The Use Of Chromate-free Passivates & Passivate Sealers On Zinc And Zinc Alloys.

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Chromate-free passivates have become necessary to avoid the use of hexavalent chromium, which is now identified as a health hazard. Forthcoming legislation will increasingly restrict use. Replacements giving equivalent corrosion protection have been developed although they are not self healing. This means that corrosion can quickly occur in damaged areas such as during Barrel plating. The use of appropriate passivate sealers can improve this situation dramatically, enabling hexavalent chromium to be avoided. EIS and scribed salt spray testing are used to test these systems.

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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 finish¹. Chromate passivates have the advantages of being cheap and 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, causing health hazards. 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 dermatitis² for workers who have regular contact with chromated coatings. These health and safety problems have led to restrictions on the use of hexavalent chromium. An example of this is the EEC automotive end of life directive, which will be implemented in Jan 2003. This will severely restrict the amount of hexavalent chromium that can be used in car production³ as only 2 g will be allowed in cars that are to be recycled. This restriction will cover cars imported as well as manufactured in the EEC. The allowed Chromate useage is a fraction of the current level. Automotive companies also have the problem that it is almost impossible to accurately determine the proportion of trivalent and hexavalent chromium deposited in a conversion coating. Thus car companies and electroplaters are now demanding zinc topcoats that are chromate free.

Alternatives To Chromium

Many non-chromium alternatives have been researched^{4&5}. 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

Trivalent chromium passivates have been more successful. These contain no hexavalent chromium and so avoid the health hazards of chromate. However they still give 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^{6&7}. Until very recently they have been limited to blue passivates which are usually based on fluoride complexes of Cr^{3+} which give coatings of limited thickness.

Advances have now been made and trivalent passivates have been formulated that give thicker insoluble inert conversion coatings that act as an effective barrier protection and give very good corrosion protection.

The product investigated in this paper is deposited from a fluoride free electrolyte to give an iridescent deposit of about the same coating weight as a conventional yellow chromate coating on electroplated zinc. To compare the corrosion resistance of the hexavalent and trivalent coating zinc plated test panels were subjected to neutral salt spray testing, (NSS) using ASTM B1117. Panels after a thermal shock step, (which is often demanded by automotive companies) were also tested. The results of this testing are given in Table 1. For this and the other testing described, zinc was plated from an alkaline non cyanide zinc electrolyte to a thickness of 9-11 microns.

	No Thermal Shock	After 1 hr @150 °C,(300 °F)
Hexavalent passivate	200 hrs	24 hrs
Trivalent passivate	210 hrs	180 hrs

Table 1. Results Of NSS Testing Of Zinc Plated Test Panels To 5% White Rust

The results illustrate that the trivalent coating has equivalent corrosion resistance to the hexavalent without heat treatment. The trivalent coating is outstandingly better after thermal shock treatment as it does not have the drastic reduction in salt spray resistance that usually happens when chromate coatings are used. This is thought to be due to a difference in the morphology of the deposit. Chromate conversion coatings crack as they dry and dehydrate. Heating increases this effect and damages the coating reducing corrosion resistance. It has also been shown that prolonged heating of chromates lowers the level of leachable hexavalent chromium reducing corrosion resistance and leaching colour^{8&9}.

In our experience thick trivalent coatings have few cracks and are largely unaffected by heat . This is illustrated in the SEM micrographs shown in figure 1.



Figure 1.SEM Photographs Of Conversion Coatings On Zinc At 1000 X Magnification.

The trivalent passivate tested may also be used with zinc/iron, zinc /nickel and zinc/ cobalt. Performance of the passivate on a zinc iron substrate was investigated using an alloy containing 0.7 % iron plated from an alkali electrolyte. This has the advantages of being cheaper than zinc nickel and easier to effluent treat whilst still giving an increase in corrosion resistance. This is illustrated by the salt spray test results given in table 2 where the trivalent passivate exceeds the performance of the hexavalent chromate and again performs particularly well after thermal shock.

	No Thermal Shock	After 1 hr @150 °C,(300 °F)
Hexavalent passivate	300	160
Trivalent passivate	320	230

Table 2. Results Of NSS Testing Of Zinc/ Iron Plated Test Panels. Hours To 5% White Rust

Electrochemical Impedance Spectroscopy, (EIS).

This technique was used to give additional corrosion test comparisons. The technique can rapidly provide 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.

Data was collected using an ACM Gill AC potentiostat equipped 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 = Charge transfer resistance of corroding substrate

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 obtained¹⁰.

Table 3 shows the results of EIS testing of plated hull test panels.

Samples	$CDL (F cm^{-2})$	Rct, (ohms cm^{-2})
Zinc + trivalent passivate	7 X 10 ⁻⁴	4.0×10^3
Zinc + hexavalent passivate	2 X 10 ⁻⁵	5.0×10^3
Zinc/iron + trivalent passivate	2.5 X 10 ⁻⁶	$1.7 \text{ X } 10^4$
Zinc/iron + hexavalent passivate	3.4 X 10 ⁻⁵	2.2×10^4

Table 3 EIS Results For Electroplated Test Panels

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 products on zinc but the results confirm that best results will be obtained on zinc/iron.

Resistance To Damage

A chromate passivate layer contains a complex mixture of trivalent and hexavalent chromium compounds¹¹. 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 properties³¹².

As trivalent coatings contain no soluble chromate compounds they are no longer self healing. This means that corrosion can 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 is normally used to produce such parts where the tumbling of the large volume of parts is likely to cause some damage during production.

Table 4 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.

Sample	Hours
Zinc + trivalent passivate	120
Zinc + hexavalent passivate	140
Zinc iron + trivalent passivate	200
Zinc iron + hexavalent passivate	150

Table 4. Results Of NSS Testing Of Barrel plated Items To 5 % White Rust.

As expected, damage has reduced salt spray resistance. However on a zinc/iron substrate the trivalent still protects at least as well the hexavalent coating. Generally it has been found that if a thick non porous trivalent coating is deposited it produces an insoluble barrier coating that is effective at retarding lateral corrosion.

A further study was made using 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. Figure 2 is a chart illustrating this.





As expected, as salt spray testing proceeds corrosion occurs and Rct falls in all cases. These results show that after barrel plating the lack of self healing properties means that corrosion resistance of the trivalent passivate on a zinc substrate is less than the hexavalent. It is also apparent that the trivalent passivate gives much better performance after heat treatment. However even after damage the trivalent product has better corrosion resistance on zinc iron than the hexavalent one.

Use Of Passivate Sealers

One way to try and increase corrosion resistance after damage is by the use of topcoats or sealers after passivation. These can help boost the trivalent performance by providing an extra barrier, increasing abrasion resistance and incorporating additional corrosion inhibitors. They can also be designed to modify lubricity of fasteners to improve the predictability of the torque and tension relationship as required for automated assembly. Two different topcoats expected to give an improvement were selected for testing and are described below.

A silicate type sealer, (topcoat 1).

This product is based on an inorganic silicate but also includes an organic additive to improve heat 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 Inorganic Sealer carried In A Lacquer Coating, (topcoat 2)

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. 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 inorganic silicon compound that is again expected to limit the corrosion of zinc where passivate is thin or missing.

Both topcoats will modify the torque tension as required by automotive specifications.

Testing

The effect of the topcoats was assessed by NSS and scribed NSS testing together with EIS. Results of neutral salt spray testing are given in table 5.

Table 5. Salt Spray Test Results For Topcoats On Zinc Plated Steel Test Panels.

	No Thermal Shock	After 1 hr @150 °C,(300 °F)
Trivalent + topcoat 1	450 hrs	300hrs
Trivalent + topcoat 2	500 hrs	400 hrs

It can be seen that each of the sealers used has a positive effect on improving salt spray resistance. The presence of these sealers on top of the conversion coating has reduced damage after heat treatment and improved resistance after thermal shock. The lacquer based topcoat 2 was the best at doing this In order to make comparisons of effectiveness after damage loads of M8 bolts were barrel processed and then neutral salt spray tested. Typical results are given in table 6.

Table 6. NSS Results to 5 % White Rust For Bolts With Topcoats Applied

Sample	Zinc	Zinc/iron
Trivalent + topcoat 1	200	270
Trivalent + topcoat 2	220	320
Trivalent passivate	120	200
Hexavalent passivate	140	150

It can be seen that both topcoats are very effective at increasing corrosion resistance where there is mechanical damage. Topcoat 2 is also particularly good at maintaining protection after heating.

Testing Of Scribed Test Panels

Scribed salt spray testing was undertaken to provide 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 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 6.

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

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

The results show that the use of these topcoats gave a substantial improvement to protection at damage points when the trivalent passivate is used on a zinc substrate.

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.

EIS Testing

Test panels were tested with topcoats applied. The results are given in table 7. Table 7 FIS results For Plated Test Panels

Table 7 EIS results for Trated rest rates.				
Samples	Rct, (ohms cm^{-2})	Rct, (ohms cm ⁻²⁾	CDL, (F)- Zinc	CDL,(F)-
	Zinc	Zinc/iron		Zinc/iron
Trivalent	4.0×10^3	$1.7 \text{ X } 10^4$	7.0 X 10 ⁻⁴	3.4 X 10 ⁻⁵
passivate				
Hexavalent	5.0×10^3	$2.7 \text{ X} 10^4$	2.0 X 10 ⁻⁵	1.4 X 10 ⁻⁵
passivate				
Trivalent +	5.3×10^3	3.6×10^4	4.4 X 10 ⁻⁵	2.5 X 10 ⁻⁶
topcoat 1				
Trivalent +	7.6×10^3	2.9×10^4	5.0 X 10 ⁻⁵	5.3 X 10 ⁻⁶
topcoat 2				

These results suggest that the application of topcoats 1 and 2 give a noticeable improvement. Capacitance results confirm the known fact that topcoat 2, (the lacquer) is thicker than topcoat 1,(the silicate).

Conclusions

It is now possible to use thick trivalent passivate to replace yellow chromates without suffering a loss in corrosion resistance. This is particularly true on Zinc/Iron substrates where the trivalent passivate tested performed especially well. These products do not have the health and safety problems associated with chromates and have the advantage of being much less damaged by heat treatment. Trivalent passivates are not self healing and the coating will have reduced corrosion resistance on zinc plated substrates after mechanical damage. Resistance to damage is much greater for trivalent deposits on a zinc/iron substrate.

The two sealers tested were very effective at increasing corrosion resistance and when used together with the trivalent product were shown to match yellow chromates on zinc after damage. The use of sealers also gives other improvements with topcoat 2, (the lacquer containing an inorganic sealer) being especially good at boosting corrosion protection after thermal shock, such as might be encountered in a car engine.

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.

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