M. E. Williams and Associates, Inc.

"Excellence in Metallurgical Engineering"

12825 385th Avenue
Waseca, MN 56093

Case Study: Chromate Conversion Coating

By

Merlin E. Williams, P.E.

Subject

Evaluation of trivalent chromate conversion coating on zinc plating to determine possible cause of discoloration of the coating upon storage of the parts. At the time of this case study, the discoloration of trivalent chromate conversion coatings was an industry wide problem that was assumed to be corrosion. It was apparent that the discoloration only happened when parts were chromated by tumbling in barrel plating drums. This study determined the nature of the problem, that the soundness of the material was not affected, but only the surface appearance. Possible causes of the problem were also determined.

The sample parts were examined by visual examination, microscopic examination, and energy dispersive x-ray analysis to determine the conditions on the surface of the zinc plating with a trivalent chromium conversion coating. This case study is a reduced sampling of the actual investigation that was conducted.

Evaluation of Die Cast Sample

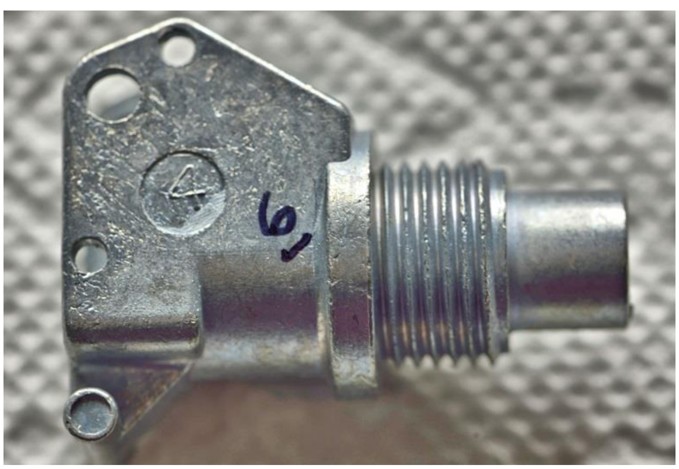


Figure 1 – Zinc Die Cast Part

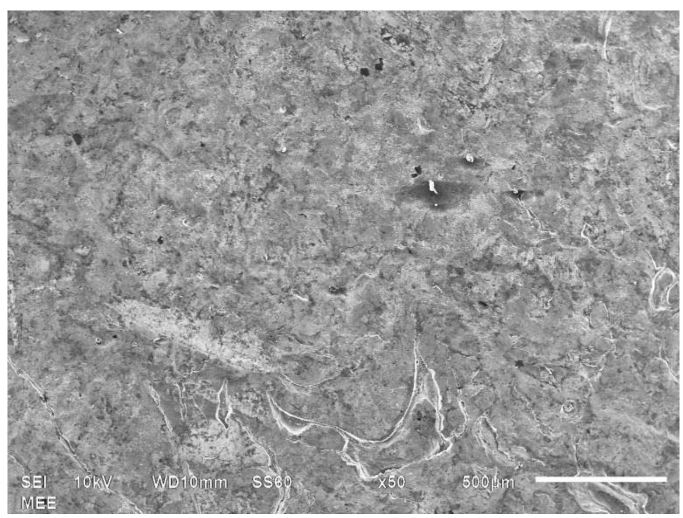


Figure 2 – 50X Analysis Area of Zinc Die Casting

A zinc die cast part, treated with trivalent conversion coating six months prior to the analysis of the surface, was examined. Figure 2 shows the area of analysis on the Zinc Die Casting. The semi-quantitative analysis results are given in Table 1, and the spectrum is shown in Figure 3.

Table 1 Raw Die Casting (Percent by Weight)	
Element	Die Cast
Carbon	5.4
Oxygen	9
Fluorine	0.5
Aluminum	4.2
Chromium	1.7
Iron	Trace
Zinc	79.2

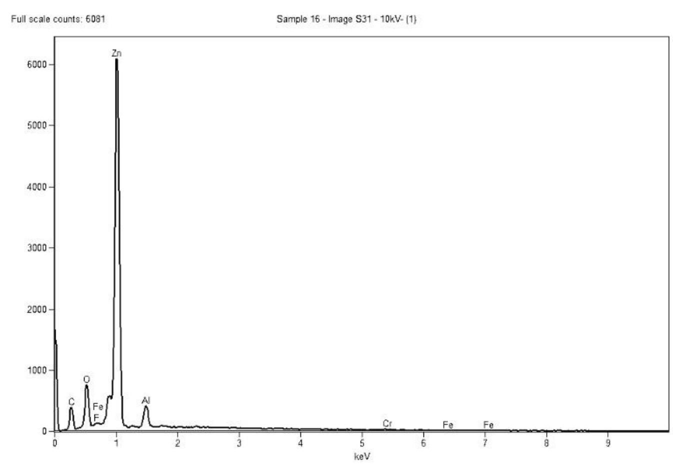


Figure 3 – Spectrum of Zinc Die Casting

Evaluation of Zinc Plated Steel Fitting

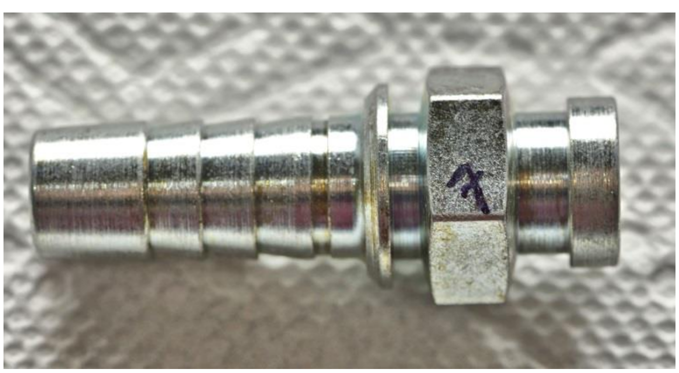


Figure 1 – Zinc Plated Steel after Five Months in Storage

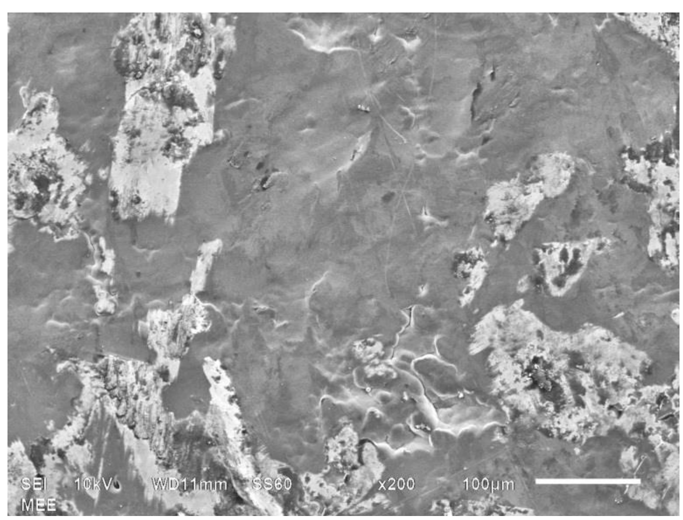


Figure 2 – 200X Zinc Plated Steel, Area 1

Zinc plated steel, Figure 1, was fabricated from 12L14 steel and plated five months prior to the evaluation with alkaline non-cyanide zinc, then given a clear trivalent chromium passivate coating. The part was stored in a Ziplock bag. Analysis Area 1 was located on the hex. The surface for Area 1 is shown in Figure 2. There was mechanical damage to the surface. The analysis locations are shown in Figure 3, and the semi-quantitative analysis results are given in Table 1.

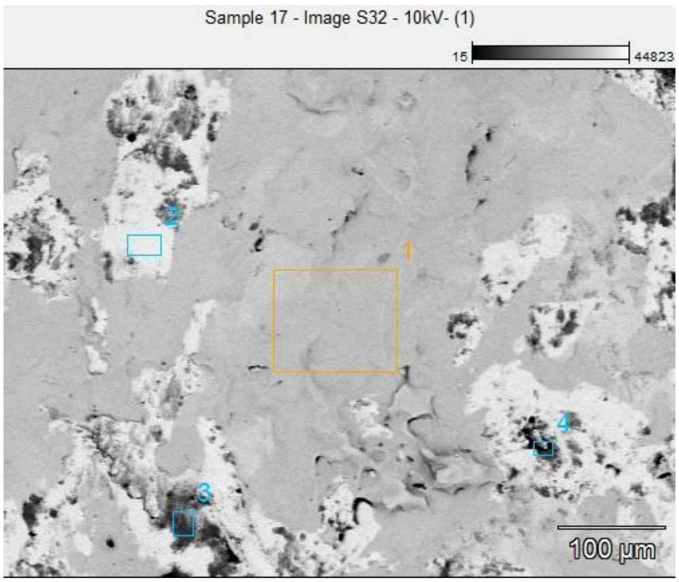


Figure 3 – 200X Zinc Plated Steel, Area 1, Analysis Locations

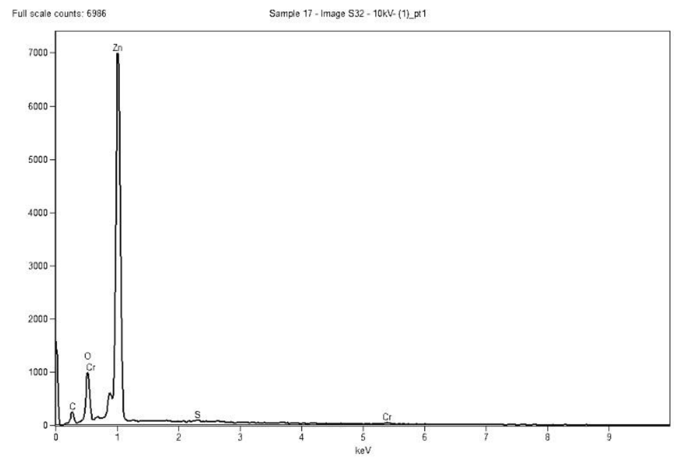


Figure 4 – Spectrum of Zinc Plated Steel, Area 1, Location 1

Table 1 **Zinc Plated Steel - Area 1 - 10kV** **(Percent by Weight)**				
Element/Location	1	2	3	4
Carbon	3.3	1.2	5.2	8.6
Oxygen	10	1.9	22.1	14.4
Fluorine			1.5	0.7
Silicon				0.7
Sulfur	0.4		0.7	0.4
Potassium			0.5	0.4
Calcium			1.5	1.2
Chromium	2.4		4.7	4.7
Zinc	84	97	63.7	68.9
Spectrum	Figure 4	Figure 5	Figure 6	Figure 7

There was no fluorine or silicon present at Location 1, but chromium was found. Location 2 was free of the conversion coating. The dark material, Figure 3, Locations 3 and 4, showed the presence of fluorine and chromium. Location 4 also had silicon. In Locations 3 and 4, the coating was thicker, allowing for better analysis.

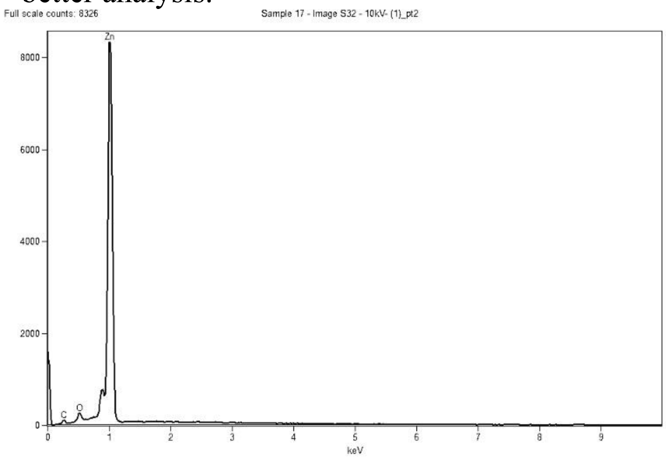


Figure 5 – Spectrum of Zinc Plated Steel, Area 1, Location 2

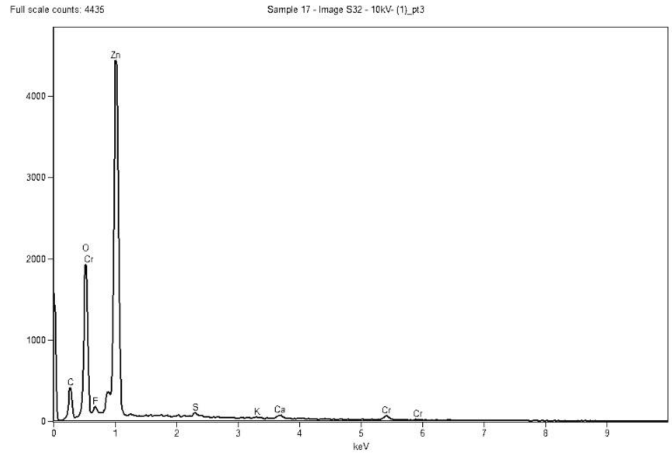


Figure 6 – Spectrum of Zinc Plated Steel, Area 1, Location 3

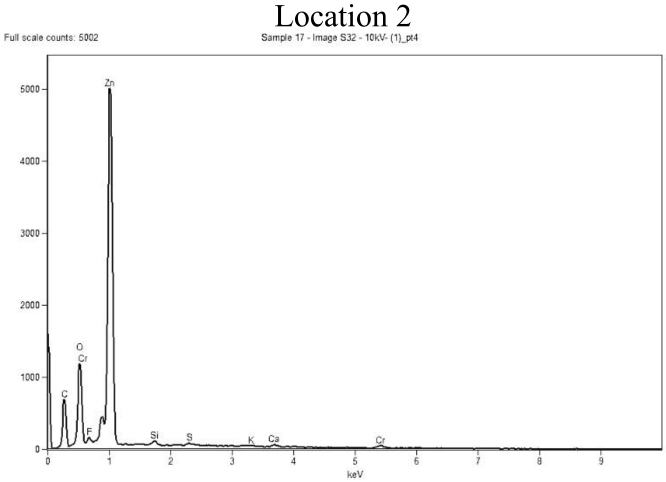


Figure 7 – Spectrum of Zinc Plated Steel, Area 1, Location 4

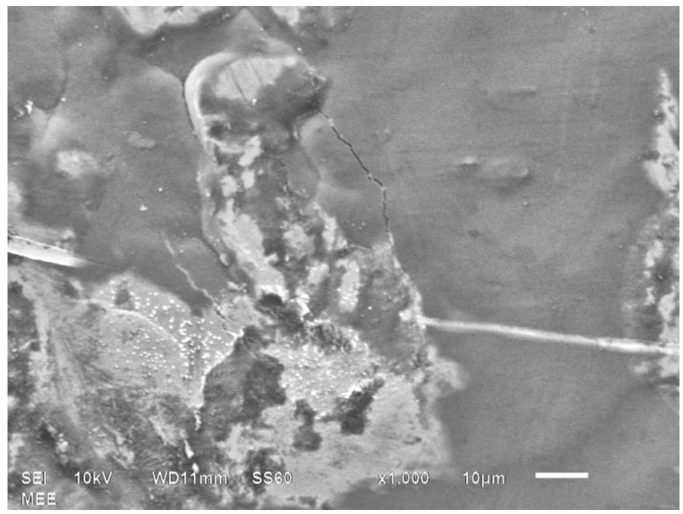
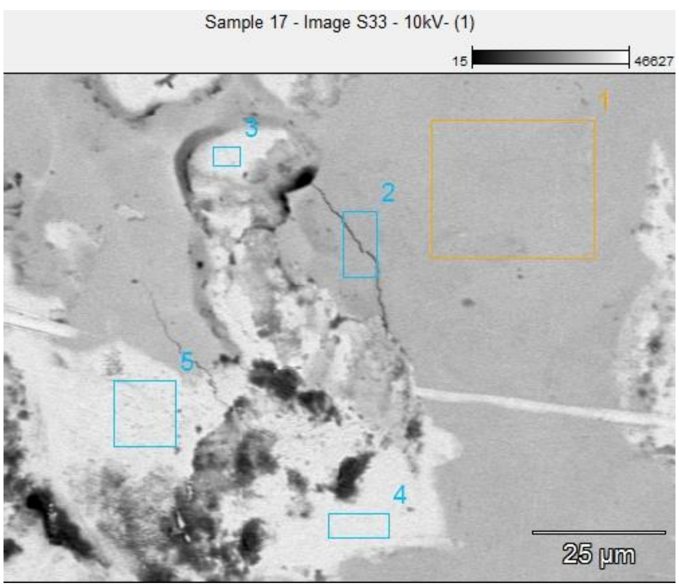


Figure 8 – 1000X Zinc Plated Steel, Area 2



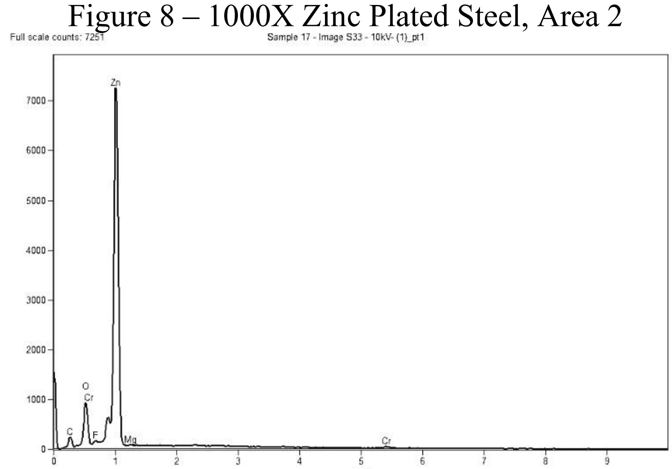


Figure 10 – Spectrum of Zinc Plated Steel, Area 2, Location 1

Figure 9 – 1000X Zinc Plated Steel, Area 2,
Analysis Locations

Zinc Plated Steel, Area 2, is shown in Figure 8. There were several cracks in the zinc plating at this location. There were very small white spheres present in a portion of the location shown. The analysis locations are shown in Figure 9. The semi-quantitative analysis result for each location is given in Table 2.

Table 2 **Zinc Plated Steel, Area 2 - 10kV** **(Percent by Weight)**					
Element/Location	1	2	3	4	5
Carbon	2.9	3.4	1.6	1.3	1.4
Oxygen	9.4	9.6	2.8	2.2	2.9
Fluorine	0.6	0.6			
Chromium	3.2	3			
Zinc	84	83.4	95.6	96.5	95.7
Spectrum	Figure 10	Figure 11	Figure 12	Figure 13	Figure 14

Locations 1 and 2 had the conversion coating, but the supplemental coating was not detected. Locations 3, 4, and 5 were free of any detectible coating.

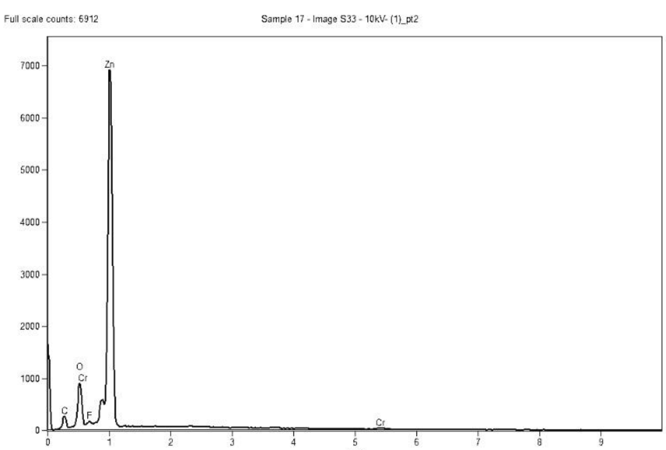


Figure 11 – Spectrum of Zinc Plated Steel, Area 2, Location 2

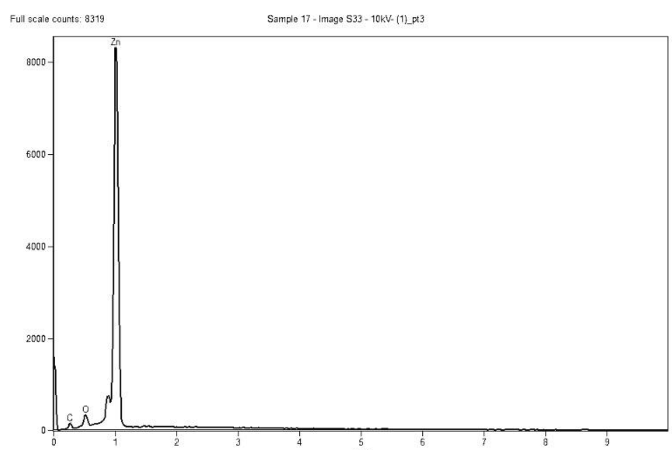


Figure 12 – Spectrum of Zinc Plated Steel, Area 2, Location 3

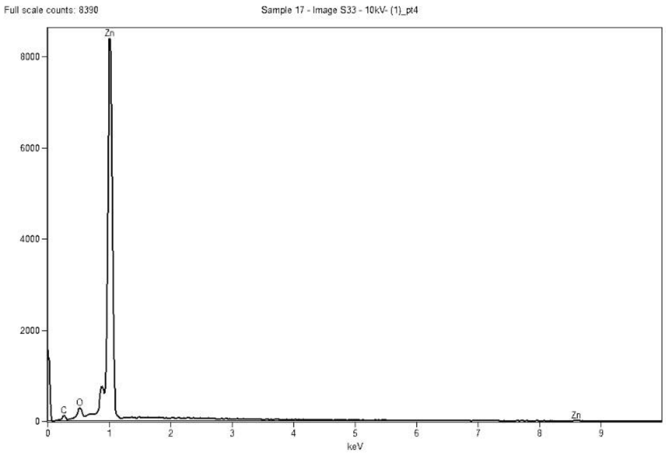


Figure 13 – Spectrum of Zinc Plated Steel, Area 2, Location 4

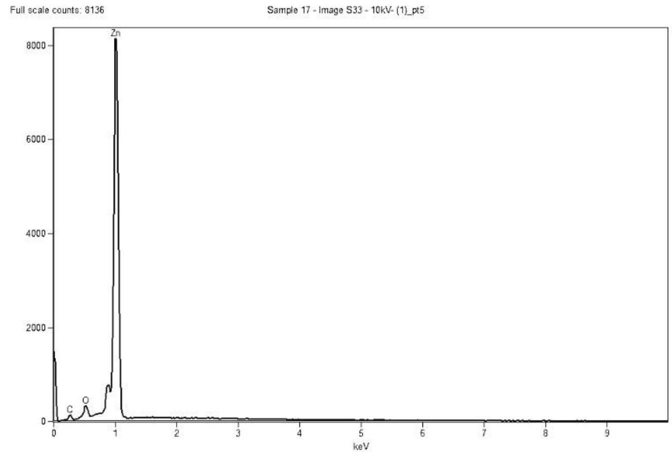


Figure 14 – Spectrum of Zinc Plated Steel, Area 2, Location 5

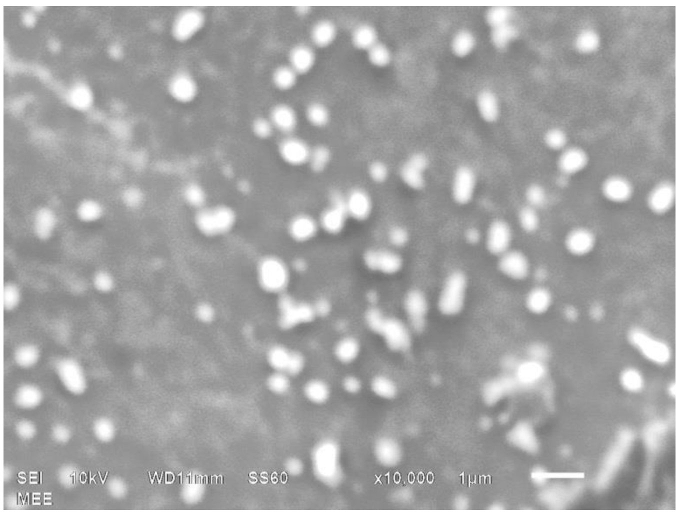


Figure 15 – 10,000X Sample 7, Area 3

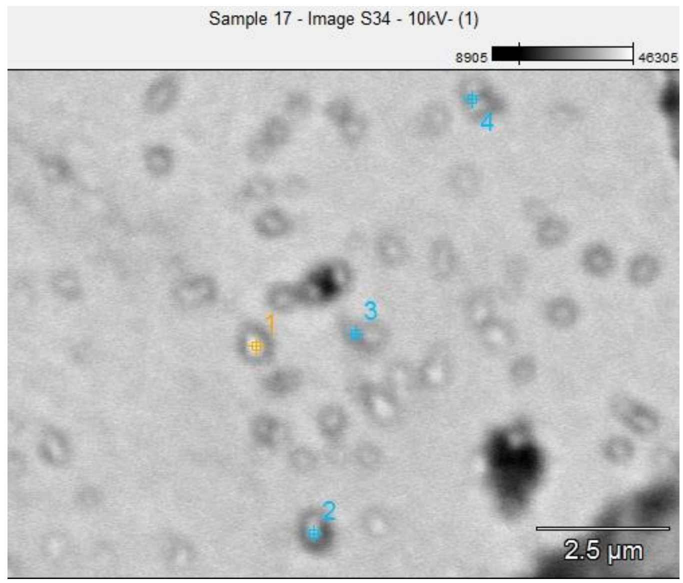


Figure 16 – 10,000X Sample 7, Area 3, Analysis Locations

Sample 7, Area 3, consisted of submicron sized particles that were seen on the surface in Area 2. Analysis was done to determine what the particles were. Table 3 gives the semi-quantitative analysis results for the four particles that were analyzed.

Table 3
Zinc Plated Steel, Area 3 - 10kV
(Percent by Weight)

Element/Location	1	2	3	4
Carbon	1.9	2.8	2.9	2.1
Oxygen	1.8	1.9	2.2	2.1
Zinc	96.3	95.3	94.9	95.7
Spectrum	Figure 17	Figure 18	Figure 19	Figure 20

The analysis of the particles showed that they were submicron-sized zinc particles.

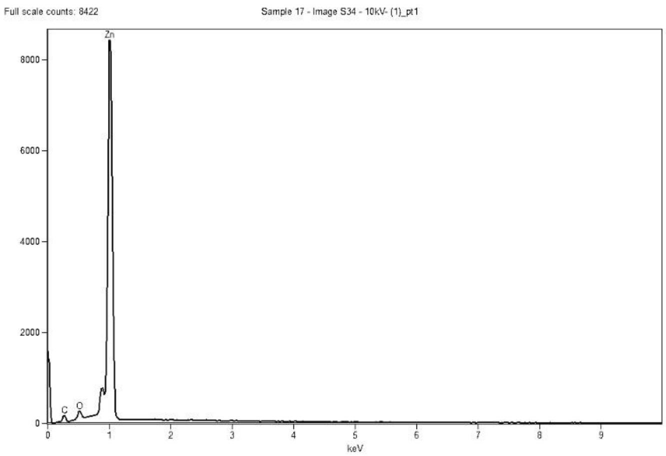


Figure 17 – Spectrum of Zinc Plated Steel, Area 3, Location 1

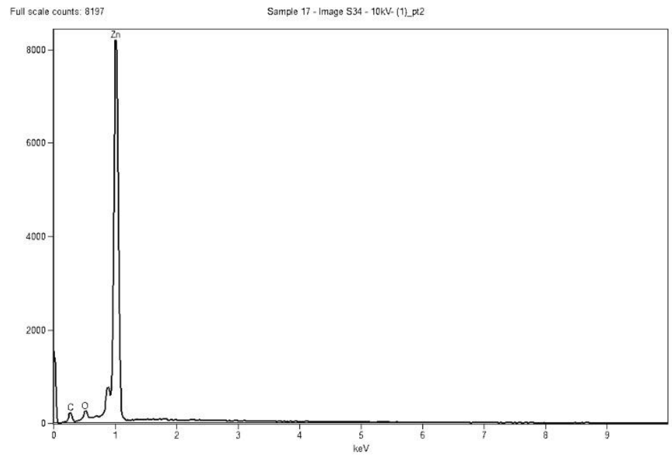


Figure 18 – Spectrum of Zinc Plated Steel, Area 3, Location 2

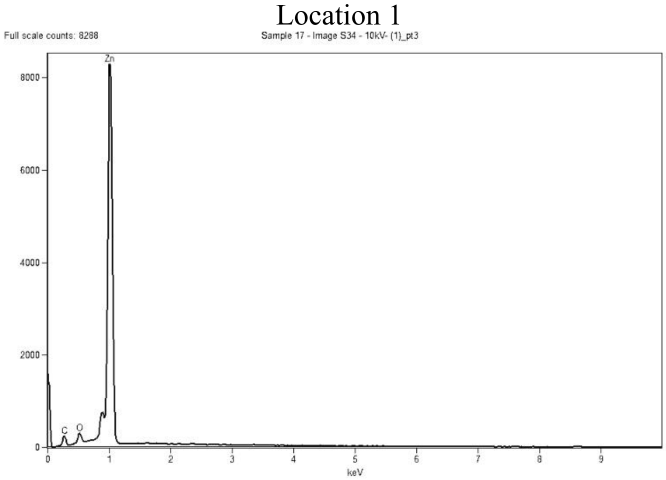


Figure 19 – Spectrum of Zinc Plated Steel, Area 3, Location 3

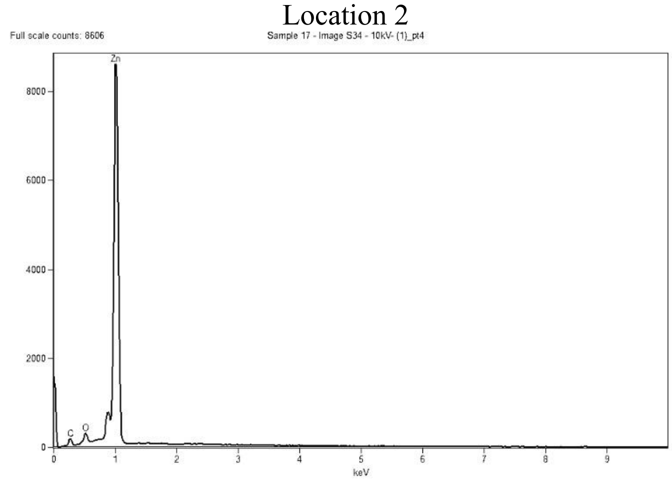


Figure 20 – Spectrum of Zinc Plated Steel, Area 3, Location 4

A full material surface evaluation was done to be sure the problem was not corrosion that would affect the finished products' use and safety.

Discussion

It is my understanding that trivalent chromium conversion coatings are not self-healing, as are hexavalent chromium conversion coatings. This fact may have been the main cause of the problem, because the discoloration only appeared on parts treated using the tumbling barrel plating equipment. The conversion coated parts examined all showed surface mechanical damage, in addition to areas with no protective coating.

Most of the locations that were free of detectable coating did not appear to have mechanical damage. The coating may have been removed from these areas by rubbing action within the barrel during the conversion coating process. There is another possibility: the processing time in the conversion coating bath may have been too short for the parts to have been completely coated. A third possibility is that something was interfering with the wetting of the zinc plating by the conversion coating bath. Incomplete coverage of the zinc plating with the conversion coating will set up differences in oxygen potential on the surface. It could not be determined if this potential would be high enough to convert trivalent chromium to hexavalent chromium, but this appeared to be happening. Upon re-examination, the zinc die cast showed red-brown discoloration starting to form, see photo below.

400X Surface of Treated Zinc Die Casting

At the time of this study, an internet search for information on oxidation of trivalent chromium revealed that others were asking the same question about conversion of trivalent to hexavalent chromium over time. This was a major problem facing the metal finishing industry but, because of studies like this one, a proprietary solution was found.