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# Electrochemical Impedance Spectroscopy Study of Corrosion of Painted Cold- Rolled and Electrogalvanized Sheet Steel for Automotive Use

By M. Dattilo, R. B. Prater, and V. R. Miller

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**Report of Investigations 9324**

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## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree celsius	Hz	hertz
cm	centimeter	kHz	kilohertz
cm <sup>2</sup>	square centimeter	μF	microfarad
cm <sup>3</sup>	cubic centimeter	μm	micrometer
deg	degree	mm	millimeter
ft	foot	mV	millivolt
g/m <sup>2</sup>	gram per square meter	ohm·cm <sup>2</sup>	ohm square centimeter
h	hour	V	volt

# ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDY OF CORROSION OF PAINTED COLD-ROLLED AND ELECTROGALVANIZED SHEET STEEL FOR AUTOMOTIVE USE

By M. Dattilo,<sup>1</sup> R. B. Prater, Jr.,<sup>2</sup> and V. R. Miller<sup>3</sup>

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## ABSTRACT

The U.S. Bureau of Mines has been conducting research on the use of waste-derived zinc as a partial replacement for pure zinc in the electrogalvanizing process. The end product of this process is automotive sheet, which has enhanced cosmetic protection over previously used cold-rolled (CR) steel. In this study, primer-coated specimens of CR and electrogalvanized (EG) steel were subjected to the on-vehicle environment and monitored periodically by electrochemical impedance spectroscopy (EIS) during immersion in 1M NaCl solution. The results of these tests were compared with immersion-only conditions. Scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) techniques were also used to evaluate the corrosion processes and compare them with atmospheric exposure specimens. EIS was found to measure the corrosion associated with on-vehicle exposure, thus providing an excellent screening technique for evaluation of the performance of EG automotive sheet steel.

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<sup>1</sup>Research chemist.

<sup>2</sup>Metallurgist.

<sup>3</sup>Group supervisor.

Rolla Research Center, U.S. Bureau of Mines, Rolla, MO.

## INTRODUCTION

During the early 1970's, one-side EG steel became available for automotive corrosion protection (1).<sup>4</sup> By the early 1980's, automakers around the globe had begun using this material to enhance the cosmetic corrosion resistance of their products, and steel manufacturers responded with plans for increased production (1).

Over the last several decades, the U.S. Bureau of Mines has investigated the use of oxidized zinc present in waste sources as a partial replacement for pure zinc in industrial processes. In the early 1980's, this was extended to electrogalvanizing; and in December 1983, a pilot-scale test showed that it was feasible for steel wire (2). The large tonnage of steel process furnace dusts and the associated zinc contained in them has naturally led to a study of extraction and process application to steel sheet.

During this time, the use of impedance spectroscopy to measure corrosion rates of organically coated metals was being developed (3-4). Classical quality control normally includes such methods as salt spray, SO<sub>2</sub> fog, cyclic tests such as the Volvo scab test, atmospheric exposure, and test tracks (5). All of these methods are subjective at best, and the first two do not relate to the real environment. Because the corrosion process is electrochemical in nature, an electrochemical technique seems most applicable.

Direct-current techniques, however, are inadequate because of the very high interfacial resistances of these coatings. Thus, impedance, being an alternating current, low perturbation technique, has been found to be much more amenable (3-4).

In this study, primer-coated specimens of CR and EG steel were compared for their corrosion properties by EIS. Results of several other investigators with polymer- and paint-coated steel showed the applicability to these materials (3-4). Three test sets of painted CR and EG steel with scribe cuts to the substrate metal were placed on-vehicle for 1-year exposure and periodically monitored by removing them from the vehicles and performing EIS during immersion in 1M NaCl solution. These specimens were compared with immersion-only conditions and with specimens that were never immersed during their atmospheric exposure.

The study was initiated to determine if an electrochemical technique could be used to monitor the corrosion performance of EG specimens used for automotive purposes. In future investigations, the performance of waste-derived materials could then be evaluated by such a method.

## EXPERIMENTAL WORK

### MATERIALS AND EQUIPMENT

Primer-painted and unpainted aluminum killed drawing quality steel was obtained from Inland Steel Corp., East Chicago, IN. The coating weight of zinc for EG specimens was 105 g/m<sup>2</sup> on one side. The steel thickness was nominally 0.762 mm. A proprietary phosphate treatment and electrocoat gray primer were applied commercially and ranged from 30 to 35 μm in thickness.

The electrochemical cells were constructed of 1.9-cm-thick acrylic sheet with a volume of 225 cm<sup>3</sup>. The primer-coated or uncoated specimens formed the floor of the cell, and the exposed area was 25 cm<sup>2</sup>. A platinum gauze electrode measuring ~4 by 2 cm was used as a counter electrode. A saturated calomel electrode (SCE) in a bridge tube with Vycor<sup>5</sup> frit acted as reference. A 0.1-μF capacitor connected by a platinum wire parallel with the SCE was used to avoid phase shifts of the potentiostat

at high frequencies. Molar NaCl solution (American Chemical Society (ACS) reagent grade) was used as immersion medium. Temperatures were ambient, 23° to 27° C.

An M368 Princeton applied research system was used to obtain EIS. This system consists of a potentiostat (model 173), a lock-in amplifier (model 5206), and an Apple IIe computer. The computer controlled the experiments, gathered the data, and plotted figures according to contained formats. Measurements were made for three separate frequency ranges. High frequencies from 20 kHz down to 10 Hz were measured by the lock-in amplifier. Lower frequencies were measured by the fast fourier transform (FFT) technique in two experiments. The 0.1- to 11-Hz range (20 frequencies) and the 0.001- to 0.1-Hz or 0.005- to 0.5-Hz range were obtained by use of a white noise-type spectrum.

Data were normally plotted as Bode phase and magnitude diagrams. Amplitudes for the three ranges of frequency were 18-mV peak for the lock-in frequencies and 20-mV peak for the FFT ranges. Total time for the measurement of all frequencies was about 2.5 h.

<sup>4</sup>Italic numbers in parentheses refer to items in the list of references at the end of this report.

<sup>5</sup>Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

## PROCEDURE

CR and EG steel painted specimens were scribed to the base metal in the shape of an X. Each crossmark measured  $\sim 2.54$  cm and was  $\sim 0.1$  cm wide giving an area of exposed metal measured at  $\sim 0.52$  cm<sup>2</sup>. The edges and back of all exposed samples were protected with electroplating tape. Three types of exposure conditions were evaluated for comparison. The first type was on-vehicle exposure for about 3 months at a time followed by removal of the specimens and measuring the EIS spectra after immersion in 1M NaCl solution for about 2 days. Three separate test sets were monitored on three vehicles. These specimens were placed on the grille and were designated as sets 1 through 3 in the text. Mileage accrued during exposure of  $\sim 1$  year was as follows: set 1—383 days, 8,245 miles; set 2—382 days, 3,692 miles; and set 3—382 days, 8,800 miles.

Driving conditions for the three vehicles were fairly similar. The set 1 vehicle was driven over State highways

approximately twice a week for a distance of 60 miles one way to a lead mill. Set 2 was exposed to local trips and occasional trips to a major city about 100 miles away. Set 3 was driven locally and to the St. Louis, MO area ( $\sim 100$  miles) occasionally and on other trips of a few hundred miles. All were more or less exposed to lower Midwest driving conditions where salt was used on the roads in winter.

The second exposure type was immersion only. These were repeated so that the results could be verified.

The third exposure type was atmospheric. Specimens were vertically oriented about 5 ft from the ground and were not protected from precipitation. A scribed set of painted specimens was exposed for 1 year and evaluated by SEM and EDX. Another set was unpainted, which was exposed 1.5 years and was tested by immersion after the exposure. These results were compared with SEM and EDX on set 3 of the on-vehicle specimens and one of the immersion-only sets after 34-day immersion.

## RESULTS AND DISCUSSION

Many painted specimens were tested without the scribe mark, but since industrial testing uses this method, only scribed specimens will be discussed in this report. By scribing the painted steel, the galvanic couple was exposed for the EG specimen, and the steel was exposed on the CR samples.

The impedance data obtained in this study were displayed as Bode plots ( $\phi$ ). The Bode magnitude plot displays the  $\log |Z|$  (log impedance modulus) versus  $\log f$  (log frequency), and the Bode phase plot shows  $\theta$  (the phase angle) versus  $\log f$ , where  $|Z|$  and  $\theta$  are defined as

$$|Z| = [(Z')^2 + (Z'')^2]^{1/2} \quad (1)$$

$$\text{and} \quad \theta = \tan^{-1} \left( \frac{-Z''}{Z'} \right) \quad (2)$$

$Z'$  is the real component of the impedance, and  $Z''$  is the imaginary component of the impedance. The advantage of this procedure is that the data for all measured frequencies can be shown, and a wide range of impedance values can be displayed. A complete description and review of impedance plot methods used for corrosion of painted metals have been given by Walter ( $\phi$ ).

Normally, if the corrosion process involves anodic dissolution of a metal, the corrosion rate is determined by

$$i_{\text{corr}} = \frac{B}{R_p} \quad (3)$$

where the parameter  $B = \frac{b_a b_c}{2.3(b_a + b_c)}$  is determined by the anodic ( $b_a$ ) and cathodic ( $b_c$ ) tafel slopes, and  $R_p$  is the polarization resistance.  $R_p$  is defined as

$$R_p \equiv \lim_{f \rightarrow 0} Z' \quad (4)$$

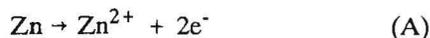
and this value is corrected for solution resistance. In cases where the cathodic process is diffusion controlled,

$B = \frac{b_a}{2.3}$  since  $b_c \rightarrow \infty$ . However, when a corrosion product coating exists on the corroding metal, these equations do not apply. This study has shown that these conditions exist; that is, a corrosion product film exists, and that  $R_p$  may not show the corrosion rate. However, other investigators have shown that the corrosion rate of steel is  $\sim 10$  times that of zinc in the atmosphere (7-8).

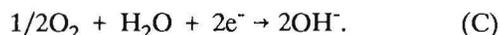
In this study, the value of  $R_p$  cannot be determined in most cases. The reason is that the values of  $Z'$  as  $f \rightarrow 0$  do not relax toward the  $Z'$  axis. This condition exists because of the Warburg impedance ( $\phi$ ), which indicates a diffusion layer of infinite thickness in the case of the CR steel specimens. For this reason, the  $\log |Z|$  values were used to relate the corrosion of EG and CR steel.

The corrosion processes measured for zinc and steel were as follows:

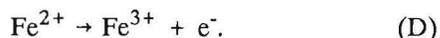
anodic -



and cathodic -



The cathodic process (reaction C) can be considered to be under diffusion control and is normally the rate controlling process. However, the existence of ferrous ions adds another important reaction for steel,



This adds to the reactions for iron and increases the complexity of the corrosion process for steel.

### ON-VEHICLE EXPOSURE

Because it approximates actual service conditions as closely as possible, the on-vehicle environment was the most important exposure type evaluated. The CR specimen from set 2, when removed from the on-vehicle environment and immersed in molar NaCl solution, yielded the Bode magnitude and phase plots shown in figure 1. The Bode magnitude plot in figure 1A has the  $\log |Z|$  as the abscissa and the  $\log f$  as ordinate. The Bode phase plot in figure 1B shows the phase relationship between the real and imaginary components.

Figures 2A and 2B show the comparable spectra from the EG specimen of set 2 over the entire test period. It can be seen from the magnitude diagrams (figs. 1A and 2A) that at low frequencies (left side) the EG specimen had greater values than the CR specimen. Also, as time of exposure increased, the CR specimen displayed lower values of  $\log |Z|$ , whereas the values for the EG specimen increased. This indicates that the EG specimen was corroding more slowly than the CR specimen and there was a divergence over time of exposure.

Visual observation of the specimens during exposure showed initially that the CR specimen began to rust in the scribe almost immediately. However, the EG specimen did not. Here two different metals, iron and zinc, are compared. Iron, of course, has a variety of colored oxidation products, which zinc does not have. After several months exposure, some small red spots appeared in the scribe on the EG specimens, but the CR specimens

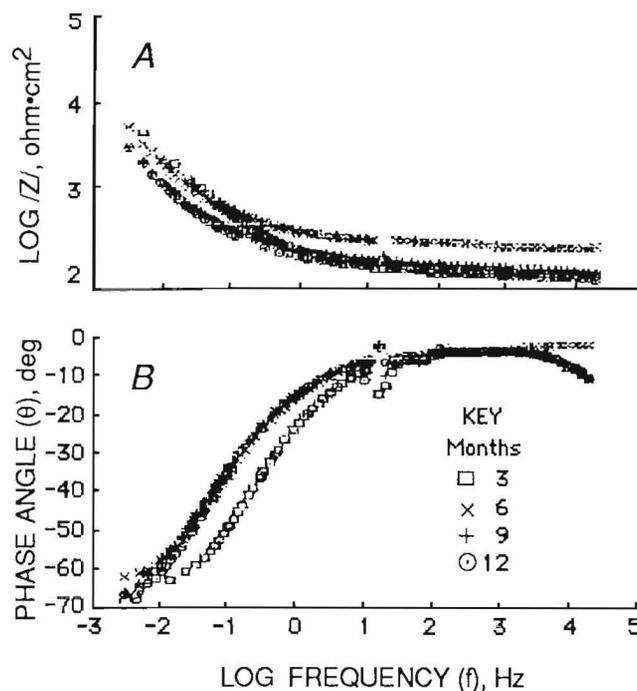


Figure 1.—Bode plot for cold-rolled steel specimen over 1-year on-vehicle exposure. A, Bode magnitude plot ( $\log |Z|$  versus  $\log f$ ); B, bode phase plot [phase angle ( $\theta$ ) versus  $\log f$ ].

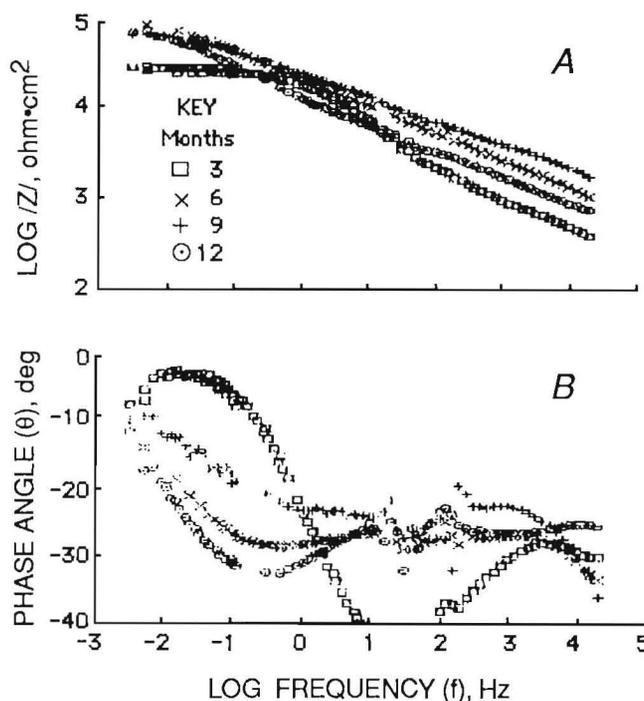


Figure 2.—Bode plot for electrogalvanized specimen over 1-year on-vehicle exposure. A, Bode magnitude plot ( $\log |Z|$  versus  $\log f$ ); B, bode phase plot [phase angle ( $\theta$ ) versus  $\log f$ ].

showed much greater coverage of corrosion products in the scribe and raised paint areas near the scribe.

The shapes of the Bode phase and magnitude plots relate to the mechanisms of corrosion (6). There are obvious differences in the CR and EG data in figures 1 and 2, and they relate to the difference in corrosion mechanisms for zinc and iron.

The data in table 1 show how the difference in values of the low-frequency impedance modulus between the EG and CR specimens did not remain uniform with exposure time. Values of the open-circuit potential (OCP) or rest potential also changed, but not necessarily in a uniform way. Predominantly, the OCP values became more positive for the EG specimens and more negative for the CR specimens with exposure time.

When comparing the data at the lowest frequency for sets 1 through 3, the following result was calculated after a 1-year exposure:

Set 1:  $|Z|$  for EG =  $3.22 \times |Z|$  for CR.

Set 2:  $|Z|$  for EG =  $11.6 \times |Z|$  for CR.

Set 3:  $|Z|$  for EG =  $10.4 \times |Z|$  for CR.

In all cases, the values of the impedance were larger for the EG specimen than for the CR specimen. However, the first set does not show an order of magnitude difference in the modulus as do sets 2 and 3. In fact, the difference in  $\log |Z|$  between CR and EG specimens shrinks after the 190-day exposure measurements as seen in table 1 for set 1. The reason for this was, that after 190 days of on-vehicle exposure, the scribed specimens for set 1 were immersed for 7 days rather than the normal 2 days used for all other measurements. The data are shown graphically in figure 3. For the EG specimen in figure 3A, the impedance shows an increase over the entire frequency range through 7 days. Less change in  $\log |Z|$  values was obtained for the CR specimen at low frequencies. The Bode phase plots in figures 3B and 3C show some variability with time during the immersion of these specimens.

During this 1-week immersion, the OCP for the CR specimen began at  $\sim -430$  mV and ended at  $-700$  mV, whereas the EG specimen's OCP began at  $-880$  mV and moved to  $-991$  mV. Because of the results of immersion after further on-vehicle exposure, it can be concluded that immersion time had a more deleterious impact upon the EG specimen than on the CR specimen. This will be fully understood after discussing the immersion-only specimens.

Table 1.—Impedance data for on-vehicle specimens

Time of exposure, days	OCP, V vs SCE	Frequency (f), Hz	Z' ohm·cm <sup>2</sup>	-Z'' ohm·cm <sup>2</sup>	Log  Z
SET 1					
CR:					
98 . . . .	-0.480	0.005	3,744	6,051	3.852
190 . . .	-600	.001	12,880	18,920	4.36
190 . . .	-600	.005	2,175	5,635	3.781
281 . . .	-616	.001	8,711	18,750	4.315
281 . . .	-616	.005	2,017	5,113	3.740
383 . . .	-594	.001	5,419	10,370	4.068
383 . . .	-594	.005	1,522	3,061	3.534
EG:					
98 . . . .	-1.029	.005	23,560	8,094	4.396
190 . . .	-.982	.001	79,810	23,620	4.920
190 . . .	-.982	.005	53,410	24,850	4.770
281 . . .	-1.017	.001	25,610	5,967	4.420
281 . . .	-1.017	.005	22,570	4,181	4.361
383 . . .	-.979	.001	36,950	7,120	4.576
383 . . .	-.979	.005	29,880	9,260	4.495
SET 2					
CR:					
105 . . .	-0.590	0.005	2,237	4,704	3.717
189 . . .	-.558	.001	7,401	10,480	4.180
189 . . .	-.558	.005	1,871	3,387	3.588
286 . . .	-.613	.001	3,618	7,644	3.927
286 . . .	-.613	.005	1,107	2,205	3.392
382 . . .	-.631	.001	3,864	7,294	3.917
382 . . .	-.631	.005	983.5	2,129	3.370
EG:					
105 . . .	-1.007	.001	34,760	9,823	4.558
105 . . .	-1.007	.005	27,750	3,308	4.446
189 . . .	-.981	.005	88,590	21,970	4.960
286 . . .	-1.014	.001	78,090	14,670	4.900
286 . . .	-1.014	.005	70,680	11,580	4.855
382 . . .	-.959	.001	94,600	13,910	4.981
382 . . .	-.959	.005	72,770	22,820	4.882
SET 3					
CR:					
189 . . .	-0.616	0.01	864.1	1,833	3.307
283 . . .	-.597	.005	1,327	1,885	3.363
382 . . .	-.621	.001	2,927	5,857	3.816
382 . . .	-.621	.005	1,081	1,729	3.309
EG:					
189 . . .	-.958	.01	82,080	32,220	4.945
283 . . .	-.981	.005	39,510	14,760	4.625
382 . . .	-1.012	.001	67,740	8,126	4.834
382 . . .	-1.012	.005	58,080	10,800	4.771
CR	Cold-rolled specimen.				
EG	Electrogalvanized specimen.				
OCP	Open-circuit potential.				
SCE	Saturated calomel electrode.				
Z	$[(Z')^2 + (Z'')^2]^{1/2}$				

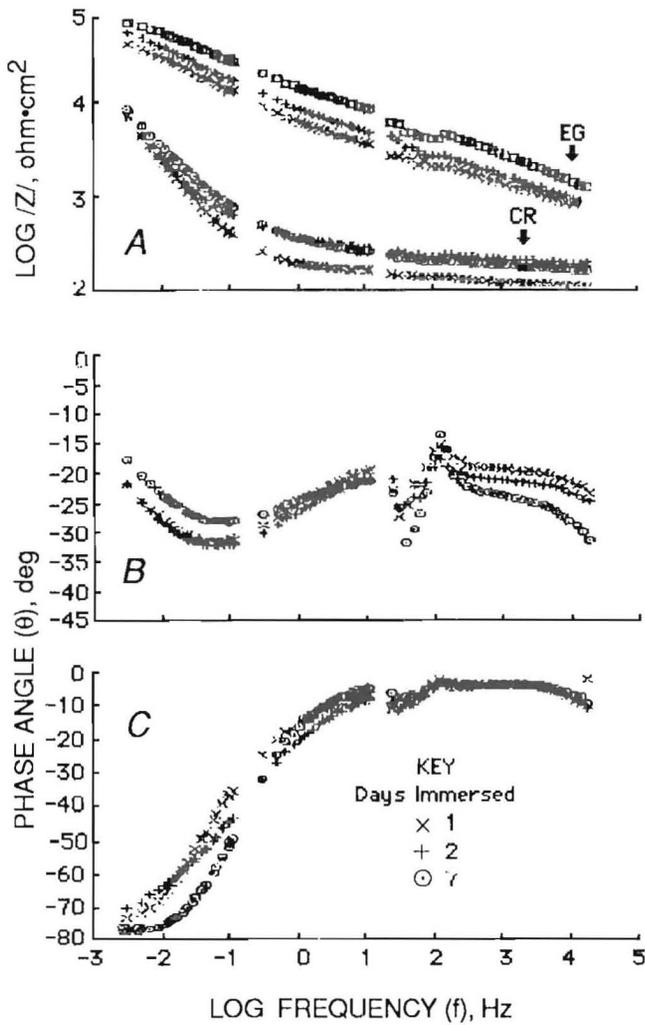


Figure 3.—Bode plots for 7-day immersion of electrogalvanized and cold-rolled steel specimens after 190-day on-vehicle exposure. A, Bode magnitude plots; B, bode phase plot for electrogalvanized specimens; C, bode phase plot for cold-rolled specimen.

After 1-year exposure and the final 2-day immersion to collect impedance spectra, the specimens from set 3 were photographed and cross-sectioned for SEM and EDX analysis. The SEM photos are shown in figures 4 and 5 for the CR and EG specimens, respectively. Figure 4A shows the normal view of the scribe on the CR specimen. Excessive corrosion is evident along with delaminated areas and raised areas of paint. Figure 4B shows the corrosion products near the paint-metal interface and the large volume of these products both in the scribe and under the paint. Raised paint areas away from the scribe are shown in figure 4C. EDX results showed only oxide corrosion products on the EG and CR specimens. No sulfur was found. This will become important when the atmospheric specimens are discussed.

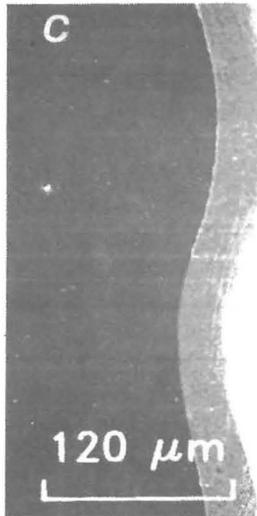
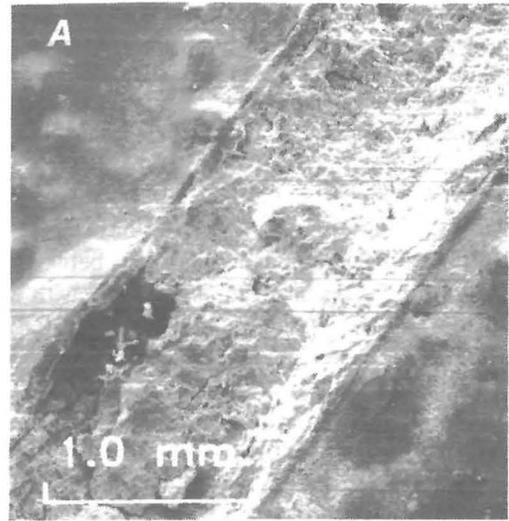


Figure 4.—Cold-rolled steel scribe area after 1-year on-vehicle exposure. A, Normal view; B, corrosion near paint-metal interface; C, raised paint areas away from scribe.

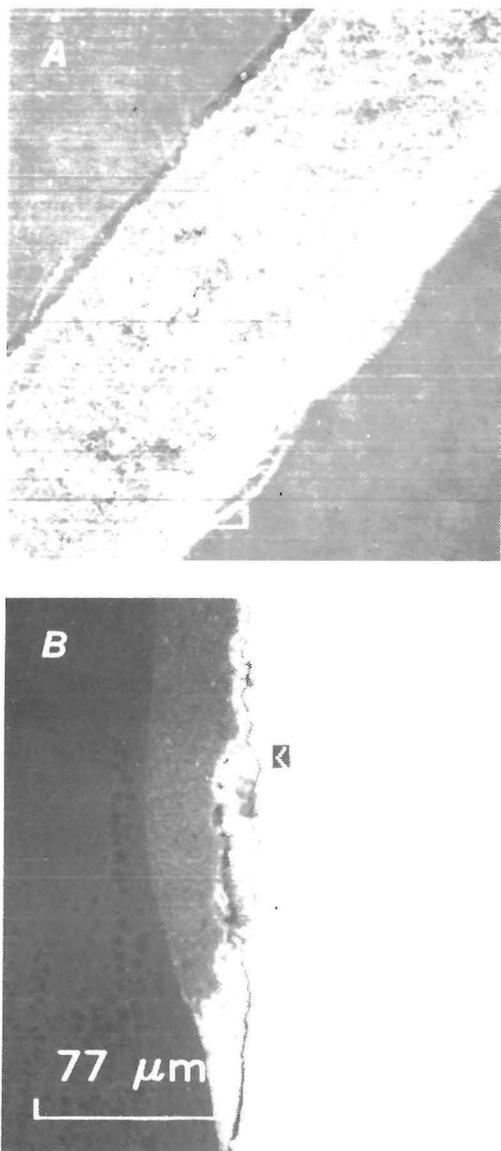


Figure 5.—Electrogalvanized scribe area after 1-year on-vehicle exposure. A, Normal view; B, corrosion near paint-metal interface.

In figure 5A, the normal view of the EG scribe shows much less corrosion than did the CR specimen in figure 4A. Also, there are no raised areas of paint. The cross-sectional view in figure 5B shows the zinc (by the use of an arrow) being about  $80\ \mu\text{m}$  from the end of the paint. Corrosion has proceeded under the paint and between zinc and paint where there still is a zinc coating present. Smaller quantities of corrosion products are evident versus the CR specimen. From these specimens, it was determined that corrosion extended about  $100\ \mu\text{m}$  back under the paint on the EG sample and  $\sim 1,000\ \mu\text{m}$  under the paint on the CR specimen.

The observed under-paint corrosion led to a question about the effect of the increase in surface area undergoing corrosion on these specimens. In comparing the Bode magnitude plots of figures 1 and 2, it is noticeable that at high frequencies on the right-hand side of the diagram, the values are greater for the EG specimen than for the CR specimen. The value of the impedance at the high frequency limit is determined by the electrolyte resistance and the sample surface area. Assuming that the electrolyte resistance remained constant, the differences between EG and CR specimen impedance at high frequency could be due to true surface area changes. Thus, it was necessary to evaluate unpainted specimens after on-vehicle exposure to verify the difference in corrosion rates. After 76 days of exposure on-vehicle, the high frequency values were almost identical and the low frequency values were initially 10 times greater for the EG specimen than for the CR specimen. Further immersion for 2 days, however, showed an increase in the low frequency values for the CR specimen and a lowering of the low frequency value for the EG specimen. At the same time, the high frequency value for the EG specimen increased slightly. This indicates that a soluble film had formed on the zinc, which was conductive, but lowered corrosion initially during immersion.

The specimens were placed back on-vehicle for another 102 days. After that period, they were tested once again by immersion and EIS. After 1-day immersion, the value of  $|Z|$  for the EG specimen was 20 times the value of  $|Z|$  for the CR specimen. Within a few days immersion, this difference was  $<10$ . Thus, it was clear that there had been a zinc corrosion product, which must have dissolved in the molar NaCl solution immersion medium, and the surface area was not causing the lowered impedance modulus for the CR specimen.

## IMMERSION ONLY

The predominant result of immersion, without prior exposure to an atmospheric environment such as on-vehicle placement, was the time dependence of the impedance spectra. Figure 6A shows the effects of immersion on the EG specimen. After 34 days, the paint has easily peeled from the surface. However, figure 6B shows adherence of the paint on the CR sample. Analysis by EDX indicated that chloride ion was prominent in the corrosion products of the zinc on the EG specimen, but absent on the CR specimen. This explains the increased corrosion rate for the EG specimen of set 1 after the longer immersion at 190-day exposure.

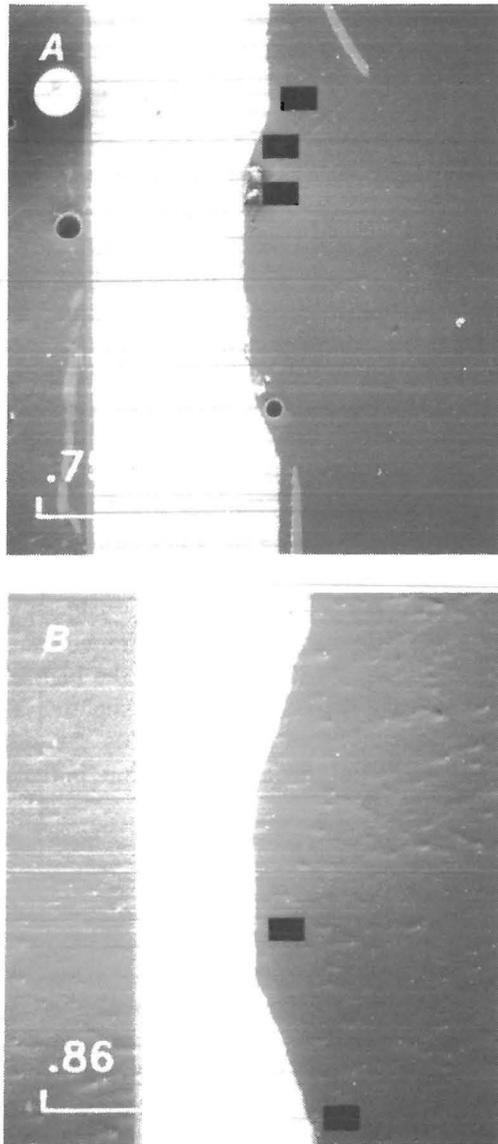


Figure 6.—Cross section of specimens after 34-day immersion. A, Electrogalvanized steel; B, cold-rolled steel.

The EIS spectra in figure 7 show the time dependence of the corrosion of immersion specimens. The CR specimen had a value of the modulus, which was 10 times that of the value for the EG specimen (fig. 7A). The phase relationship was quite different from on-vehicle specimens as shown by figure 7B indicating mechanistic differences.

After long immersion (~172 days), the situation was reversed with the EG specimen having the higher impedance modulus (fig. 7C). Also, the phase relationship has changed, but still does not appear to be similar to the on-vehicle specimens (fig. 7D).

During this immersion test, the pH of the medium was monitored. This would lend information concerning the types of corrosion products and their subsequent effect on the specimen. Within 1 day of immersion, the CR specimen displays rust, which is iron oxide-hydroxide presumably in the ferrous state initially. Oxidation by atmospheric oxygen produces ferric iron. Ferric hydroxides have known acidic character because of hydrolysis reactions. The initial pH was ~5.6. Within 2 weeks, the pH for the EG medium was 7.16, and the pH for the CR medium was 6.67. This shows the acidic character of the iron corrosion products and the neutral-basic character of the zinc corrosion products.

The trend of pH difference continues. After 172 days of immersion, the pH of the EG medium was 8.6, and the pH of the CR medium was 6.1. A recent article (9) suggests that the lowered pH in carbon steel crevices was due to hydrolysis of the ferric ions. These acid conditions and the fact that ferrous ions act as scavengers for oxygen increase the corrosion and cause the creepback of scribed specimens in the salt spray test.

During immersion, the initial condition was short lived, lasting 1 month or less. After 1 month, there was a continuous increase in the impedance for EG specimens and a continuous decrease in impedance for the CR specimens. If one stops an immersion test before the crossover point, different conclusions will be drawn.

For the reasons cited, it appears that immersion only is a poor test method for atmospheric or on-vehicle service corrosion of EG or CR steel.

#### STATIC ATMOSPHERIC SPECIMENS

Sulfur was found to be a dominant factor in the corrosion products of both EG and CR scribed specimens. This was presumably due to atmospheric sulfur oxides from combustion. No sulfur was present on the on-vehicle specimens. Sample orientation affected the distribution of corrosion products. The scribed specimens were used after 1-year atmospheric exposure to yield the SEM and EDX information.

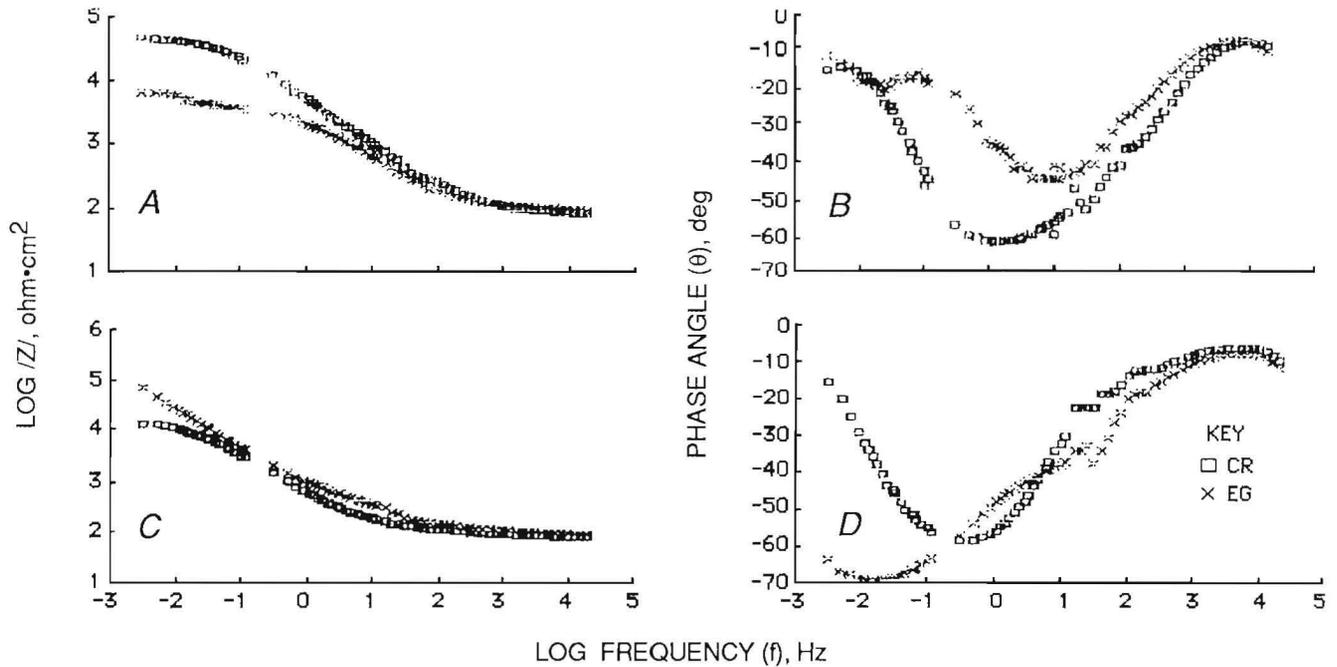


Figure 7.—Bode plots for specimens after 1- and 172-day immersion. A, Bode magnitude, 1 day; B, bode phase, 1 day; C, bode magnitude, 172 days; D, bode phase, 172 days.

Figure 8 shows the cross section of the scribe for the EG (fig. 8A) and CR specimens. Both were oriented vertically to be similar to on-vehicle specimens, and this is especially noted in figure 8B, where corrosion products overlap the paint. Copious quantities of corrosion products were present in the scribe of the CR specimen, and very little corrosion was evident under the paint, which was not the case on the on-vehicle samples. In fact, the corrosion extended only  $80\ \mu\text{m}$  under the paint on this CR specimen and was  $225\ \mu\text{m}$  under the paint on the EG specimen. This appears to be due to the affinity of the sulfur oxides for zinc. There was red rust in the scribe for the EG specimen, which was more extensive than on the on-vehicle specimens.

Because of the presence of sulfur in the corrosion products of these specimens, the corrosion proceeded differently than it did on-vehicle. Under-paint zinc corrosion products showed almost 10 times the amount of sulfur as did the under-paint corrosion products of the CR

specimen. In the scribe, the factor dropped to about two. The pH was 8 for the EG specimen's immersion medium after 1 day, which was much higher than the immersion of unexposed specimens.

After 1.5-years exposure, unpainted specimens were tested by EIS under immersion. After 1-day immersion, the Bode plots showed the EG specimen had a value for the modulus at 0.001 Hz, which was 16.4 times the value for the CR specimen. Figure 9 shows the Bode plots. The high frequency value for the CR specimen was higher on the right side of figure 9A. This indicates that the corrosion products were more resistive than the EG specimens. After longer immersion, the high frequency value for the CR specimen dropped, indicating reaction of these products by hydrolysis. This was also seen by the pH changes in the CR immersion medium. After 1 day, the value was pH 4.8, which began to rise by the second day to pH 5.4.

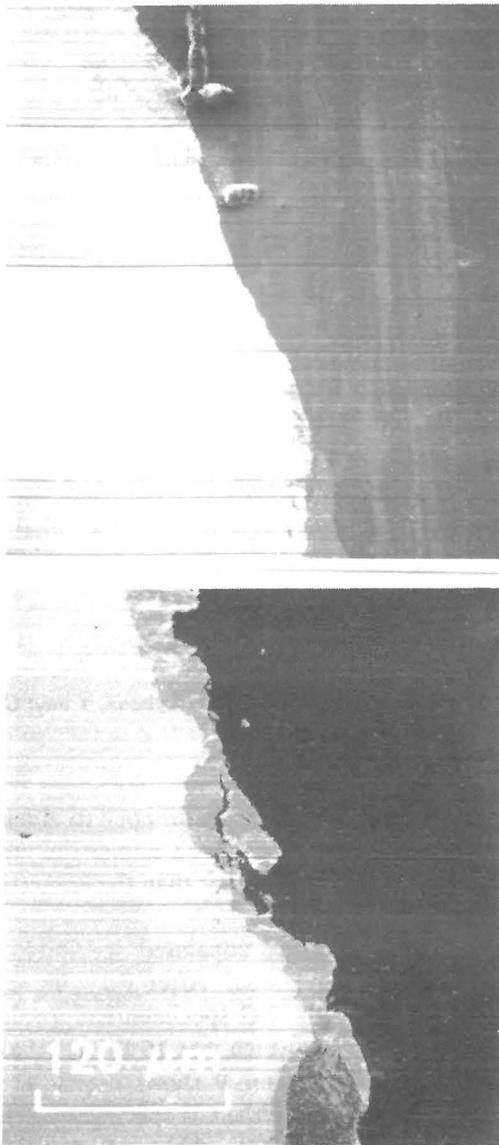


Figure 8.—Cross section of electrogalvanized and cold-rolled specimens after 1-year atmospheric exposure. A, Electrogalvanized; B, cold-rolled.

Table 2 shows the difference in OCP for the immersion only and atmospheric exposed specimens. There are striking similarities for the EG unpainted specimens OCP values for both exposed and unexposed conditions. However, the CR specimens have drastically different values owing to the presence of corrosion products on the exposed specimen. The OCP values of immersion-only specimens were more positive with time for the EG specimen and the CR specimen because of corrosion product formation.

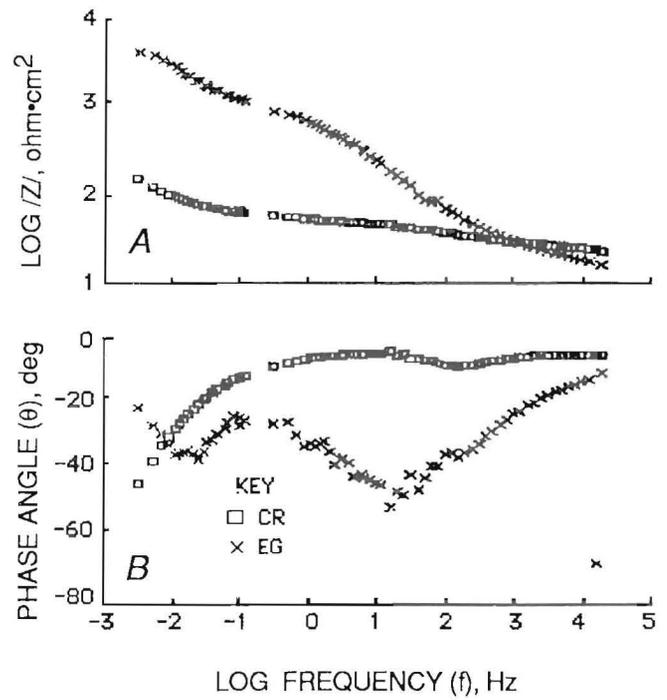


Figure 9.—Bode plots for atmospheric exposure specimens. A, Bode magnitude plot; B, bode phase plot.

Table 2.—Open-circuit potentials for immersion-only specimens and atmospheric-exposed specimens

Specimen	OCP, V vs SCE	Time of immersion, days
Scribed immersion only:		
CR .....	-0.696	172
CR .....	-.752	1
EG .....	-.893	172
EG .....	-1.044	1
Unpainted immersion only:		
CR .....	-.700	1
EG .....	-1.079	3
Unpainted 1.5-year atmospheric exposure:		
CR .....	-.555	1
CR .....	-.578	2
EG .....	-1.061	1
EG .....	-1.072	2

CR Cold-rolled specimen.  
 EG Electrogalvanized.  
 OCP Open-circuit potential.  
 SCE Saturated calomel electrode.

Chloride ion caused paint separation on the EG specimens, but not the raised areas of paint as seen on the CR specimens. When comparing the CR specimens from on-vehicle and atmospheric exposure, the raised paint was evident on both, but the depth of penetration was five times greater for the on-vehicle specimens.

The mechanistic implications of the impedance spectra have been discussed at length by Walter (6). Surveying

the spectra for CR and EG specimens immersed in moist NaCl solution, one can conclude that diffusion impedances are definitely obtained. Though no modeling has been performed on the data gathered as yet, the authors are presently attempting this aspect by using the equivalent circuit models as seen in the literature (3-4, 6).

## SUMMARY AND CONCLUSIONS

The investigation of the corrosion of scribed CR and EG primer-coated steels by three separate testing conditions has resulted in a better knowledge of the effects of exposure. Without any doubt, the on-vehicle environment was the most applicable for evaluation of these materials. Coupling this exposure with short-period immersion to obtain electrochemical impedance spectra provided a method to measure corrosion rates. Comparison of this method with the immersion of unexposed specimens showed that the wrong conclusions could easily be drawn by use of the latter method alone. There were significant differences in the corrosion mechanisms as evidenced by the phase angle versus frequency relationship.

When comparing the three sets of test specimens from on-vehicle exposure, there are some similarities and some differences. Most notably, the value of  $|Z|$ , except in one case, increases with time for the EG specimens. CR specimens appear, in general, to show a decrease in  $|Z|$  versus time. For both EG and CR specimens, the atmospheric and on-vehicle exposure yield the more similar results. Although sulfur was not present in both exposures, the spectra do not differ drastically for these two test conditions. Chloride appeared to have more impact on the zinc corrosion than on the steel corrosion.

Atmospheric exposure yielded different corrosion phenomena near the paint-metal interface than did the on-vehicle specimens. The absence of immersion periods may account for the difference, but that does not seem likely. The presence of sulfur in the corrosion products appears to be the key difference. Gaseous sulfur oxides have a different affinity for zinc than for iron. Also, it was obvious that times of wet precipitation caused copious corrosion products to form at the scribe for the CR specimen and under the paint in the zinc layer for the EG specimen. This difference in mechanism of corrosion for zinc and steel still translated to a tenfold difference in the  $|Z|$  at the lowest frequency.

Continuous immersion of EG specimens showed extensive creepback of the paint from under-film attack. Chloride ion was assumed to be the reason for this.

Continued on-vehicle, immersion, accelerated atmospheric, and normal atmospheric testing may answer some of the questions that have arisen in this study. However, the results show that for service exposure of automotive sheet, be it EG or not, EIS yields corrosion information that relates directly to the performance of this material.

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