The Effect of Sealers on Increase Of Corrosion Resistance of Chromate-free Passivates on Zinc & 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 passivates 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.

A wide range of chromate conversion coatings is 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 selfhealing properties.[3]

Chromate passivates also have the advantage of being cheap, easy to apply and amenable to effluent treatment. Consequently, 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 considered 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 led 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 automobile production.[5] As a result, 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 marketplace inasmuch as none meets all the electroplater's needs.

Trivalent chromium passivates have been more successful. They are much less hazardous than chromates containing hexavalent chromium, while still giving an acceptable level of corrosion protection. They are also relatively cheap and easy to treat as effluents. 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}, and yield 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 offer very good corrosion protection.

Zinc-plated test panels.

Because 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 and other items for automotive use that 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.

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 iridescent hexavalent chromium-free conversion 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 percent iron in the deposit. Zinc-iron was selected because it is known to provide an increase in corrosion performance while being easy to treat as an effluent 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 µm thickness.

The trivalent passivate used was fluoride-free and capable of providing a similar coating weight to a yellow hexavalent passivate. Table 1 shows a comparison of corrosion resistance as assessed by neutral salt fog testing, using ASTM method B117.

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

Fig. 1—Equivalent electrical circuit, where WE = Working electrode, RE = Reference electrode, CDL = Capacitance of the double layer, Rct = Resistance of coating and Rsol = Resistance of solution.

Table 1
Results of Salt Fog Testing Of Steel Test Panels by ASTM B117

Sample	Hr to 5% white rust
Zinc + trivalent passivate	200
Zinc + hexavalent passivate	200
Zinc-iron + trivalent passivate	270
Zinc-iron + hexavalent passivate	250

Table 2
Results of Salt Spray Testing of Barrel-Plated Items

Sample	Hr to 5% white rust
Zinc + trivalent passivate	72
Zinc + hexavalent passivate	120
Zinc-iron + trivalent passivate	120
Zinc-iron + hexavalent passivate	150

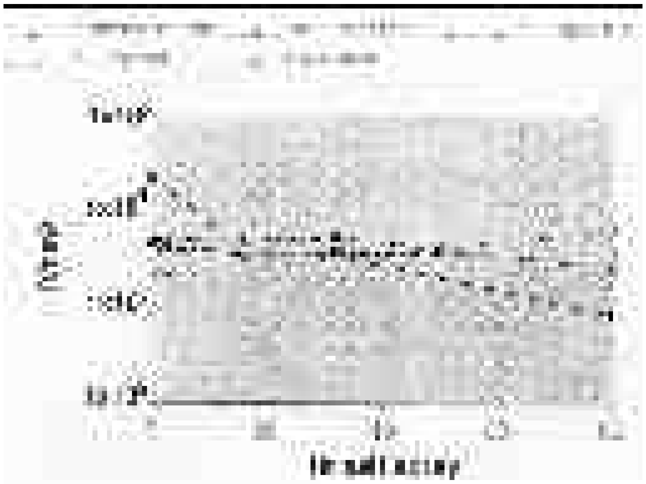

Fig. 2—Variation of resistance of coating during salt spray testing of zinc-plated bolts.

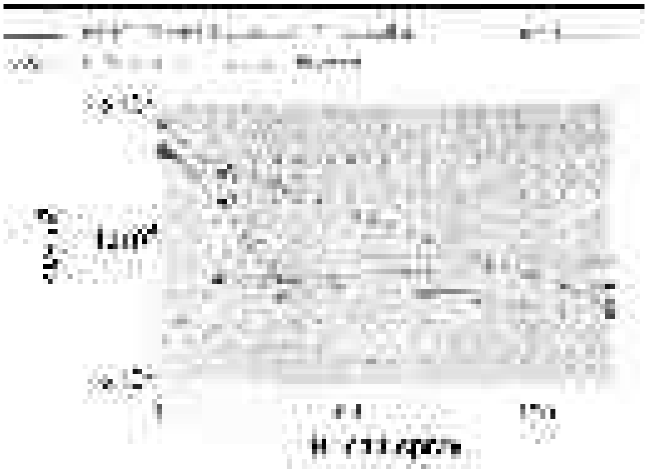

Fig. 3—Variation of resistance of coating during salt spray testing of zinc-iron-plated bolts.

Table 2 lists 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.

It can be seen that, as expected, the performance of the trivalent passivate has been reduced more than the hexavalent coating 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 passivate performance by providing an extra barrier, increased abrasion resistance and by incorporating additional corrosion inhibitors.

Topcoats Tested

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

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 °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.

Organic Clear Lacquer Coating

Lacquers can provide a hard barrier coating, providing 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 also available.

Stoving lacquers that have much higher levels of chemical crosslinking offer very good corrosion resistance, but application is more difficult because an oven capable of maintaining temperatures of about 150°C is needed, and stripping of any rework 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 µm) 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 µm. The product can be stripped on a standard cleaning line in case of rework 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 corrosion resistance.

Silane-based Coating

Silanes have been proposed as replacements for chromates.[8] The silane develops covalent 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 aluminum before paint application. Used at only one percent concentration and applied at room temperature, it is easy to use and stable for at least six weeks.

Table 3
Salt Spray Test Results
For Topcoats on Steel Test Panels

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

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}

Testing

The performance of these topcoats on zinc-plated steel test panels was first tested by normal salt fog test. The results are shown in Table 3. It can be seen that each of the sealers used seems to have a positive effect on improving salt fog resistance.

As already discussed, ASTM B117 is not always a very good prediction of salt fog resistance of barrel-plated components. 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 make 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 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 were collected using a potentiostat equipped with appropriate software. A platinum auxiliary electrode and a silver/silver chloride reference electrode were used, and neutral salt solution was used as the electrolyte. An immersion time of 15 min was used for equilibration. The EIS spectrum was collected over a frequency range of 0.1-20,000 Hz, using a potential perturbation of ±10 mV around the rest potential.

An equivalent circuit used to model corrosion by the software is shown in Fig 1. Nyquist plots were generated for each sample, using the software to generate values for CDL and Rct. Rct is directly related to corrosion resistance, while CDL is influenced by porosity and thickness of the coating. The higher the Rct values and the lower the CDL values, the better the corrosion resistance obtained.[11]

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}

Table 6
Comparison of Bolts After 150-hr 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

Testing of New Test Panels

Panels were kept for 48 hr after plating, immersed for 15 min in the sodium chloride electrolyte, then tested. Results are given in Tables 4 and 5.

The higher resistance and lower capacitance results obtained on a zinc-iron substrate suggest that corrosion resistance will definitely be higher on 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 passivates.

The application of topcoats produced 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 topcoat 3 had only a negligible effect, while topcoats 1, and especially topcoat 2, provided a definite improvement.

EIS Testing of Bolts

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

These bolts were then placed in a salt fog cabinet and tested intermittently after exposure. This was intended to follow any changes and search for degradation of the coatings. The results obtained were tabulated and are shown in Figs. 2 and 3.

Discussion

It can be seen that, in general, resistance of the coating fell, indicating degradation and faster corrosion as the test progressed. Greater corrosion protection is predicted for the zinc-iron substrate, particularly for the trivalent passivate.

The sealers used had a variable effect. Topcoat 1 showed an increase in coating resistance throughout the test. Topcoat

Table 7
Comparison of Scribed Test Panels After 200 hr Salt Spray

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

2 (as expected for a thicker barrier coating) provided an initial large increase in Rct. This was quickly reduced, however, as the test progressed and initial corrosion occurred. The results obtained for Topcoat 3 were unusual. Initially, resistance was actually lower than with 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 for the other samples. It is possible that this may have been caused by the reaction of the silane's being slower than expected.

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

After 150 hr of salt fog testing, the bolts were examined visually and assessed for white corrosion on a scale of 1-10, with 1 being absence of corrosion. The comparison is given in Table 6 and 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 the 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 subjected to neutral salt fog testing and comparisons made. After 200 hr exposure, they were examined in detail, again on a rating of 1-10, with 1 being absence of visible corrosion. As expected, the corrosion observed was principally at damaged areas and exposed edges. These results are listed in Table 7. An example of the differences that can be seen is shown in the photograph, comparing two zinc-plated test panels.

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 gain information on degradation of the coating of real components during corrosion. Scribed panel testing further illustrated that the use of sealers provided improvement to protection at damage points.

These results suggest that topcoats 1 and 3 were 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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Paul Upton received a Bsc (hons) degree in applied chemistry in 1984. He has worked in the research laboratory of MacDermid Inc., in Birmingham England, since 1986. Since 1990, as a senior research chemist, he has primarily worked on formulating and developing organic coatings for decoration and protection of electroplated and other metallic substrates. As part of this role, he has written and presented papers on the subject.