The Effect Of Sealers On Increasing The Corrosion Resistance Of Chromate Free Passivates On Zinc And Zinc Alloys

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In recent years chromate free passivates have been developed to avoid the use of hexavalent chromium which is now designated as a class 1 carcinogen. Some now give equivalent corrosion protection although they are not self healing. This means that corrosion can quickly occur in damaged areas i.e. during Barrel plating. This paper shows that the use of passivate sealers can improve this situation dramatically enabling hexavalent chromium to be avoided. This is illustrated by corrosion testing including EIS and scribed salt spray testing.

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Introduction

A wide range of chromate conversion coatings are currently used as topcoats on zinc and zinc alloy plated components. They inhibit corrosion of the sacrificial zinc layer and act as a barrier greatly increasing corrosion protection as well as in some cases improving the decorative finish [1].

A chromate passivate layer contains a mixture of trivalent and hexavalent chromium compounds[2]. Some of the hexavalent chromium compounds are more soluble than the trivalent ones and are capable of leaching to the metal surface after scratching so that the chromate protection will be renewed in this area. Thus chromates are said to be self-healing. Iridescent or Yellow passivates contain much more hexavalent chromium than blue passivates and so have much better self-healing properties[3].

Chromate passivates also have the advantages of being cheap and being easy to apply and effluent treat. Thus it is not hard to understand why products of this type have been used for at least 50 years.

Unfortunately hexavalent chromium is toxic. Inhalation and ingestion are carcinogenic while continual exposure to low levels of hexavalent chromium on the skin leaching from passivates has been shown to cause contact dermatitis[4]. These health and safety problems have lead to restrictions on the use of hexavalent chromium with such measures as the EEC automotive end of life directive being implemented which will severely restrict the amount of hexavalent chromium that can be used in car production[5]. Thus electroplaters now need alternatives to chromate passivation.

Many non- chromium alternatives have been researched[6&7] . Replacements including vanadates, molybdates, silanes, titanates , rare earth salts and organic films have met with only limited success in the market place as so far none fulfill all the electroplater's needs.

Trivalent chromium passivates have been more successful. These are much less hazardous than chromates which contain hexavalent chromium whilst still giving an acceptable level of corrosion protection. They are also relatively cheap and easy to effluent treat. Trivalent chromium passivates have been developed and introduced into the market over the last 20 years[8&9]. Until very recently they have been limited to blue passivates which are usually based on fluoride complexes of Cr^{3+} which give coatings of only limited thickness. Iridescent trivalent passivates have now been formulated that give thicker relatively insoluble inert conversion coatings that act as an effective barrier protection and give very good corrosion protection.

As these coatings are no longer self healing corrosion is likely to occur and spread quickly from damage sites. This can be a particular problem in producing fasteners etc for automotive use which generally have demanding corrosion specifications. Barrel plating normally produces such parts where the tumbling of the large volume of parts is likely to cause some damage during production.

One way of trying to improve resistance to damage is to modify the trivalent passivate layer by the use of passivate sealers. This paper explores whether this approach is effective.

Trivalent Coatings Without Topcoats

A leading hexavalent chromium free conversion iridescent coating was compared to a traditional yellow chromate. Both were applied on top of a zinc and a zinc alloy electroplated substrate. The zinc alloy selected was zinc/ iron containing 0.7 % iron in the deposit. Zinc/iron was selected because it is known to give an increase in corrosion performance whilst being easy to effluent treat and quite economical to run . Zinc was plated from an alkali zinc electrolyte. All of the comparisons detailed below were made on electroplated substrates of 9-11 microns thickness.

The trivalent passivate used included was fluoride free and was capable of giving a similar coating weight to a yellow hexavalent passivate. Table 1 shows a comparison of corrosion resistance as assessed by neutral salt spray testing using ASTM method B1117.

Table 1 .Results of salt spray testing of steel test panels by ASTM B117

Sample	Hrs to 5% white rust
Zinc + trivalent passivate	200
Zinc + hexavalent passivate	200
Zinc/iron + trivalent passivate	270
Zinc/iron + hexavalent passivate	250

The results confirm that the trivalent coating is an adequate replacement for the hexavalent one in this test.

Table 2 gives typical results of testing real components,(bolts in this case) that have been processed in bulk in a barrel and so have inevitably suffered damage in production.

Table 2. Results Of Salt Spray Testing Of Barrel plated Items.

Sample	Hrs to 5% white rust
Zinc + trivalent passivate	72
Zinc + hexavalent passivate	120
Zinc/iron + trivalent passivate	120
Zinc/iron + hexavalent passivate	150

Thus it can be seen that as expected the performance of trivalent passivate has been reduced more than the hexavalent because the hexavalent coating is self healing and the trivalent one is not.

Addition of a topcoat or sealer after passivation could be expected to help boost the trivalent performance by providing an extra barrier, increased abrasion resistance and incorporating additional corrosion inhibitors.

Topcoats Tested

A variety of chemically different topcoats can be employed. Examples were selected as follows:

A silicate type sealer.

This product is based on an inorganic silicate but also includes an additive to increase abrasion resistance. Applied by dip at 65 ^{0}C it is designed to give a glassy barrier coating having an alkaline pH. This has an inhibiting effect on zinc corrosion so may limit corrosion of areas where the chromium coating is thin or has been removed.

An organic clear lacquer coating.

Lacquers can provide a hard barrier coating giving extra abrasion resistance and an improved decorative finish as well as an increase in corrosion resistance. Lacquers can also act as good primers for any subsequent painting.

A water based lacquer was selected to fit the process requirements. Stoving or air drying lacquers are are available.

Stoving lacquers that have much higher levels of chemical crosslinking can give very good corrosion resistance but application then becomes more difficult as an oven capable of maintaining temperatures of about 150 ^{0}C is needed and stripping of any reworks and barrel contacts becomes more difficult. When a stoving lacquer is applied there will be damage to the passivate film and a higher coating thickness of lacquer,(approximately 5 microns) will be needed to counter this and give good results.

To give greater ease of application on an average barrel line an air drying lacquer was selected. The product selected has low viscosity so that it can easily be applied without causing drips at the expected coating thickness of 0.5-1 micron. The product can be stripped on a standard cleaning line in case of reworks and can be dried at low temperatures to avoid thermal damage of the passivate coating. It incorporates an additional organic corrosion inhibitor and is capable of a small degree of post application oxidative crosslinking to boost resistance.

A silane based coating.

Silanes have been proposed as replacements for chromates[8]. The silane covalently bonds to the surface and to any subsequent paint . Very thin coatings of less than 10 nm usually result[10] . The product selected was modified with inorganic transition metals and was deposited at pH 2. It has been used as an alternative for chromate rinsing of phosphated iron and aluminium before paint application. Used at only 1% concentration and applied at room temperature it is easy to use and stable for at least 6 weeks.

Testing

The performance of these topcoats on top of a zinc plated steel test panels was first tested by normal salt spray testing. The results are given in table 3.

Table 3. Salt Spray Test Results For Topcoats On Steel Test Panels.

Sample	Hours to white rust failure
Trivalent + topcoat 1	330
Trivalent + topcoat 2	400
Trivalent + topcoat 3	300

It can be seen that each of the sealers used seems to have a positive effect on improving salt spray resistance.

As already discussed ASTM B117 is not always a very good prediction of salt spray resistance of barrel plated components. In order to find additional information alternative tests were investigated. Comparisons were made on zinc and zinc/iron plated substrates .

1) *Electrochemical Impedance Spectroscopy, (EIS).*

This technique can be used to give corrosion test comparisons rapidly providing numerical values rather than relying on subjective visual assessment. Data can be collected throughout the corrosion process showing any changes in the sample as they occur. Neutral salt spray solution was used as the test electrolyte for the results presented in this paper, but a variety of other corrosive test solutions may be employed.

2) *Scribed salt spray testing* .

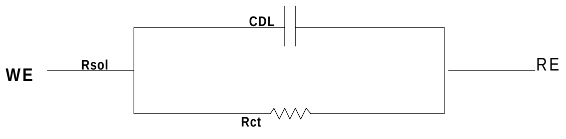
Testing of scribed steel test panels with untaped edges was undertaken to provide extra information about corrosion performance after damage.

EIS Testing

Data was collected using an ACM Gill AC potentiostat equiped with Sequencer 4 software. A platinum auxiliary electrode and a Silver/Silver Chloride reference electrode were used and neutral salt spray solution was used as the electrolyte. An immersion time of 15 minutes was used for equilibration. The EIS spectrum was collected over a frequency range of 0.1-20,000 Hz using an potential perturbation of + or -10 MV around the rest potential.

An equivalent circuit used to model corrosion by the software is given below in fig 1:

Fig 1. Equivalent electrical Circuit.



WE= Working electrode.
RE= Reference electrode.
CDL= Capacitance of the double layer.
Rct = Resistance of coating
Rsol = Resistance of solution

Nyquist plots were generated for each sample using the software to generate values for CDL and Rct.

Rct relates directly to corrosion resistance whilst CDL is influenced by porosity and thickness of the coating. The higher the Rct values and lower the CDL values the better the corrosion resistance obtained[11].

Testing Of New Test Panels

Panels were kept for 48 hrs after plating, then immersed for 15 minutes in the sodium chloride electrolyte and then tested. Results are given in tables 4 & 5.

Table 4 EIS Results For Zinc/Iron Plated Test Panels

Samples	CDL (F)	Rct, (ohms cm^{-2})
Trivalent passivate	3.4×10^{-5}	1.7×10^{4}
Hexavalent Passivate	1.44×10^{-5}	2.7×10^{4}
Trivalent + topcoat 1	2.5×10^{-6}	3.6×10^{4}
Trivalent + topcoat 2	2.8×10^{-7}	1.1×10^{5}
Trivalent + topcoat 3	5.6×10^{-5}	1.5×10^{3}

Table 5 EIS results For Zinc Plated Test Panels.

Samples	CDL (F)	Rct, (ohms cm^{-2})
Trivalent passivate	7.0×10^{-4}	4.0×10^{3}
Hexavalent Passivate	2.0×10^{-5}	5.0×10^{3}
Trivalent + topcoat 1	4.4×10^{-5}	5.3×10^{3}
Trivalent + topcoat 2	8×10^{-6}	2.6×10^{4}

Trivalent + topcoat 3	5.0×10^{-4}	1.3×10^{3}

The higher resistance and lower capacitance results obtained on a zinc/iron substrate suggest that corrosion resistance will definitely be higher on a zinc/iron rather than a zinc substrate. The capacitance results suggest that thicker or less porous coatings are obtained on the zinc/iron than on pure zinc for the trivalent passivate. A comparable performance would be expected from the hexavalent and the trivalent passivate.

The application of topcoats gave a noticeable improvement. CDL results confirm the known fact that topcoat 2, (the lacquer) is thicker than topcoat 1,(the silicate) which is thicker than topcoat 3, (the modified silane). The results of these tests on new panels suggested that 3 has had only a negligible effect whilst 1 and especially 2 gave a definite improvement.

EIS Testing Of Bolts

A further study was made using real components. These were M8 sized threaded bolts which were plated in a small barrel using approximately 2 kg of bolts processed in the same manner each time. Thus the bolts had been exposed to normal processing damage. EIS spectra were collected from sample bolts 48 hours after plating. Again a neutral salt spray electrolyte was used.

These bolts were then placed in a salt spray cabinet and tested intermittently after salt spray exposure. This was intended to follow any changes and search for degradation of the coatings.

The results obtained were tabulated and are given in figures 2 &3.

Fig 2. Variation Of Resistance of Coating During Salt Spray Testing Of Zinc Plated Bolts.

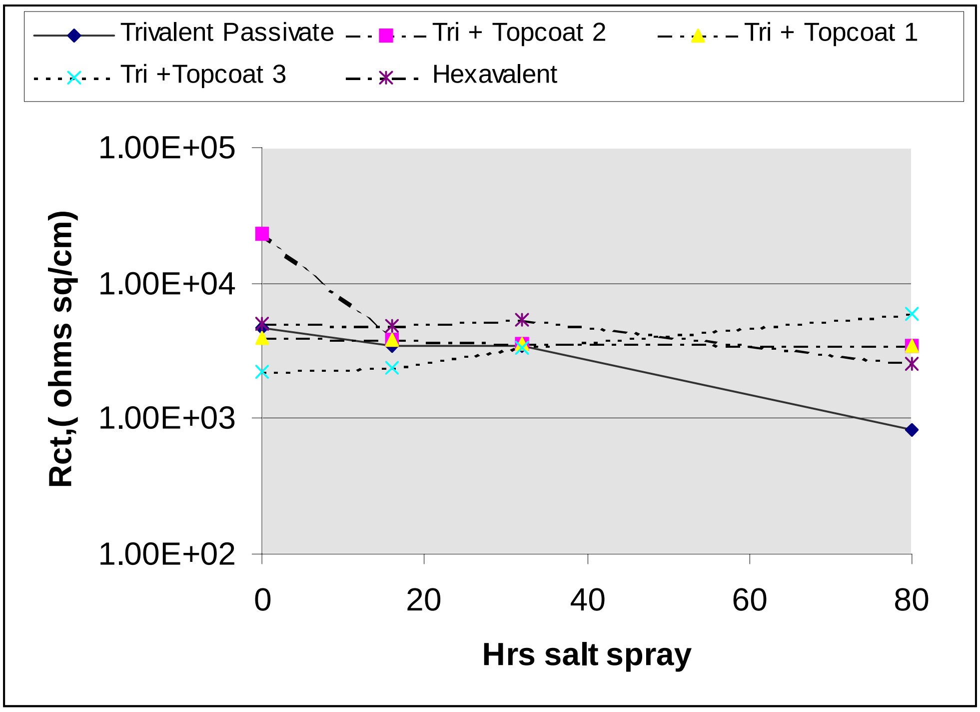
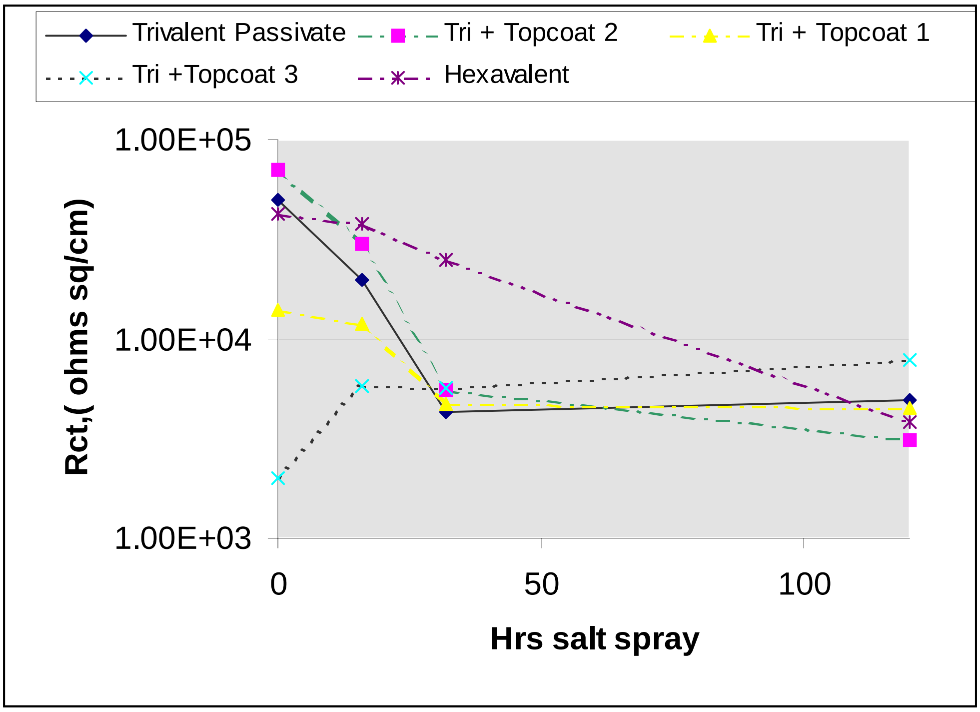


Fig 3. Variation Of Resistance of Coating During Salt Spray Testing Of Zinc/Iron Plated Bolts.



Discussion of Results.

It can be seen that resistance of the coating fell indicating degradation and faster corrosion as the test progresses. Greater corrosion protection is predicted on the Zinc/Iron substrate particularly for the trivalent passivate.

The sealers used had a variable effect. Topcoat 1 gave an increase to coating resistance throughout the test. 2,(as expected for a thicker barrier coating) gave an initial large increase in Rct. However this was quickly reduced as the test progressed and initial corrosion occurred. The results obtained for topcoat 3 were unusual. Initially resistance was actually lower than the passivate only, but as the test progressed in both cases this steadily increased to the point that at the end of the test period corrosion was predicted to be slower than the other samples. It is possible that this may be caused by the reaction of the silane being slower than expected.

The hexavalent coating apparently gave better protection than the trivalent in these tests but when topcoats were used this was negated.

After 150 hrs salt spray testing the bolts were examined visually and assessed as to state of white corrosion on a scale of 1-10 with 1 being absence of corrosion. The comparison is given in table 6.

Table 6. Comparison Of Bolts After 150 Hours Salt Spray Testing.

Sample	Zinc	Zinc/ Iron
Trivalent passivate	8	4
Hexavalent passivate	4	3
Trivalent + topcoat 1	4	3
Trivalent + topcoat 2	5	5
Trivalent + topcoat 3	3	2

This is as expected from the EIS results.

Testing Of Scribed Test Panels

Scribed salt spray testing was undertaken to give more information about corrosion protection in damaged areas. Electroplated panels were cross scribed with a scalpel through to base metal. In a separate area of the panel a 6H pencil was drawn in an approximate straight line to give a lesser amount of damage. Edges were left exposed to provide some idea what might happen at sharp edges.

The panels were neutral salt spray tested in a test cabinet and comparisons made. After a period of 200 hrs exposure they were examined in detail and again an a rating of 1-10 applied with 1 being absence of visible corrosion. As expected the corrosion observed was principally at damaged areas and exposed edges. These results are given in table 7.

Table 7. Comparison Of Scribed Test Panels After 200 hrs Salt Spray Exposure.

Sample	Zinc	Zinc/ Iron
Trivalent passivate	6	3
Hexavalent passivate	4	3
Trivalent + topcoat 1	3	2
Trivalent + topcoat 2	5	3
Trivalent + topcoat 3	4	3

An example of the differences that can be seen is given in the photograph below comparing two Zinc plated test panels.

Trivalent + Topcoat 1 **Trivalent Passivate**

Photograph Of Scribed zinc plated Test panels After 200 hours Salt Spray Testing.

Conclusions

The use of topcoats improves the performance of trivalent passivates and their resistance to damage to the point where they can replace yellow Chromate coatings. This is especially true on Zinc/Iron substrates where the trivalent passivate tested performed especially well .

EIS testing suggests that the passivate film obtained for the trivalent product may be substantially thicker or less porous on Zinc/Iron than Zinc plated surfaces. It was also possible to use the technique to give information on degradation of the coating of real components during corrosion.

Scribed panel testing further illustrated that the use of sealers gave an improvement to protection at damage points.

These results suggest that topcoats 1 and 3 were the most effective at increasing corrosion protection of trivalent passivates in barrel plating applications. Topcoat 2 which was shown to give very good protection in normal salt spray testing may be more effective in rack plating applications.

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