Alternatives to Chromate as a Conversion Coating for Electronic Enclosures

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Nortel Networks had been using chromate conversion coatings for corrosion protection on electronic enclosures. As EMI protection requirements became more stringent, the yellow chromate did not provide electrical conductivity to enable the enclosure to protect the electronic equipment from environmental EMI nor inhibit the equipment EMI from radiating to the environment. Research was conducted to find an alternative that would provide a replacement conversion coating. The molybdenum phosphate coating was determined to provide a cost effective treatment that provided adequate corrosion protection to the zinc plated steel with superior electrical conductivity and environmental improvements.

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Introduction

Hexavalent chromate solutions have been used for years to protect the zinc plated steel components of telecom equipment. The application of chromate to the electronic enclosure was especially important not only to delay the mechanical consequences of corrosion but to defer the decay of EMC integrity due to the corrosion of the underlying metals to their oxides. With the onset of higher signal speeds of the electronics, the higher operating temperatures of the densely packaged equipment and the movement of telecom equipment into an unprotected environment, the chromate protection was fast becoming inadequate and a new environmental protection system needed to be installed.

The Original Configuration

The electronic substrates essential to the signal switching are stored in a zinc plated steel box like structure fitted with a face plate.

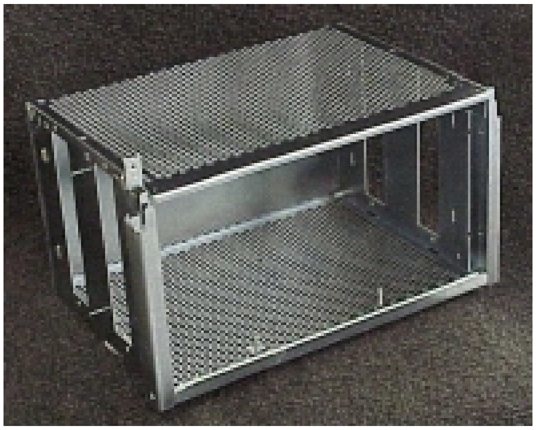

Figure 1 - Zinc Plated Steel Box

This enclosure acts as a Faraday cage that prevents electromagnetic energy from either entering or exiting the interior electronics assembly area. To accomplish this end, the electronics must be completely and continuously surrounded by electrically conductive material. The enclosure sides are assembled using chromated zinc plated steel panels. The intersections of the panels are gasketed to maintain electrical contact and assure electrical continuity. This is where chromate no longer fulfills the design intent for EMC integrity.

The face of the panel ends are yellow chromated. Upon assembly of the backpanel and faceplate to the side panels, a beryllium copper gasket that is tin lead plated is assembled at the interfaces. The gasket has "spurs" to assure penetration through the chromate to the zinc/steel underlayment so that electrical continuity can be maintained.

As the switching speed of the electronic system increased into mega and gigabit frequency and the signal power changed, the EMI protection requirements, as set by the FCC (Federal Communications Commission), became more stringent. This stricter regimen coincided with the stronger signal generated by the electronics and greater EMI susceptibility of some of the components in the system. As a result it was becoming increasingly difficult to consistently conform to FCC regulations as the system was configured. Investigation demonstrated that the material composition of the gasket system was the apex of the pattern of non-conformance. Configuring the same gasket with clear chromate enabled the system to be in conformance. This strongly indicated that the yellow chromate was a major cause of deviation.

New Test Criteria

The salt fog test as is specified by ASTM B 117 gives some meaningful information about the corrosion behavior of metals but none about the electrical conductivity of the metals' surface. The approach was taken that the gasket interfaces were essentially an electrical connector so why not test the finished gasket surfaces as a connector finish? The test for environmental stability of electronic connections in an unprotected environment is the Battelle Class IV mixed flowing gas test (See Table 1).

Table 1 - 1000 Hour Battelle Class IV Test

1)	Chlorine	20ppb.
2)	Hydrogen Sulphide	100ppb.
3)	Nitrogen Dioxide	200ppb.
4)	Sulphur Dioxide	200ppb.
	70% relative humidity	at 30°C

The relatively low concentration of gases needed for this experiment was supplied by means of permeation. Permeation tubes were prepared by condensing the high purity gases in dry ice method and ethanol alcohol, then encapsulating them in Teflon tubes. After the tubes are removed from the dry ice bath and allowed to reach room temperature, a gas phase is developed causing the gases to permeate the walls of the Teflon. In order to maintain the permeation rate, a gas/ liquid phase must be present inside the tubes.

Unlike the connector joint, the gasket joint is not "gas tight" so we prepared the gasket joint with 10 days of 85°C/85% RH environment exposure. The Battelle test was run for 1000 hours. The salt fog test was run for 100 hours (Bellcore specification). Samples were removed periodically and checked visually and electrically for surface conductivity and contact resistance. Some samples were also examined with SEM (Scanning Electron Microscopy) and EDX (energy-dispersive X-ray) to survey metal ion changes. Samples were evaluated in terms of times to white and red corrosion, initial electrical properties and changes of those properties.

The search for an alternative to chromate began with the evaluation of conductive paints.

Conductive Paints

Several classes of conductive paints were tested under the conditions described above. These paints have been recommended as conductive metal protectants at the interface of the gasket. Several organic vehicles and conductive pigments were represented in the test. For several causes the conductive paints failed long term electrical conductivity tests and the material as a class was not chosen to replace the chromate.

Other Plating Alloys

In the hope that the protection function provided by the yellow chromate be achieved by merely changing the plating alloy and thus eliminating the conversion coating altogether, plating metals and alloys other than zinc were investigated. Among them were variations of electroplated nickel, electroless nickel, trivalent chrome, zinc iron and zinc nickel alloys.

Steel coupons were plated with the above alloys. Half the samples of the zinc alloys were treated with yellow chromate. Steel samples were also plated with zinc (both the alkaline and cyanide process) and treated to yellow chromate to be used as a baseline. All the samples were exposed to both the salt fog and the mixed flowing gas environmental stress tests and evaluated as described above. The results (see Table 2) indicated that the nickel coatings were not as conductive as the yellow chromated zinc samples.

Table 2 - Surface Resistivity on Samples before and after Environmental Testing

Sample Type	Surface Resistivity (Ω/ft)	
	Before	After
Zinc/Nickel	168.75	281.25
AlkalineYellow Chromate	225	281.25
Cyanide Yellow Chromate	281.00	600.00
MolyPhos	168.75	150.00

The zinc nickel alloy coupons were surprisingly robust to the stress tests. The conductivity and visible signs of corrosion were such that it seemed to be the superior strategy. If retention of conductivity and corrosion resistance were the only criteria of success this alloy, both chromated and non chromated, would have been selected. At the time this part of the program was carried out (1995) zinc nickel alloy plating was not well understood at all and only one specialized plater could be located which made the process out of line with the cost targets. Furthermore, when a zinc nickel alloy plated shelf was chromated the color of the surface ranged from magenta to blue which seriously disconcerted the designers. We decided to defer the alternative plating strategy until cost and control issues could be resolved.

Since the alternative plating strategy was deferred the research team decided to explore the advances in alternate conversion coatings.

Criteria for Alternative Conversion Coatings

By the time we started to search for an alternative conversion coating to hexavalent chrome there developed considerable public concern and regulatory activism regarding the adverse effects of hexavalent chromates on health and the environment. We predicted that there would be continuing activism against such chemicals and processes. To avoid a situation where any alternative process we may develop could be restricted in the future, we decided to look for the least environmentally aggressive and health threatening conversion coating and process that would fulfill our design intent. At this time the National Consortium for Manufacturing Sciences (NCMS) published a report on alternative coatings to chromate for aluminum. The report revealed an excellent environmental profile of the alternative conversion coatings as well as the several chromate processes. When the entire process was characterized, many had as bad or worse environmental profiles as the chromate.

The same report described the salt fog corrosion tests on aluminum with one of the evaluating factors being electrical conductivity. The test results, when juxtaposed on the environmental profiles of the processes, gave little evidence that an alternative to the chromate conversion coating for zinc plating, that met the design intent of the program, would be found. We realized that zinc's corrosion process and products are different from aluminum but experience said that the NCMS report was a good indicator of success.

We decided to evaluate the most conforming of the processes. Then the AESF journal started reporting on the work of P.T. Tang et al from the Technical University of Denmark on a molybdenum phosphate conversion coating. Subsequent correspondence with the Danish research group provided enough information to include molybdenum phosphate in the test cohort.

Before the actual testing program started a table of product criteria was developed to evaluate the coatings. The essential elements were:

1. The coating had to have lower contact resistance and surface resistivity than chromate.

2. The coating had to meet the ASTM B117 salt fog criteria after 96 hrs. exposure. The contact resistance and surface resistivity deviation had to be less than that for yellow chromate.

3. The coating had to have less deviation of contact resistance and surface resistivity than yellow chromate after 250 hours exposure to 85°C/85% RH coupled with 1000 hours mixed flowing gas exposure.

4. The alternative coating had to maintain this electrical conductivity to the electronic system at an operating temperature of > 75°C for 20 years.

5. The alternative coating had to be paintable with either a liquid or electrostatic powder coating within 24 hours of application.

6. The coating process had to be safe to apply and the process residues had to be rendered environmentally acceptable to dispose.

7. The coated products had to be safe to handle by users and at the end of life, the coated product had to be disposed of via acceptable disposal channels.

8. The coating had to be applicable within the envelope of skill and equipment envelope of the contractor for the chromate.

9. The coating application had to be cost neutral to the application of yellow chromate.

The Evaluation Program

Molybdenum phosphate coating, a titanium coating and the yellow chromate coating were applied to steel coupons plated with alkaline zinc, cyanide zinc and zinc nickel. The coated and plated samples were then exposed to the salt fog and the modified Battelle Class IV environment as described above. Five coupons of each sample class were examined visually and tested electrically at the beginning, periodically throughout and at the end of each test; the results were recorded (see Table 3). The molybdenum phosphate met all of the product criteria.

Samples of both molybdenum phosphate and chromated zinc plated steel were exposed to 10 day exposure temperatures of -20,+ 25 , and +90°C, allowed to equilibrate to 23°C and tested for durability (ASTM B571) and microhardness (ASTM B578). All samples passed. Results of the molybdenum phosphate and the chromated coincided.

One coupon of each sample class for each environmental test from the start point and end point were examined with scanning electron microscopy and EDX.

The molybdenum phosphate was recommended as an alternative conversion coating because it met all the pre set product criteria. Other conversion coatings may provide better corrosion resistance than molybdenum, but the literature research gave indications that in one or more aspects they would not meet the product criteria template, especially the electrical conductivity requirements.

Additional Benefits

The molybdenum phosphate coating, as applied and tested in this program, has at least five times better surface conductivity and one-fifth the contact resistance of yellow chromate. During application research, we also discovered this electrical property allowed the use of a conformable conductive gasket rather than the expensive and environmentally unfriendly tin lead plated beryllium gasket needed for yellow chromate. This change increased first pass yields in manufacturing, reduced assembly time and improved conformance to FCC EMI rules. A significant cost reduction benefit ensued.

Further process and product tests revealed that an organic coating could be applied within one hour of application of the molyhdenium phosphate coating or alternatively an electrostatically applied powder coating could be used, thereby providing additional cost and environmental benefits.

Conclusion

The investigation to find an alternative to yellow chromate, triggered by the need to find a coating which provided significantly better EMI shielding properties, was successfully completed with the selection of molybdenum phosphate. In addition, this conversion coating, when used for electronic enclosures, also provided significant gains in environmental protection, process safety, manufacturing cost savings, finished product cost savings, extended operating temperature range, feasible painting alternatives and overall product appearance. All of this was achieved with a replacement coating process which was as simple to implement as the well entrenched chromate based process, produced significantly less toxic waste by-product and was a cost neutral plating process as compared to hexavalent chromate.

We view our investigation as a major success and in 1999, Nortel Networks began to utilize molybdenum phosphate on new product initiatives.

In addition, the success of our research with steel has initiated research to include a similar process alternative for aluminum.

Table 3 - Results of The Evaluation Program

Type of Coating	Before	Change in Contact Resistance (OHMS)				
		After 10 days 85°C/85%RH	Plus X Days In Gas Chamber			
			10 DAYS	20 DAYS	30 DAYS	40 DAYS
Zinc/Nickel	0.0095	0.0024	0.0045	0.0011	0.0001	0.0058
Alkaline Yellow Chromate	0.0056	0.0069	0.0005	0.0016	0.0044	0.0063
Cyanide Yellow Chromate	0.0070	0.0039	0.0140	0.0005	0.0289	0.0380
MolyPhos	0.0067	0.0138	0.0334	0.0051	0.0138	0.0038