

Case Studies of Blistering Problems in Zinc-plated Steel and Zinc-plated Die-cast Zinc Alloy Parts

by Z. Panossian* & J.V. Ferrari

This paper presents two case studies of blistering problems in zinc-plated steel and zinc-plated die-cast zinc alloy parts. An optical microscope and a scanning electron microscope (SEM) connected to an energy-dispersive spectrometer (EDS) system were used to examine and analyze the surface and the cross-section of the plated parts. In addition, the plating baths were analyzed and the entire plating processes, including pre-treatment steps, were evaluated. It was concluded that the blistering was caused by different factors. For zinc-plated steel parts, it was caused by inadequate pre-treatment and for zinc-plated die-cast zinc alloy parts, by poor substrate surface quality.

Introduction

This work originated from one of the technological services carried out by PRUMO** at a company that dealt with zinc cyanide plating baths. Two case studies of blistering problems in the electroplating are discussed:

Case I: Zinc-plated steel parts coated with epoxy-based varnish. The blisters only appeared during the varnish curing process.

Case II: Zinc-plated die-cast zinc alloy (Zamac 5) parts. The blisters appeared during the electroplating process.

Case I: Blisters in the zinc-plated steel parts

The plater applied the zinc coating onto the steel parts using a cyanide zinc plating process. After that, the parts were chromated and sent to the customer, who then applied varnish to them. The varnishing process was as follows:

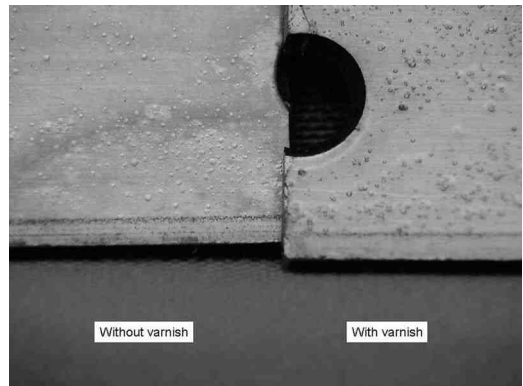


Figure 1—Surface view of a blistered part with and without varnish layer. The blisters remain visible after removal of the varnish layer, indicating that it is not present at the zinc/varnish interface.

- Light brushing
- Chemical cleaning by immersion in perchloroethylene vapor at 127°C (261°F)
- Electrostatic application of the epoxy-based varnish
- Oven curing at 220°C (428°F). The temperature of the parts during this process was around 200°C (392°F).

Experimental procedure and results. Samples of the parts with and without blisters were submitted to the following tests and analysis.

The varnish layer on a surface of a part showing blisters was removed with the appropriate organic solvent. After this procedure, the blisters were still visible, as can be seen in Figure 1.

After removing the varnish layer, the blistered surface was also examined with a scanning electron microscope

Nuts & Bolts: What This Paper Means to You

For the last few years, this journal has updated past articles from the 1960s and 1970s related to troubleshooting in the field. This paper shows that such work is still ongoing, as we read about a couple of case histories from a mobile-troubleshooting lab in Brazil. This paper presents two case studies of blistering problems in zinc-plated steel and zinc-plated die-cast zinc alloy parts.

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** PRUMO $\text{\textcircled{D}}$ Mobile Units Project for Technological Service for Micro and Small Businesses, created in Brazil in 2001 aiming to offer technological support for the metal finishing businesses. The project is conducted by a trained team with the support of a mobile laboratory which had facilities to carry out several types of tests and analyses such as plating bath analysis, thickness measurement and Hull cell tests, with the intent of solving the detected problems.

(SEM). Figure 2 shows the results, indicating the presence of blisters. This same surface was analyzed by energy dispersive spectroscopy (EDS) connected to the SEM. Through this analysis, it was possible to verify the presence of the following elements: zinc, chlorine and oxygen. Very probably, the chlorine originated from chemical cleaning in perchloroethylene. This solvent can decompose, yielding hydrochloric acid, which is aggressive to zinc, and phosgene, which is toxic.¹

The cross-sections of the blistered parts were examined with an optical microscope. The blisters were present at the steel/zinc interface as shown for two separate sites in Fig. 3. No part surface defect could be seen that correlated with the blistering.

The cyanide zinc plating bath (rack formulation) used for plating the blistered parts was analyzed by an energy dispersive X-ray fluorescence bath analyzer (ED-XRF) and by titrimetric analysis. The results obtained and the required composition range of the bath are presented in Table 1.

The possibility of hexavalent chromium contamination in the plating bath was checked. Hexavalent chromium is a frequent contaminant of almost all bright zinc plating baths because of the widespread use of chromate bright dips. As little as 5 ppm can cause blistering in the coating.² However, no hexavalent chromium was detected.

The entire zinc plating process, including pre-treatment steps, was inspected in order to identify possible operational procedures that would cause the blistering problem. During this inspection, the presence of an oil layer on the surface of the alkaline cleaner was verified. This could lead to oil contamination of the parts as they were removed from the bath.

We also found that the parts were placed on racks only after the pre-treatment (degreasing and pickling) and immediately before the immersion of parts into plating bath. This was done without using gloves, which caused the contamination of the part surfaces. Further, some of the parts remained exposed to atmospheric moisture long enough to allow the onset of corrosion, forming a thin layer of rust.

Discussion. We concluded that the blistering arose from hydrogen gas that was trapped at the steel/zinc interface. This occurred at weakly bonded areas between the steel and zinc, which were localized adhesion faults.

The process inspection indicated that the adhesion faults were caused by inadequate pre-treatment procedures. The chemical surface preparation involved:

- Immersion alkaline cleaner (65 to 100°C; 149 to 212°F) (The oil layer observed on the cleaning solution contaminated the part surfaces during their removal from the cleaning tank)
- Cold water rinse
- 50% hydrochloric acid pickle (room temperature)
- Double cold water rinse
- Alkaline water dip (neutralizer)
- Manual racking

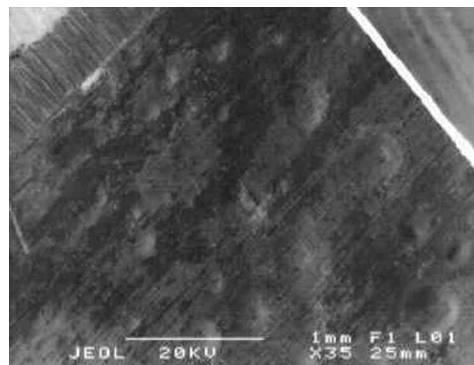


Figure 2—Blisters shown in Fig. 1 without varnish. SEM, magnification: 35X. No etching.

Table 1
Composition of the Cyanide Zinc Bath

Component	Composition	
	Required range, g/L (oz/gal)	Analysis, g/L (oz/gal)
Zinc (Zn)	6.0 - 12.0 (0.8 -- 1.6)	18.5 (2.5)
Total sodium cyanide (NaCN)	10 ± 15 (1.3 -- 2.0)	7.8 (1.0)
Caustic soda (NaOH)	150 (20.0)	141.2 (18.8)
Sodium carbonate (Na ₂ CO ₃)	Not specified	24.4 (3.2)
Ratio (Total NaCN/Zinc)	1.0 - 1.5	0.4

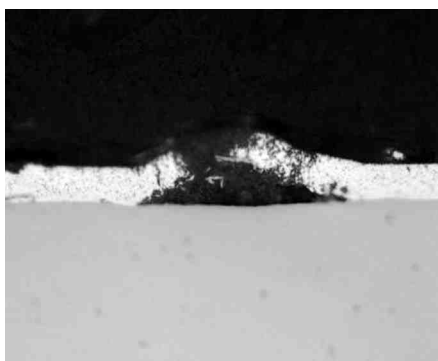


Figure 3—Cross-sections of blistered parts showing separation at the steel/zinc interface. Magnification: 1000X. No etching.

After racking, the plating was not done immediately and, for this reason, the surface of the parts dried. This was inadequate, as it promoted mild corrosion of the surfaces of the parts.

It should be noted that adhesion problems are not always easily detected. The adhesion faults can be localized and, in this case, they were not detected by traditional bending tests. However, they were quickly detected during baking of the zinc-plated parts. Hydrogen atoms, incorporated during pickling and electroplating, tended to migrate and, when they encountered localized adhesion faults, were trapped and recombined into molecular hydrogen. As the molecular hydrogen formed in the localized adhesion faults, the pressure increased, causing blisters,^{3,4} as illustrated in Fig. 4. It is for this reason that, in the present case study, the blistering occurred during the varnish curing process.

Improvements in the pre-treatment process were recommended to the plater, including the continuous removal of the oil layer from the alkaline cleaner bath and racking the parts for plating from the beginning of the production process.

A change in the bath composition and operating conditions can also control the hydrogen uptake during plating. The reduction of the total sodium cyanide-to-zinc ratio will increase the cathodic current efficiency of zinc bath, and therefore reduce the hydrogen

uptake. This was the reason for maintaining a lower ratio than what is specified (Table 1). However, this did not solve the problem as small amounts of hydrogen could still cause blisters if the localized adhesion faults were not eliminated.

Usually, hydrogen embrittlement is a major concern when plating zinc on high-strength steel. During the pickling and plating processes a considerable amount of hydrogen uptake can occur.⁵ It has been recognized that the codeposition of hydrogen can cause failures in high-strength steel, leading to hydrogen damage and causing delayed fracture in service. A hydrogen embrittlement relief treatment after zinc plating is mandatory.

Delayed fracture does not occur in low-strength steel, thus, it is not usual practice to submit this type of steel to hydrogen embrittlement relief treatment. However, the hydrogen uptake occurs regardless of the steel type. In any event, this treatment is necessary when zinc-plated steels are painted or varnished and heat cured. In this case, hydrogen damage occurs through blistering. If the zinc coating exhibits localized adhesion faults, the blisters will be formed at the steel/zinc interface. In turn, if the zinc coating has good adhesion, the blisters can be formed at the zinc/varnish interface. If hydrogen embrittlement relief treatment is not possible, the hydrogen uptake during the zinc plating process must be otherwise hindered. For this purpose, the following is recommended:

- Avoid acid pickling by keeping the parts well oiled before electroplating, in order to avoid rust formation; or adopt mechanical cleaning.
- If pickling is desired, suitable corrosion inhibitors in the acid pickling bath should be used in order to reduce hydrogen uptake.
- Keep the total NaCN-to-Zn ratio as low as possible in order to increase the current efficiency of the plating bath and therefore to reduce the hydrogen uptake during plating. Although this procedure was adopted by the plater, it did not solve the problem.
- Hold the temperature at the upper end of the operational temperature range.
- Increase the caustic soda concentration to the upper end of the concentration range.
- Decrease the current density as much as possible within the operating range.

Case II: Blisters in the zinc-plated die-cast zinc alloy parts

Die-cast zinc alloy (Zamac 5) parts were barrel plated in a cyanide zinc bath. Heavy blistering occurred during plating. Under the same plating conditions, parts made of the same alloy but with a different design showed no blistering. It is important to note that the pre-treatment for Zamac 5 parts is quite different from that for carbon steel. Here, the chemical surface preparation involves the following steps:

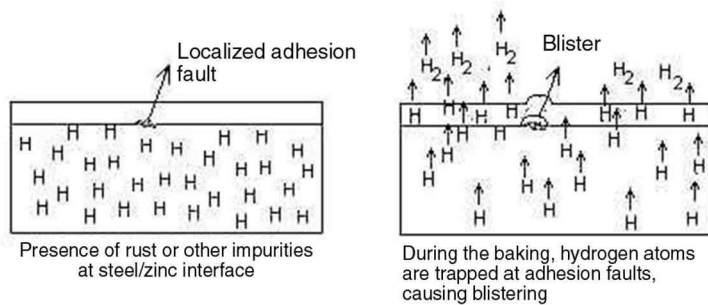


Figure 4—Schematic illustration of blistering a localized adhesion fault at the steel/zinc interface.

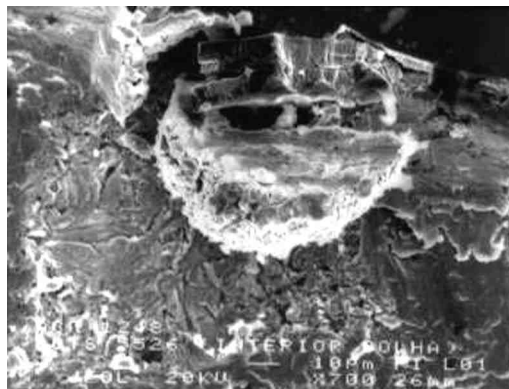


Figure 5—A blister after removal of the zinc coating. The scratches are due to the tool used. Magnification: (Left) 100X; (Right) 700X. No etching.

- Immersion in alkaline cleaning solution;
- Cold water rinse
- Double cold water rinse
- Alkaline water dip (neutralizer)
- Load the parts into the barrel.

The plating was not done immediately and, for this reason again, the part surfaces dried. This procedure was inadequate as it promoted mild corrosion of the parts.

Experimental procedure and results. Both blistered and non-blistered parts were subjected to the following tests and analyses. A blister was examined with a scanning electron microscope after mechanically removing the zinc coating (Fig. 5). It was possible to verify the presence of solid products on the die-cast zinc alloy surface where the blister was removed. These products were subjected to EDS analysis by a spectrometer connected to the SEM. The presence of the following elements was verified: zinc, aluminum, copper, silicon (elements present in the zinc alloy) and oxygen. The latter indicated the presence of corrosion products.

The cross-section of a blistered part was also examined. The surface of the die-casting exhibited several defects, pores (Fig. 6) and small cracks (Fig. 7). In some regions, these defects were very pronounced. At these points, the detachment of the coating from the substrate was observed (Fig. 8). Regions with and without defects were subjected to EDS analysis and the results indicated a higher oxygen content in the defects.

The cross-section of parts with a different design and which showed no blisters was also examined with the SEM. No defects were observed near the substrate/coating interface (Fig. 9).

The barrel cyanide zinc-plating bath was also analyzed. Hexavalent chromium contamination of the bath was not detected. The results obtained and the required composition range of the bath are presented in Table 2.

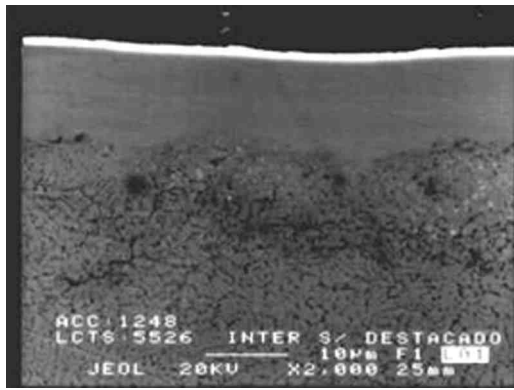


Figure 6—Cross-section of a blistered part, showing high porosity in the die-cast alloy. Magnification: 2000X. No etching.

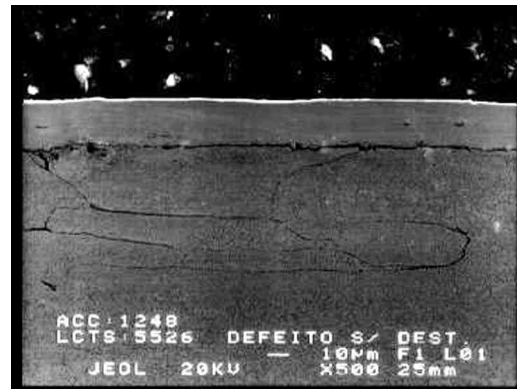


Figure 7—Cross-section of a blistered part showing cracks in the die-cast alloy. Magnification: 500X. No etching.

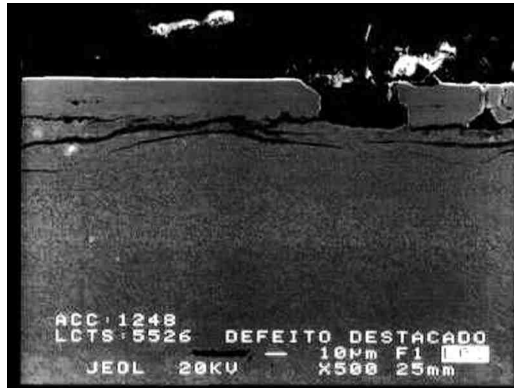


Figure 8—Cross-section of a blistered part. Cracks in the die-cast alloy caused the detachment of the coating. Magnification: 500X. No etching.

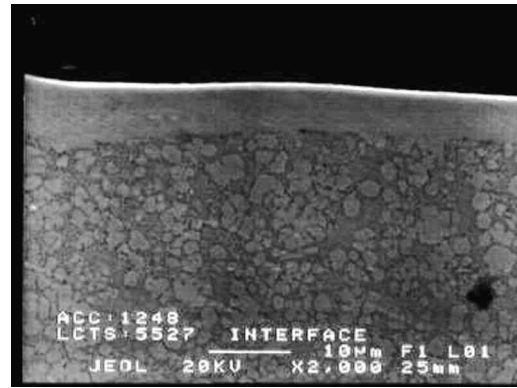


Figure 9—Cross-section of parts with a different design which showed no blisters. No defects were observed on the zinc alloy surface. Magnification: 2000X. No etching.

As with the carbon steel parts, the entire zinc plating process was inspected. The parts were found to be dried after pre-treatment, placed in the barrel and electroplated.

Discussion. The blistering arose from hydrogen gas trapped at the die-cast zinc alloy/zinc interface. As with the steel parts, this occurred at weakly bonded

areas of the zinc coating. In this case, defects on the die-cast zinc alloy surface were the cause of the adhesion faults.

After the pre-treatment steps, when the parts were dried, chemicals from cleaning processes probably remained on the surface defects of the die-cast alloy and caused corrosion. Later, during plating, the plated zinc could not adhere to the voluminous corrosion products, causing the trapping of molecular hydrogen and thus causing blister formation.

If the zinc die-cast parts had not been dried before barrel plating, the blistering intensity at the very least would be lower, and this would suggest other causes of the problem. The presence of superficial defects like porosity and microcracks on the substrate surface can cause atmospheric moisture absorption by capillary effects, leading to the occurrence of corrosion in the defects. This can occur between the casting and plating processes, that is, during storage and transport. Thus, to hinder blistering of the zinc die-cast

Table 2

Composition of the Barrel Cyanide Zinc Bath

Component	Composition	
	Required range, g/L (oz/gal)	Analysis, g/L (oz/gal)
Zinc (Zn)	15.0 - 30.0 (2.0 -- 4.0)	16.9 (2.2)
Total sodium cyanide (NaCN)	50 ± 60 (6.7 -- 8.0)	56.4 (7.5)
Caustic soda (NaOH)	150 (20.0)	115.9 (15.5)
Sodium carbonate (Na ₂ CO ₃)	Not specified	13.8 (1.8)
Ratio (Total NaCN/Zinc)	2.0 - 2.5	3.3

parts, it is recommended that the surface quality of the die-castings be improved. Further, drying of parts after cleaning should be avoided.

Conclusion

The blistering in the two case studies was caused by different factors. The blistering of the zinc-plated steel parts arose from inadequate pre-treatment, while the blistering of the zinc-plated die-cast parts arose from poor quality of the substrate surface.

Acknowledgment

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Solvents for Ultrasonic Cleaning continued from page 47

by Bogdan Niemczewski*

Table 2
Average Electrical Power Drawn by the Generators
in the Five Solutions Studied

Solvents	Average electrical power, W Cleaner frequency, kHz		
	25 (A)	40 (B)	40 (C)
NMP	382	423	817
Carbitol	357	364	707
Methyl Carbitol	345	385	739
Clenvex AS 105	368	334	655
Freon TE	430	300	582

about the latter material owing to its being possibly hazardous to human health. Hydrocarbon solvent mixtures are not recommended by the author for use in ultrasonic cleaning.

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Conclusions

The initial requirement to be met by a solvent used for cleaning is, of course, good solubility for the given impurity. Having met this requirement and using a cleaner operating at about 40 kHz (and not at 25 kHz), three of the solvents tested in this work may be successfully used in ultrasonic cleaning, N-methylpyrrolidone (NMP), carbitol and methyl carbitol. However, there are serious reservations