Protective Action of Chromate Conversion Coatings

By R. Šarmaitis and E. Juzeliūnas

The results of investigating the corrosion resistance of zinc in an aerated 5 percent NaCl solution with a pH of 7 show that colorless and iridescent chromate conversion coatings sustain a decrease in the cathodic process, i.e., the reduction of oxygen. Olive chromate coatings also retard the rate of partial anodic dissolution, The chromate coatings had no effect on the value of the anodic Tafel constant. A Cr^{6+} compound in the coating increases the initial rate of zinc oxidation. Visual changes in chromated surfaces originate by the corrosion of zinc. Black spots and stains are indicators of uniform corrosion, whereas white spots are the result of crevice corrosion.

Zinc surfaces are chromated in acid solutions that contain Cr^{6+} and/or Cr^{3+} to increase resistance to corrosion. Chromate coatings are widely used for passivating protective and decorative zinc elect redeposits. Investigation of the protective properties of conversion coatings exposed to a neutral electrolyte has both practical and theoretical aspects. The density of the corrosion current (i_k) is a measure of the protection against corrosion supplied by the coating. Measurements of the voltage and current assist clarification of the mechanism of the protective action.

The purpose of our study was to investigate the protective properties of chromate conversion coatings (CCC) containing different amounts of Cr^{6+} when zinc is exposed to a neutral, aerated sodium chloride solution.

Experimental Procedure

A 5 percent NaCl solution with a pH of 7, prepared with analytical grade, high-purity salt and distilled water, was the corrosion medium. The pH was adjusted with dilute HCl solution. The working electrode was made of high-purity (99.998 percent) zinc with an exposed area of 1 cm’, pressed into a Teflon housing. Before each experiment, the zinc surface was abraded with a fine emery paper surfaced with 1-2 µm abrasive particles, wiped with filter paper, degreased with Vienna lime and rinsed in distilled water. To apply a conversion coating, the specimen was immersed in a chromating solution for 30 see, rinsed in distilled water and dried for 24 hr at room temperature. The reference electrode was prepared in the same manner. Its potential was monitored by measurements with a silver chloride electrode and converted to the hydrogen electrode scale.

Galvanostatic measurements were made with an automated laboratory unit that provided computer control and graphically displayed experimental data, which could be printed by an alphanumeric printer. During measurements, the ohmic drop was automatically compensated.

In order to determine polarization resistance (R_p), we obtained potentiodynamic current-voltage relationships near the corrosion potential (E_k). A polarographic analyzer with a recording unit was used for this purpose. The potential sweep rate was set at 0.5 mV/sec while measurements were made at steady state conditions.

Colorless, iridescent and dark olive chromate coatings were applied in solutions prepared with proprietary salts. Total salt concentrations are given in the table. To determine the Cr^{6+} content, the coatings were dissolved for 30 sec in a 1M solution of NaOH at 65 “C and the Cr^{6+} was established by an iodometric titration using 0.005 M sodium thiosulfate. The table shows the amounts of Cr^{6+} found in each coating.

The microstructure of chromated zinc surfaces was studied by microprobe X-ray analysis using a microanalyzer.

Results and Discussion

Figs. 1-4 show quasi-stationary polarization values set at galvanostatic current pulses of about 10 msec, but decreasing with increasing polarization current. The slope (b_a) of the Tafel plots of chromated zinc at low polarization levels have the same value (0.04 V). The anodic Tafel plot for non-chromated zinc (Fig. 4) also has the same slope. The value of 0.04 V for b_a is typical for the zinc electrode’” and consistent with the multi-step charge transfer with slow splitting-off of the second electron. Therefore, it can be suggested that the chromate conversion coatings do not affect the mechanism of the anodic dissolution of zinc in the low polarization range.

The data in Figs. 1-2 show that changes in current-voltage characteristics occur, depending on exposure time. If the coating contains no Cr^{6+} (Fig. 3), there is no significant change with increasing exposure time from 1.5 min to 5 hr. However, values of i_k obtained by extrapolating the lines in Figs. 1 and 2 decreased with increased exposure time for coatings containing Cr^{6+}.

Because of the large difference between the standard potentials of the Zn/Zn^{2+} and O_2/OH^- electrodes the corrosion of zinc under the conditions we employed should occur at a limiting diffusion flow of oxygen. This behavior should also occur for chromated zinc because the conversion coatings have no substantial effect on E_k (Figs. 1-4). Because the standard potentials of the Zn/Zn^{2+} and Cr^{3+}/Cr^{6+} electrodes also are large, the superpositioning of the Cr^{b+}—Cr^{3+} process is possible in the presence of Cr^{6+}. This

Amount of Cr^{6+} Found in Each Coating

Coating	Chromating bath cone. of salts, g/L	pH	Cr^{6+} content of coating, mg/m^2
Colorless	18-26	2-3	None found
Iridescent	50-70	1.6-2.0	32
Dark olive	60-90’	2.7-3.1	200

‘This solutlon also contained 35-45 g/L of CrO_3 and 35-45 g/L of NaCOOH.

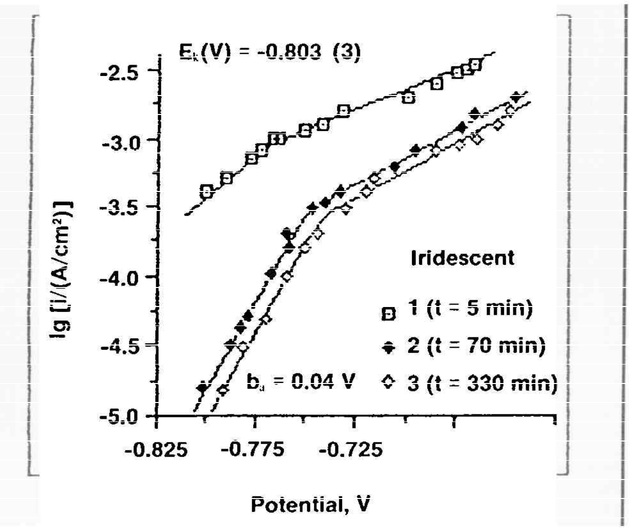

Fig. 1—Current-voltage characteristics of zinc with an iridescent chromate conversion coating exposed in 5 percent NaCl solution for 5,70 and 330 min.

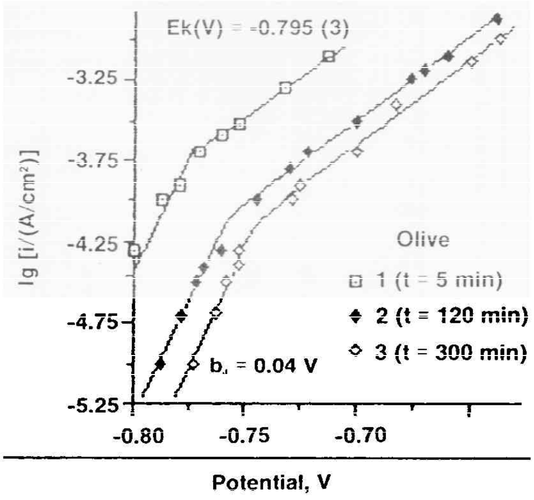

Fig. 2—current-voltage characteristics of zinc with an olive chromate conversion coating ex-posed in 5 percent NaCl solution for 5, 120 and 300 min.

reduction process can cause an increase in ik, at first (Figs. 1-3). However, ik must fall when the amount of Cr^{6+} decreases. It should be noted that an additional reduction of Cr^{6+} can also explain the "self-healing" effect observed in practice when a chromate coating recovers in mechanically damaged locations. Deposition of insoluble Cr^{3+} compounds on active (mechanically damaged) spots results from the increase in corrosion current, i_k, at the initial stage of corrosion when Cr^{6+} is present in the coating. "Self-healing" may be observed at this time.

The degree of corrosion-rate acceleration by the Cr^{6+}—Cr^{3+} process must depend on the mobility of Cr^{6+} in the coating. This supposition was confirmed by experimental data obtained with newly formed chromate coatings, which would be expected to have Cr^{6+} ions in a more mobile state than dried coatings. The current-voltage relationships for newly formed iridescent coatings proved to be much higher, initially, than those shown in Fig. 1.

Because of the relatively long time required to obtain current-voltage data, changes in ik are difficult to follow by the procedure used during our study. A more suitable approach would be to establish polarization resistance ($R_p = \Delta E/\Delta i$) as ΔE approaches zero. For a limiting diffusion flow of oxidant, the relationship between R_p and i_k is as follows:[3]

$$i_k = b_a/(2.303\ R_p)$$

According to ik calculations frOm measured values of R_p, it follows that the zinc corrosion rate without a chromate coating drops in time to a limiting value that likely is related to the accumulation of corrosion products on the surface. The rate-retarding effect of such products is associated with the prevention of oxygen access to the zinc surface.[4] The initial value of ik for chromated zinc with Cr^{6+} in the coatings is close to the value for non-chromated zinc, but drops sharply to a limiting value. On the other hand, the zinc dissolution rate in the absence of Cr^{6+} decreases negligibly. Thus, it is suggested that the decrease in the oxidation rate of zinc with a Cr^{6+}-containing chromate coating is determined, first of all, by the presence of Cr^{6+}, rather than closing of pores by zinc corrosion products as noted previously.’

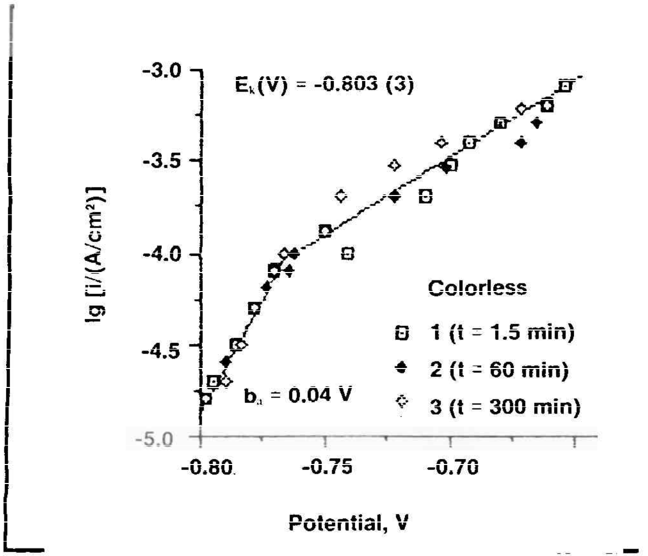

Fig. 3—Current-voltage characteristics of zinc with a colorless conversion coating exposed in 5 percent NaCl for 1.5, 60 and 300 min.

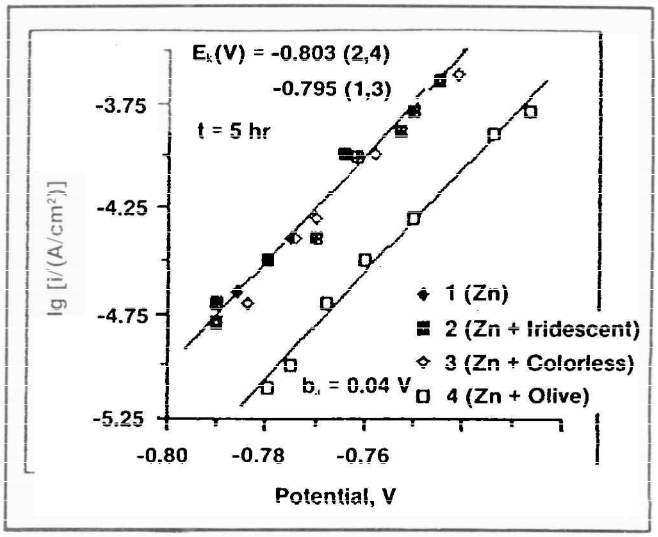

Fig. 4—Comparison of current-voltage characteristics of zinc with ar without chromate conversion coatings exposed 5 hr in 5 percent Na solution.

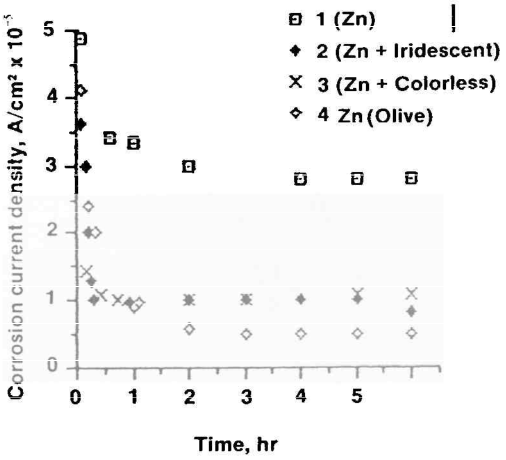

Fig. 5—Variation of corrosion current density with time in 5 percent NaCl determined from polarization resistance measurements for Zn and Zn with colorless, iridescent and olive conversion coatings.

Fig. 6- Corroded surface of zinc with iridescent chromate coating after exposure in aerated (neutral) 5 percent NaCl solution for 106 hr. Magnification 1 cm = 150 µm.

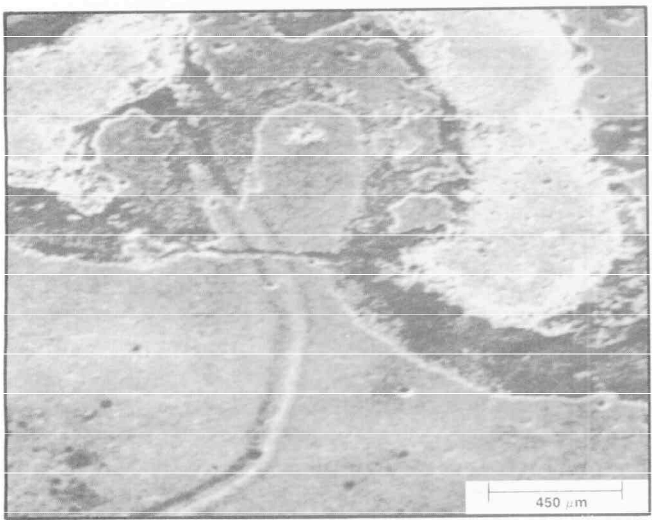

Fig. 7—The area in Fig. 6 after dissolution of the corrosion products with 0.2M CrO_3.

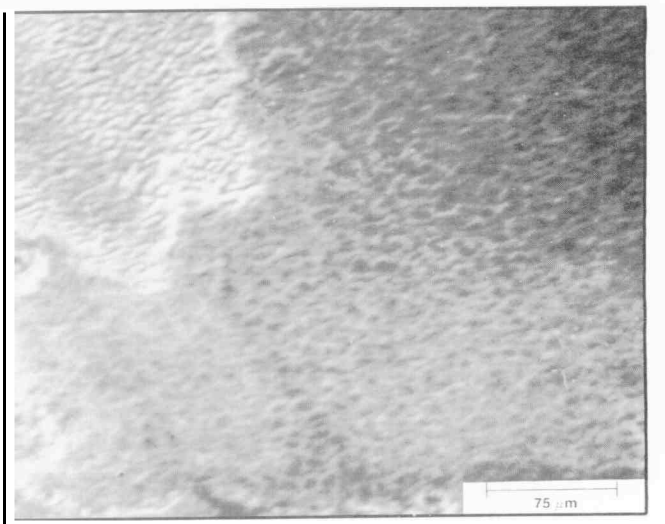

Fig. 8-Surface of zinc with an iridescent chromate coating after exposure in aerated (neutral) 5 percent NaCl for 106 hr and dissolution of corrosion products from a black slain. Magnification: 1 cm = 25 µm.

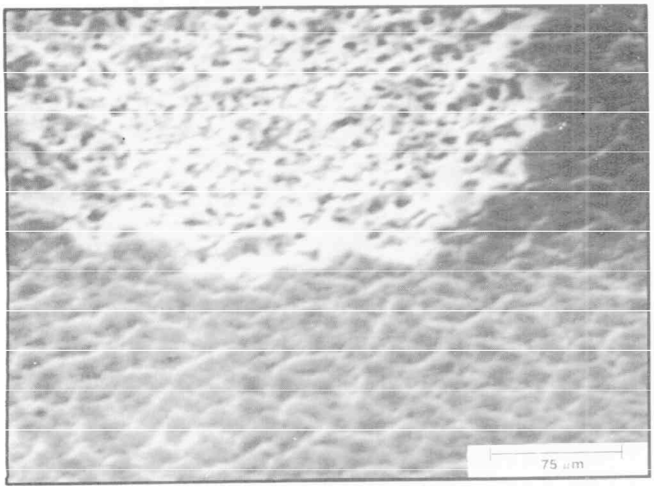

Fig. 9—Surface of zinc with an iridescent chromate coating after exposure in an aerated (neutral) 5 percent NaCl solution for 106 brand dissolution Of corrosion products from a white spot. Magnification: 1 cm = 25µm.

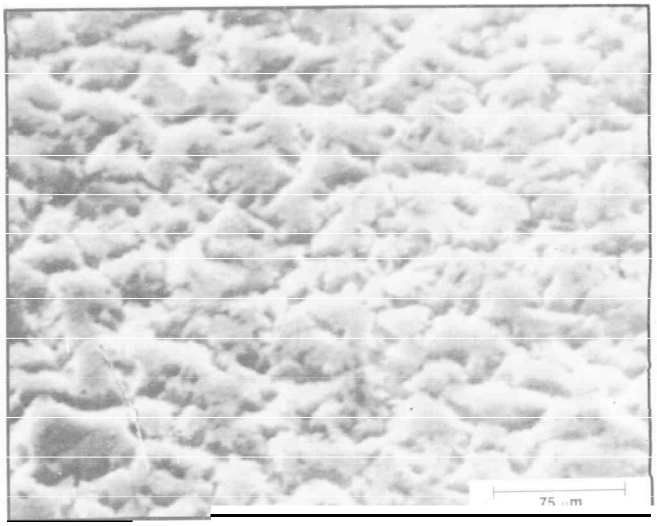

Fig. 10—SEM photograph of zinc with an iridescent chromate coating. Magnification: 1 cm = 25 µm.

Fig. 11—SEM photograph of zinc with an olive chromate coating. Magnification: 1 cm = 25 µm.

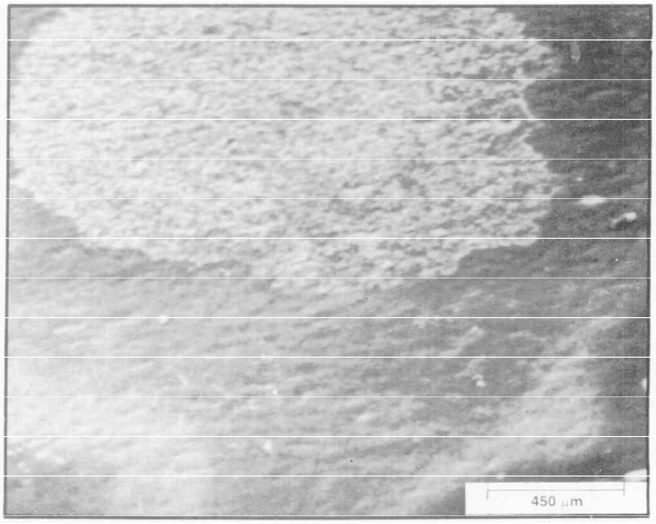

Fig. 12—Black spot on zinc coated with an iridescent chromate film and exposed in an aerated (neutral) NaCl solution. Magnification: 1 cm = 150 pm.

The corrosion-inhibition efficiency of our coatings may be expressed by the degree of protection (W):

$$W = 100 \quad (i_{k,Zn} - i_k)/i_{k,Zn}$$

where i_k and $i_{k,Zn}$ are corrosion current densities for zinc with and without a conversion coating, respectively. From the data in Fig. 5, limiting values of corrosion-inhibition efficiency is 60 percent for the colorless and iridescent chromated zinc samples and 80 percent for the olive-colored chromated zinc.

Fig. 4 shows that current-voltage curves obtained after 5 hr of immersion of the colorless and iridescent chromated zinc electrodes virtually coincide with the 5-hr immersion data for non-chromated zinc. Thus, these chromate coatings have no substantial effect on the partial dissolution of zinc, whereas their protective properties are determined by the retardation of cathodic process, i.e., oxygen access to the metal surface. Fig. 4 also shows that the dark olive chromate coating reduces the rate of partial anodic dissolution.

Our results agree with a previous report’ on the role of conversion coatings, which concludes that such coatings mainly reduce the rate of oxygen discharge and have a significantly smaller effect on the rate of anodic dissolution. However, results in the cathodic region should be interpreted cautiously because there may be a superposition of the discharge process of both zinc corrosion products and the hydroxides produced on the surface during the chromating process.

Study of the microstructure of chromated zinc surfaces has shown that visual changes during corrosion tests can be attributed to corrosion of the zinc substrate (Figs. 6 and 7). Black spots and stains are indicators of uniform corrosion whereas white spots indicate crevice corrosion (Figs. 8 and 9).

All kinds of chromated and non-chromated zinc surfaces exhibit local areas of zinc dissolution at individual anodically active spots. Chromate coatings reduce the anodic activity of zinc surfaces, but iridescent coatings create fewer sites than colorless chromate coatings (Figs. 10 and 11).

In most cases, the corrosion process begins in anodically active spots (Fig. 12) with the formation of a fine dispersion of zinc hydroxide (black spots and stains). Depending on the corrosive environment, the zinc hydroxide is transformed into hydroxychloride, hydroxysulfate or hydroxycarbonate compounds of zinc (Figs. 13 and 14). The resistance of these compounds to dissolution in specific solutions determines the corrosion resistance of the zinc. Their influence is associated with a decrease in the active surface that supports the cathodic process of oxygen reduction and the anodic process of zinc ionization.

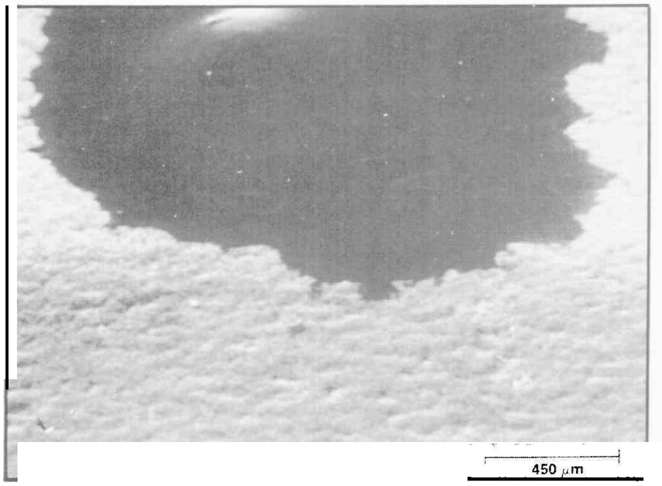

Fig. 13—The area in Fig. 12 after exposure for 10 hr.

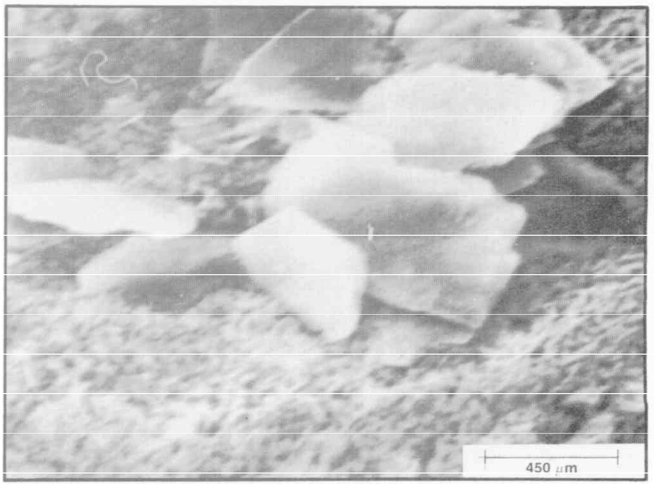

Fig. 14—The area in Fig. 12 after exposure for 43 hr.

Data on the protective characteristics of zinc obtained in a neutral solution do not necessarily coincide with the results of long-term exposure or salt spray tests. For example, tests in a salt spray chamber have shown that the first appearance of white corrosion products is proportional to the amount of Cr^{6+} in the chromate coating,[6,7] whereas Fig. 5 indicates that colorless and iridescent coatings containing different amounts of Cr^{6+} exhibit the same protection from white “rust”.

Conclusions

The anodic Tafel constant for zinc with colorless, iridescent and olive chromate conversion coatings in naturally aerated, 5 percent NaCl solution is 0.04 V, which is the same as the value for zinc without a conversion coating. Cr^{6+} compounds in the conversion coating accelerate the oxidation of zinc during the initial stage of immersion in a NaCl solution.

Colorless and iridescent chromate coatings protect zinc by decreasing the cathodic reaction, i.e., the reduction of oxygen. Olive chromate coatings also decrease the rate of partial anodic dissolution of zinc.

Visual changes in chromated zinc surfaces during corrosion tests are the consequence of zinc corrosion. Black spots and stains are indicators of uniform corrosion whereas white spots are the result of crevice corrosion.

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