxidant and inorganic acids as major components. The solution was made highly acidic with pH in the range 1.5~1.8 and was operated at ambient temperature. In order to understand the process the formation mechanism of the conversion coating is proposed here for discussion.

Taking Zn-Cr alloy coatings as an example, when such a coating is immersed into an above mentioned solution, zinc from the outer layer of the alloy preferentially dissolves and reacts with hydrogen ions within the alloy-solution interface.

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \qquad (1)$$

Chromium content near alloy surface is enriched and activated; its dissolution takes place after being oxidised by permanganate. This can be represented simplistically by;

$$5Cr + 3MnO_{4-} + 24H^+ \rightarrow 5Cr^{3+} + 3Mn^{2+} + 12H_2O \qquad (2)$$

A portion of Cr(III) is then further converted by permanganate to Cr(VI).

$$10Cr^{3+} + 6MnO_{4-} + 11H_2O \rightarrow 5Cr_2O_7^{2-} + 6Mn^{2+} + 22H^+ \qquad (3)$$

Reactions (1) and (2) can be regarded as predominating reactions, during which hydrogen ions within the alloy-solution interface are consumed quickly and this results in a rapid increase of pH in the interface. When pH attained a critical value a complex chom gel, which contains Cr(III) and Cr(VI) oxo/hydroxo species, and probably zinc hydroxide and zinc chromate species as well. The conversion layer will include some form of manganese species. Reference to Porbaix diagram Figure 5 for manganese indicates that is can undergo reactions, not only by oxidation, with the formation of layers of MnO_2, Mn_2O_3, and Mn_3O_4 or soluable derivatives MnO_4, and MnO_4^{2-}, but also by reduction with the formation of the hydroxide $Mn(OH)_2$. When such formed gelatinous layer is dried it dehydrates, yielding a dense layer of conversion film which contains Cr(III) and Cr(VI) oxides.

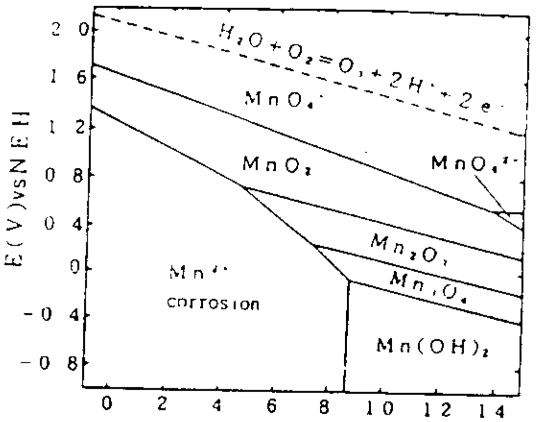

Fig 5: Potential - pH diagram for Mn-H_2O system at 298K

When the base alloy coating is Zn-Ni-Cr rather than Zn-Cr the following reaction takes place in parallel with the above oxidation reactions;

$$5Ni + 2MnO_4\text{-} + 16H^+ \rightarrow 2Ni^{2+} + 5Mn^{2+} + 8H_2O \qquad (4)$$

Corrosion Tests

Electrochemical corrosion tests

The results of the electrochemical corrosion tests are shown in Table 3. For the as-plated coatings, slightly lower corrosion currents obtained for the Zn-Cr alloy than for single metal Zn, although the protection is broadly similar. Passivating the Zn-Cr alloy with a permanganate treatment and the Zn coating with chromate treatment, reduce the corrosion rates and shift the corrosion potentials in the positive direction. A comparison between these two conversion coatings suggests greater improvement of corrosion resistance was offered by Zn-Cr with permanganate treatment.

The as-plated Zn-Cr-Ni and Zn-Ni displayed similar order of corrosion current with the Zn-Ni showing slightly lower value. However, the corrosion currents were reduced by half as compared to Zn and Zn-Cr alloys. Also it can be seen that the corrosion potentials were more positive in comparison with those for Zn-Cr containing same amount of chromium, indicating the alloy have become more noble as a result of alloying with nickel. Low corrosion currents were measured for chromated Zn-Ni and permanganated Zn-Cr-Ni alloy coatings. This result combined with knowledge obtained from the studies of passivated Zn and Zn-Cr indicates that in the conversion coating nickel content in the form of nickel oxides enhance the corrosion resistance of conversion coatings. However, it is clearly apparent that the chomrate passivation treatment to Zn-Ni coatings provides much superior protection than those of permanganate treatment to Zn-Cr-Ni alloy coatings. The chromate coating treatment achieves a considerable shift in corrosion potential and corrosion current. It is believed that the coating of hydrated chromium oxide provides a very stable barrier and the incorporated reservoir of residual hexavalent chromium provides an oxidising passivator to film repair, thus achieving continued corrosion protection even at high anodic potentials before the coating eventually starts to breakdown. This fact suggest that the oxident used in this study is not sufficiently powerful to oxidise Cr(III) to Cr(VI) at the level required.

Salt spray corrosion tests

The as-deposited and permanganate passivated Zn-Cr and Zn-Cr-Ni have been compared with Zn and Zn-Ni commercially produced and chromated to give similar conversion coating colour (yellow iridescent) to permanganated Zn-Cr and Zn-Cr-Ni. The results of these are summarised in Table 4. From the table it can be seen that the as-deposited Zn-Cr and Zn-Cr-Ni coatings showed much better resistance to white rust and red rusts than those commercially produced Zn and Zn-Ni coatings. All the passivation treatments produced significant improvements in corrosion performance over that of as-deposited coatings. The permanganate treated Zn-Cr coatings provided better resistance to white rust as compared to chromated Zn coatings, however , both coatings showed similar resistance to red rust.

As shown in Table 4 , the chromate passivation coating on Zn-Ni alloys achieved a superior corrosion performance than those of the permanganate passivation coatings on Zn-Cr-Ni alloys, with times to white and red rust of 480 and 1416 hours respectively. The salt spray test therefore suggests that these permanganate conversion coatings produced on Zn-Cr and Zn-Cr-Ni alloy coatings can be used as alternatives to the conventional chromate conversion coatings generated on Zn coating.

The results are in good agreement with electrochemical corrosion test.

Conclusion

Good quality deposits of Zn-Cr and Zn-Cr-Ni alloys can be obtained from an acid zinc bath based on chromium (III).

The formation of conversion coatings has been achieved on Zn - 4% Cr and Zn - 4% Cr - 13% Ni alloys electrodeposits by simple immersion into acidic permanganate ($KMnO_4$) solution.

Auger electron spectroscopy and x-ray photoelectron spectroscopy revealed that the conversion coating thickness is about 0.5μm and mainly composed of Cr(III), Cr (VI), zinc and manganese oxides. This composition resembles the composition, the valence and the bonding in the conversion film obtained using chromate treatment. The unpassivated coatings of Zn-Cr and Zn-Cr-Ni alloys gave improvement in corrosion performance over the commercially produced Zn and Zn-Ni alloy coatings.

Three appears to be good agreement between the salt spray and electrochemical corrosion tests. Both tests show that passivating the Zn-Cr and Zn-Cr-Ni alloy coatings with permanganate produces an improvement in the corrosion performance over the unpassivated alloys and chromated Zn. However, the tests indicate similar trends that the chromated Zn-Ni coatings are markedly.

References

1. Wilhelm, E. J., *U.S. Patent 2,035,380,* (1936)
2. Anderson, E A, *Proc. Am. Electroplaters' Soc.,* 31, (1943) 6
3. Farr, J.P.G., Kukarni, S.V., *Trans. Inst. Met. Fin.,* 44, (1966) 21
4. Ostrander, C.W., *Plating,* 38, (1951) 1033
5. Short, N.R., Abibsi, A., Dennis, J.K., *Trans. Inst. Met. Fin.,* 67 (1989) 73
6. Shears, A.P., *Trans. Inst. Met. Fin.,* 67, 3, (1989) 67
7. Sizelove, R.R., *Plating and Surf. Fin.,* 78, 3, (1991) 26
8. Kodak, P., *Plating and Surf. Fin.,* 76,3, (1989) 30
9. Heller, R.J., and Roy, C.H., *Plating and Surf. Fin.,* 73, 11, (1986) 22
10. Bittner, A., *Surf. and Coatings Australia.,* 27,5, (1990) 6
11. Toxicological Profile for Chromium, *Agency for Toxic Substances, U.S. Public Health Service, Report No. ATSDR/TP-88/10,* jULY, (1989)

12. Holmes, J., *Met. Fin.*, 87, 11, (1989) 65
13. Barnes, C., Carter., V.E., Ward, J.J.B., and Sehmbhi, T.S., *IMF Annual Conference*, May, (1982) 283
14. Albanese, J. A., *Plating and Surf. Fin.*, 77, 5, (1990) 120
15. Freeman, D.B., Phosphating and Metal Pretreatment, *IndustrialPress Inc., New York,* (1986)
16. Paatsch, W., *Met.Fin.*, 83, 6, (1985) 79
17. Wilcox, G.D., Gabe, D.R, and Warwick, M.E., *Corrosion Reviews*, 6, 4, (1988) 577
18. Wilcox, G.D. and Gabe, D.R., *Bri. Corro. J.*, 22, 4,(1987) 254
19. Wilcox, G.D. and Gabe, D.R., *Met. Fin.*, 86, 9 (1988) 71
20. Baldwin, K.R., Robinson, M.J., and Smith, J.E., *Bri. Corros. J.*, 29, 299 (1994)
21. Stern, M., *Corrosion. J.*, 14, 9, 440 (1958)
22. Watson, A., Su, Y.J., El-Sharif, M.R. and Chisholm, C.U., *Trans. IMF.*, 71,1,15 (1993)
23. El-Sharif, M.R., Su, Y.J., Watson, A. and Chisholm, C.U., *Int. Conf. Asia 92.*, Singapore, 185 (1992)
24. Biestek, T., Weber, J., *Electrolyte and Conversion Coatings*, Portcullies Press, 1976

Table 2 - Surface appearance of conversion films generated on Zn-Cr and Zn-Ni-Cr alloys (obtained from 5g/l $KMnO_4$ solution pH = 1.5 ~ 1.8, 25°C)

Type of Alloy	**Immersion Time (sec)**	**Chromium content of alloy % (wt)**		
		2%	**6%**	**10%**
Zn-Cr	10	very light yellow	light iridescent	iridescent
	20	light yellow	iridescent	iredescent
	40	light yellow	iridescent	dark iridescent
	60	dark yellow	dark iridescent	brown-iridescent
	90	yellow-brown	brown-iridescent	brown-iridescent
Zn-Cr-Ni	10	yellow	iridescent	dark iridescent
	20	yellow	iridescent	iridescent-blue
	40	dark yellow	iridescent-blue	blue
	60	yellow-brown	iridescent-blue	blue
	90	yellow-brown	dark blue	dark blue

Table 3 - Electrochemical corrosion test

Coatings	**Treatment**	**E_{corr} mV (SCE)**	**βa mV**	**R_p Ω cm^2**	**i_{corr} mA/cm^2**
Zinc	as-deposited chromated (iridescent)	-1063 -965	12.4 5.3	233.1 434.2	2.31×10^{-2} 5.30×10^{-3}
Zn-Cr (4% Cr)	as-deposited Permanganated (iridescent)	-1041 -933	18.1 13.4	379.7 1870.9	2.07×10^{-2} 3.11×10^{-3}
Zn-Ni-Cr (14% Ni, 4% Cr)	as-deposited Permanganated	-960 -922	23.0 15.7	830.4 11175.7	1.20×10^{-2} 6.1×10^{-4}
Zn-Ni (14% Ni)	as deposited chromated	-1083 -881	35.9 28.6	1180.9 236001	9.66×10^{-3} 5.26×10^{-5}

Table 4 - Results of time to white and red rust in salt spray test

Treatment	**Salt Fog Corrosion ASTM B117 (Time, hours)**							
	Zinc		**Zinc-Chromium**		**Zinc-Nickel- Chromium**		**Zinc-Nickel**	
	WR	**S.RR**	**WR**	**SRR**	**WR**	**SRR**	**WR**	**SRR**
As-deposited	6	120	48	216	50	380	24	360
Permanganate			120	300	188	600	-	-
Chomate	98	300	-	-	-	-	480	1416

WR: White rust, SRR: Spots of rest rust.