Rapid Assessment of Automotive Epoxy Primers by Electrochemical Techniques

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An epoxy primer commonly used in the automotive industry was applied cataphoretically (using different times and potentials) over metallic substrates, and was investigated by means of different techniques such as accelerated cathodic disbonding, EIS, and AC/DC/AC tests. The variables considered in this study were the metallic substrate (cold rolled steel and phosphatized cold rolled steel), the thickness (20 and 25 μm), and finally the deposition potential in the cataphoretic cell (140 V and 190 V). The primer performed better when applied over phosphatized steel at the maximum thickness and when the lowest cataphoretic potential was used. Primer quality results obtained by the different techniques used in this study were quite similar and led to almost the same conclusions, although the AC/DC/AC and cathodic disbonding techniques provided results in less time than the EIS technique.

INTRODUCTION

Protecting automobiles against corrosion is of great importance from the point of view of the national economy and the private car owner.

Rust that starts at an interior surface of a body panel, penetrates the steel sheet, and eventually shows through as rust on the exterior exposed surface is known as perforation corrosion. The term cosmetic corrosion is applied to an attack which starts at the exterior surface, usually at regions where the paint film is damaged.[1]

The concern of automobile manufacturers about corrosion protection can be summed up by General Motors' 10-5-2 target, which stands for 10 years protection against perforation, 5 years against cosmetic corrosion, and 2 years against engine compartment corrosion. Such targets are achieved mainly by the use of cataphoretic epoxy coatings applied to phosphatized steel or phosphatized galvanized steel (today steel substrate is still used for a few parts of the automobile body).[2]

The mechanism by which an organic coating protects a metallic material from the environment is a complex process which is not well understood. Many properties of polymers (processability, curing conditions, application conditions on substrate, electrical, chemical, thermal and mechanical properties, and environmental stability) affect their suitability and reliability as protective organic coatings. A review of the literature reveals that the protection offered by an organic coating can be ascribed to one or more of the following mechanisms: (1) depression of the anodic and/or cathodic reaction; (2) introduction of a high electrical resistance into the circuit or the corrosion cell; and (3) as a barrier to aggressive elements (oxygen, water, and ions).[1,3-7]

At present, for the diagnosis and evaluation of coating films, several techniques can be used: (a) an external visual observation test; (b) testing the color and gloss of coating films; (c) the adhesion test; (d) mechanical tests of abrasion-resistance and by stress-strain curve; (e) resistance to natural exposure; (f) accelerated corrosion tests; and (g) electrochemical tests.

Various electrochemical techniques are used for evaluating the performance of organic coating/metal systems. The application of electrochemical impedance spectroscopy (EIS) to coated metals has resulted in new

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Table 1—Type of Substrate, Primers, Application Potentials, Curing Temperatures and Coating Thickness of Samples Used in the Study

Samples	Substrate	Anticorrosion Pigment Type	Deposition Potential (V)	T Curing (°C)	Film Thickness (μm)
A . . .	Steel	Pb	140	180	20
P	Steel	Pb	140	180	25
Q . . .	Phosphatized steel	Pb	190	180	25
M . . .	Steel	Pb	190	180	25

information concerning their degradation in corrosive environments. In recent years, EIS has been shown to be a useful technique in the study of the corrosion performance of polymer-coated metals.[1, 3-13]

In predicting the material properties concerning interaction stability, the main problem arises from the complexity of the total process itself. Due to this complexity, the main routines of interaction testing and material assessment were experimentally developed by using different exposure processes and property measurement techniques. The principal types of exposure processes are the accelerated aging test and field exposure experiments (which must be planificated for long times and are very expensive to run). Property measurement can be taken electrochemically, mechanically, and chemically. Only when the exposure process and measurement test are well defined and programated will it be possible to obtain information about the coating degradation process and obtain reproducible results that are not time consumptive.

Therefore, there is an express interest in rapid assessment methods for practical applications which provide an early indication of corrosion processes in the surface of coated metallic substrates. Hollaender et al.[14-16] developed a rapid method for testing coated metal which consisted of a combination of DC and AC measurements (AC/DC/AC procedure). After the first AC measurement, the test sample is treated for a short time by a constant cathodic current (DC) and, following that, an AC spectrum is recorded again. The change in the spectrum characteristics can be attributed to a coating degradation (pore formation) and a delamination process in the metallic surface due to hydrogen production (if the cathodic polarization is high enough).

The work presented here will concentrate on: (1) the evaluation of an epoxy primer applied to different metallic substrates (cold rolled steel and phosphatized cold rolled steel) with two thicknesses (20 and 25 μm) and two deposition potentials in the cataphoretic cell (140 and 190 V), using different techniques in order to determine anticorrosion properties; (2) the development of an electrochemical test procedure (AC/DC/AC) which can be applied to coated metals and offers results in a short time; and (3) to compare the different evaluation procedures applied to the coated metals in order to know whether the conclusions offered by each of them concur.

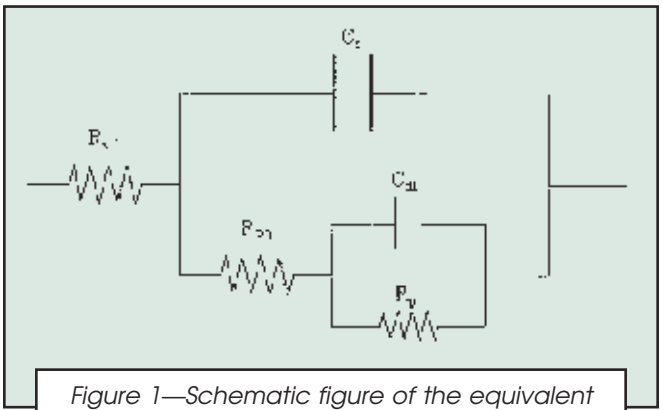


Figure 1—Schematic figure of the equivalent circuit used to modelize results of coated samples.

EXPERIMENTAL

Materials

A commercial anticorrosive epoxy coating (containing lead as the anticorrosive pigment) was cataphoretically deposited on two types of substrate: steel and phosphatized steel. The conditions of the cataphoretic process, sample identification, primer type, curing conditions, and substrate type are summarized in *Table* 1. The test panels (20 × 20 cm × 0.25 mm) were pretreated by mechanical cleaning (polishing), degreased in acetone solution, and rinsed with distilled water. Anodes were placed parallel to the working electrode (steel panel) at a distance of 1.5 cm. Coatings were deposited galvanostatically at different current densities and different times in order to obtain two film thicknesses: 20 and 25 μm. The temperature was controlled throughout the whole cataphoretic process. Other cataphoretic conditions applied were an anode/ cathode ratio of 1:4 and a bath temperature of 28ºC.

After removing the coated samples from the cataphoretic bath, they were cured for 10 min at 180°C, as shown in *Table* 1.

Testing Methods and Equipment

Electrochemical Impedance Spectroscopy: EIS tests were carried out on coated samples exposed to 3.5 wt% NaCl in distilled water for periods up to six months. The three-electrode electrochemical cell was obtained by standing a glass cylinder on the sample sheet and filling it with the test solution. The exposed surface area was 16.6 cm^2. A carbon sheet counter electrode and an Ag/AgCl saturated calomel were used as a reference electrode.

The AC impedance data was obtained at the free corrosion potential using an Autolab PSTAT 30 potentiostat and frequency response analyzer. The

impedance tests were carried out over a frequency range of 100 kHz down to 1 mHz using 10 mV amplitude of sinusoidal voltage inside a Faraday cage in order to minimize the external interference on the system. The impedance spectrum was analyzed using Zplot software.

The equivalent circuit model, shown in *Figure* 1, was employed to analyze the EIS spectra. The circuit consisted of a working electrode (metal substrate), a reference electrode, electrolyte resistance R_s, pore resistance R_{po}, coating capacitance C_c, polarization resistance R_p, and double layer capacitance C_{dl}.

Fitting the EIS data to the circuit determined the values of the equivalent circuit elements. The chi-squared parameter of the fit was usually below 0.1.

CATHODIC DISBONDING: The cathodic disbonding test involved scribing the sample through the paint down to the bare metal. The scribe marks were made at right angles to form a 2 × 2 cm cross. An electrochemical cell, filled with 3.5 wt% NaCl aqueous solution, was then placed over the cross and a voltage of –0.59 V (cathodic polarization) versus Ag/AgCl reference electrode was applied for 24 hr in order to accelerate the reduction of water-dissolved oxygen at cathodic sites to form hydroxide ions.[12] After the cathodic treatment, an adhesive tape was applied over the coating in the vicinity of the cross and pulled off to reveal the extent to which cathodic polarization produces disbondment. Determination of the degree of disbondment produced by cathodic polarization of five samples usually shows good reproducibility.

Measurements were made of the average dimension of the disbonding away from the scribe in millimeter units. The value dx/dt is calculated by dividing this dimension by the duration of the test in hours, which was 24 hr. Note that no observed disbonding defines a default value of 10^{-4} mm/hr.

AC/DC/AC: The AC/DC/AC procedure consisted of a combination of DC and AC measurements. First, an AC test was applied to the sample under the same conditions as described previously in the EIS section. This measurement allows the present state of the test sample to be determined.

After the first AC measurement, the test sample was treated for a short time by a constant cathodic potential (–3 V) for 30 min (DC). Following the potential, the sample was turned off and allowed to relaxate until it again reached a new steady state and the potential was once more stabilized. Normally, this step is performed in one hour. Finally, a new EIS measurement (AC) was applied to the sample in order to determine the new present state. A schematic representation of the AC/DC/AC procedure is shown in *Figure* 2.

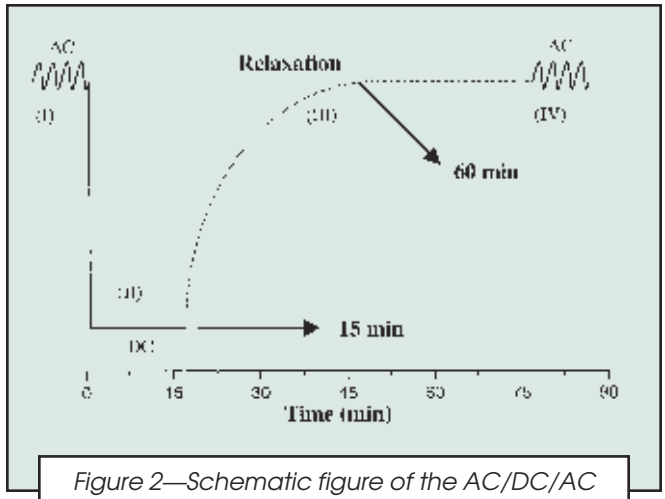


Figure 2—Schematic figure of the AC/DC/AC test procedure vs. time.

This test sequence was repeated at least 20 times, which means that more than 24 hours were needed for this purpose. The AC/DC/AC procedure was absolutely automated in PSTAT 30 Autolab equipment.

Experimental results obtained from EIS measurements were modelized using the equivalent circuit shown in *Figure* 1 with the same procedure as previously described.

ACCELERATED CYCLIC TEST: The cyclic test applied to the sample consisted of three consecutive steps, which are as follows:

(1) Four hours in salt fog chamber, in accordance with ASTM B117.

(2) Four hours at ambient exposure (temperature 18-28°C and relative humidity 40-60%), in accordance with DIN 50014-23/50-2.

(3) Sixteen hours in humidity chamber at 40 ± 3°C and 100% relative humidity, in accordance with DIN 50017 KK.

Coated samples were previously scribed through the paint down to the bare metal. The scribe marks were made at right angles to form a 6 × 6 cm cross.

Table 2—Comparative Table of Rankings for Samples Performance (with Different Thickness, Substrate, and Application Potential) in Each Type of Test

Samples	EIS	Cathodic Disbonding	AC/DC/AC	Cyclic Test
Thickness				
A (20 µm)	Worse	Worse	Worse	—
P (25 µm)	Better	Better	Better	Slightly better
Substrate				
M (steel)	Worse	Worse	Worse	Worse
Q (phosph. steel) . . .	Better	Better	Better	Better
Potential				
M (190 V)	Worse	Worse	Worse	Worse
P (140 V)	Better	Better	Better	Better

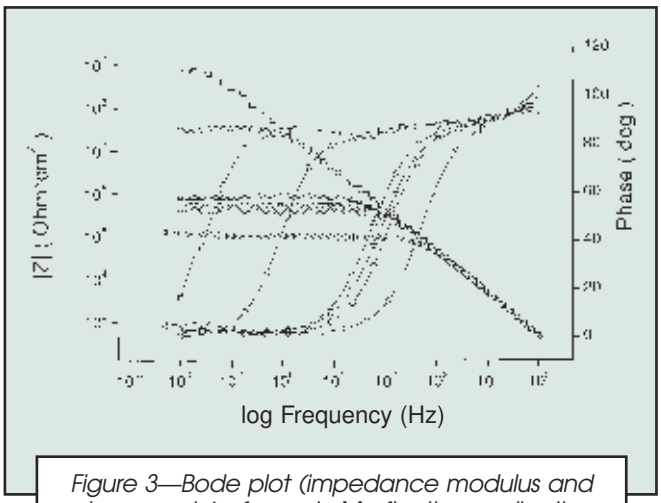


Figure 3—Bode plot (impedance modulus and phase angle) of sample M after the application of AC/DC/AC cycles (❑—99 min, O—372 min, Δ—462 min, ∇—734 min, ◊—1459 min, and +—2940 min of exposure to AC/DC/AC test).

The samples were evaluated after 20 and 40 cycles of exposure and consisted of two measurements:

(1) *Corrosion*: normally determined by measuring the distance between the center of the scribed line and the furthest points where the cataphoretic coating has been delaminated.

(2) *Blistering*: typically determined by measuring the distance between the center of the scribed line and the furthest points where the cataphoretic coating had been damaged by blistering.

Equivalent Circuit Interpretation: It is generally assumed that the elements of the equivalent circuits are in correlation with the corrosion properties of the system.[17]

The pore resistance, R_{po}, is a measure of the porosity and degradation of the coating. R_{po} values are related to the number of pores or capillary channels perpendicular to the substrate surface through which the electrolyte reaches the interface.[11] Although the R_{po} can increase with immersion time, probably as a result of pore or defect blockage by corrosion products, it usually decreases.

Some authors have found three regions in the time dependent decreases of R_{po}. It initially decreases rapidly, then slowly (displaying a plateau), and then again rapidly, coinciding with the appearance of the second semi-circle. They explain the plateau by making the assumption that the number of pathways formed is approximately constant with time.

The capacitance of the coating, C_c, should be a measure of the water permeation into the coating. It is defined as:

$$C_c = \varepsilon \varepsilon_o A/d \quad (1)$$

where ε is the dielectric constant of the coating, ε_o is the permittivity of vacuum, A is the area of the coating exposed to the electrolyte, and d is the thickness. The coating capacitance will usually change during electrolyte absorption because the dielectric constant of water is approximately 20× greater than that of a typical coating. C_c usually increases at the initial stage of exposure, and seems to be a measure of water absorption. When the coating has been exposed for a long time it can be correlated to disbonding and degradation.

The polarization resistance, R_p, and double layer capacitance, C_{dl}, are two parameters used to specify the disbonding of the topcoat and the onset of corrosion at the interface. The specific polarization resistance is associated with the charge transfer behavior of the metal substrate. R_p, like C_{dl}, can only be calculated well when at least two time constants are evident in the spectrum.

C_{dl} is a measure of the area over which the coating has disbonded. It can be accurately measured only at advanced stages of coating deterioration. The trend of C_{dl} is complex. A change in the C_{dl} value can be

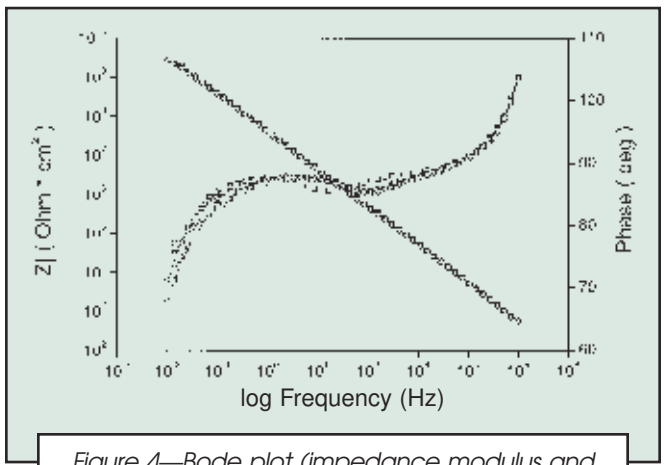


Figure 4—Bode plot (impedance modulus and phase angle) of sample P after the application of AC/DC/AC cycles (❑—0 min, O—271 min, Δ—633 min, ∇—815 min, ◊—1268 min, and +—2880 min of exposure to AC/DC/AC test).

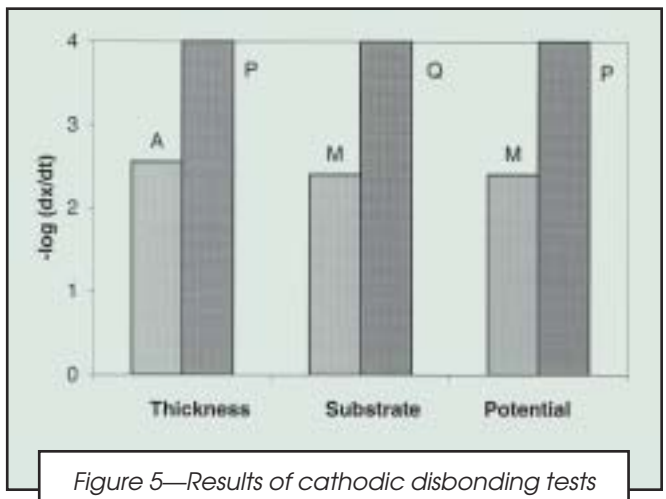


Figure 5—Results of cathodic disbonding tests of the different samples used in this study (thickness comparison A-20 μm vs. P-25 μm; type of substrate comparison M-steel vs. Q-phosphatized steel; application potential comparison M-190 V vs. P-140V).

associated with the competition between disbonding and corrosion product accumulation at the interface. The C_{dl} value increases as water spreads at the interface and the delaminated area extends. On the other hand, the accumulation of the corrosion product at the interface reduces the area of the double layer capacitor, which will lead to a decrease in the C_{dl} value. Therefore, the change of C_{dl} may depend on which factor, the disbonding or the corrosion product accumulation, was more dominant during the corrosion process. However, it should be pointed out that both the increase and the decrease in C_{dl} are the result of corrosion development at the metal surface and a constant C_{dl} is an indication of a stable interface.[6]

RESULTS AND DISCUSSION

Different electrochemical techniques (EIS, AC/DC/AC, and cathodic disbonding) were used to determine the quality of the primer deposited, with changes being made to some parameters in the process (the thickness and the cataphoretic potential), over two types of metallic substrates (steel and phosphatized steel).

Although the quality of a primer takes into account various complex characteristics (permeability, adherence, passivation capacity, etc.), the techniques used in this study proved to be capable of discriminating between the different aspects. These techniques (including accelerated cyclic tests) showed similar results regarding the quality of the primer (*Table* 2). Nevertheless, the AC/DC/AC technique proved to be much faster than traditional EIS, while giving similar results.

As can be seen in *Figures* 3 and 4, the coatings are affected to a different degree by the imposed cathodic stress. Both figures present the effect (in Bode diagrams) of the AC/DC/AC cycles over the coated samples. *Figure* 3 presents the results of a primer that is significantly affected, while *Figure* 4 shows the results of an unaltered sample which remains unaffected over time, having the same capacitive behavior after 20 AC/DC/AC cycles (2880 min) as it had initially. It is important to note that the effect of the cathodic stress can be seen in the middle and low frequency part of the corresponding impedance spectra.

Figure 5 shows the cathodic disbonding results of the different samples tested. It can be seen that the highest adherence was given when the primer was applied to the phosphatized substrate (sample Q) or to the steel substrate but at the lowest potential (sample P), and both with the greatest thickness.

The results that we present correspond to a comparison between samples, where one of the application parameters (thickness, substrate type, or application potential) has been changed.

Thickness

Figures 6 a-c show the evaluation of R_{po}, R_p and C_{dl} versus time for samples A (20 µm) and P (25 µm) obtained by EIS after different periods of exposure to electrolyte. *Figures* 7 a-c show the evolution of the same

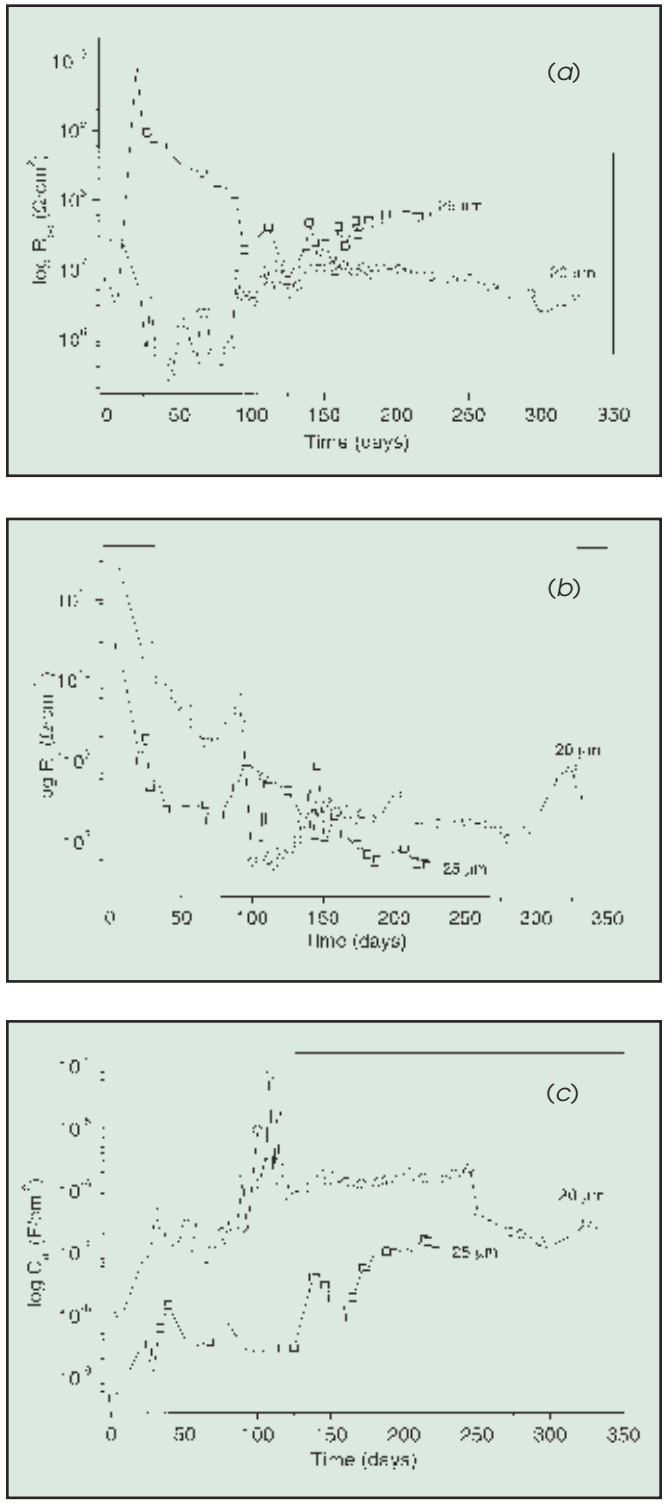
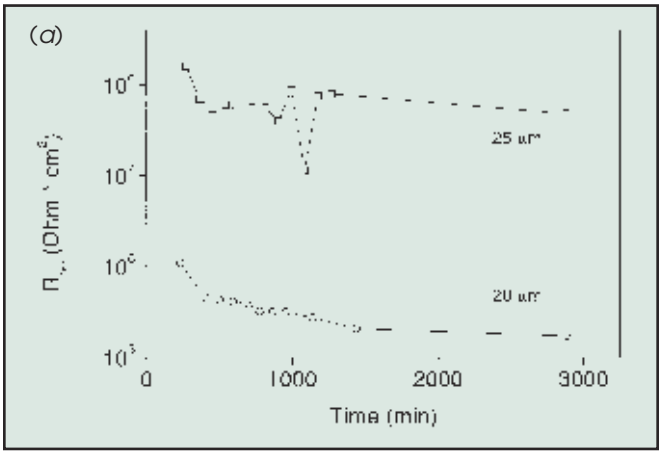
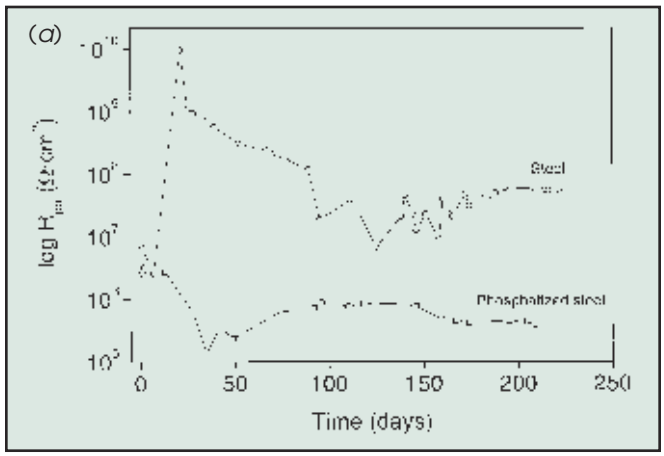
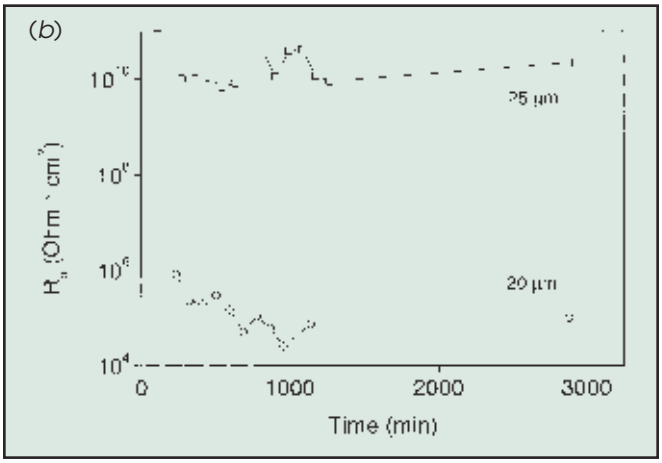
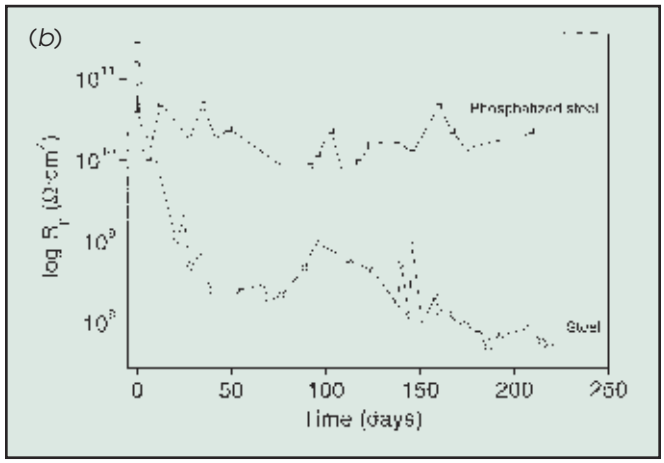


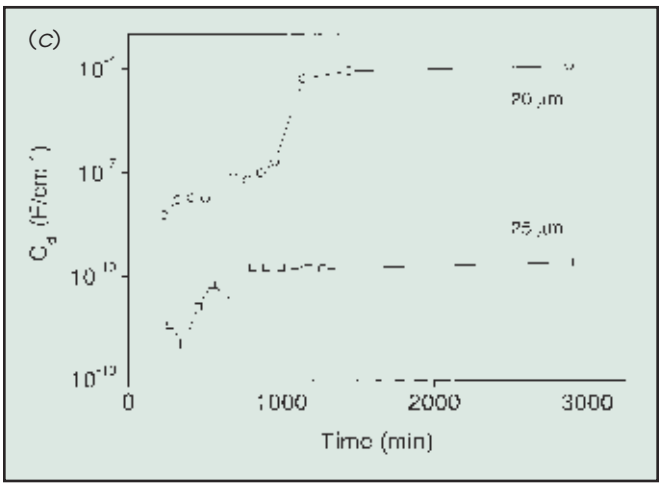
Figure 6—Effect of primer thickness A (20 µm) vs. P (25 µm). Parameters of the equivalent circuit from EIS tests: (a) pore resistance R_{po}, (b) polarization resistance R_p, and (c) double layer capacitance C_{dl}.











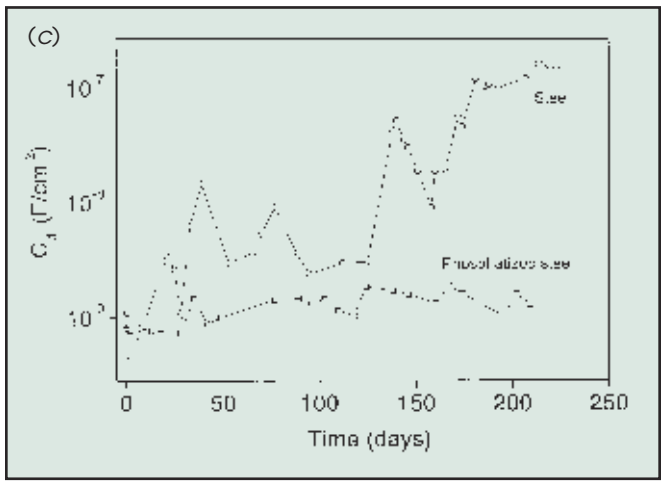


Figure 7—Effect of primer thickness A (20 µm) vs. P (25 µm). Parameters of the equivalent circuit from AC/DC/AC tests: (a) pore resistance R_{po}, (b) polarization resistance R_p, and (c) double layer capacitance C_{dl}.

Figure 8—Effect of type M (steel) vs. Q (phosphatized steel) substrate. Parameters of the equivalent circuit from EIS tests: (a) pore resistance R_{po}, (b) polarization resistance R_p, and (c) double layer capacitance C_{dl}.

Table 3—Corrosion and Blistering Results of Samples Tested in 20 and 40 Cycles in Accelerated Cyclic Tests (Thickness Comparison A-20 µm vs. P-25 µm; Type of Substrate Comparison M-steel vs. Q-phosphatized Steel; Application Potential Comparison M-190 V vs. P-140 V)

Samples	Corrosion		Blistering	
	20 cycles	40 cycles	20 cycles	40 cycles
A	0.5	2	1	2
M	0.5	2	1	3
P	0.5	2	0.5	2
Q	0.5	0.5	0.5	0.5

parameters versus time (and corresponding number of cycles) obtained by the AC/DC/AC technique.

The results presented in both figures correspond. Sample P had higher R_{po} values than sample A, while its C_{dl} values were lower. The trends of R_p obtained by the EIS technique for both samples were quite similar, while R_p values of sample P obtained by AC/DC/AC were much higher than those in sample A.

Samples with a higher thickness P (25 µm) had fewer pores and were less degraded with the exposure time to electrolyte than sample A (20 µm). The initial increase of C_{dl} (in both EIS and AC/DC/AC techniques) indicated that the metal-coating interface was very active at low exposure times and that a disbonding process probably took place in the primer-metal interface. The delamination produced was greater in the sample with lower thickness.

The cathodic disbonding test shows how samples with a higher thickness P (25 µm) present maximum adherence to the metallic substrate while sample A (20 µm) shows less adherence.

Anticorrosive properties of the primer seem to be increased when higher thicknesses are applied due to a lower permeability and a greater adherence to the substrate.

Accelerated cyclic tests (*Table* 3) do not offer different results for these samples. The number of testing cycles was probably not enough to discriminate between their characteristics.

Substrate

Figures 8 a-c show the evolution of R_{po}, R_p, and C_{dl} versus time for samples M (steel) and Q (phosphatized steel) obtained by EIS after different periods of exposure to electrolyte. *Figures* 9 a-c show the evolution of the same parameters versus time (and the corresponding number of cycles) obtained by the AC/DC/AC technique. The results presented in both figures are coincident. The trend of the different equivalent circuit parameters for sample Q was almost constant with the exposure time. At the same time, sample M showed a decrease in the resistances, R_{po} and R_p, with time and an increase in the capacitance, C_{dl}.

Anticorrosive coating performance is much higher when the epoxy primer is applied to a phosphatized steel substrate than when it is applied to other substrates, such as steel. It can be clearly seen that the phosphatized coating interface is much more stable than the steel one (the trend of R_p and C_{dl} are almost invariable for the phosphatized sample).

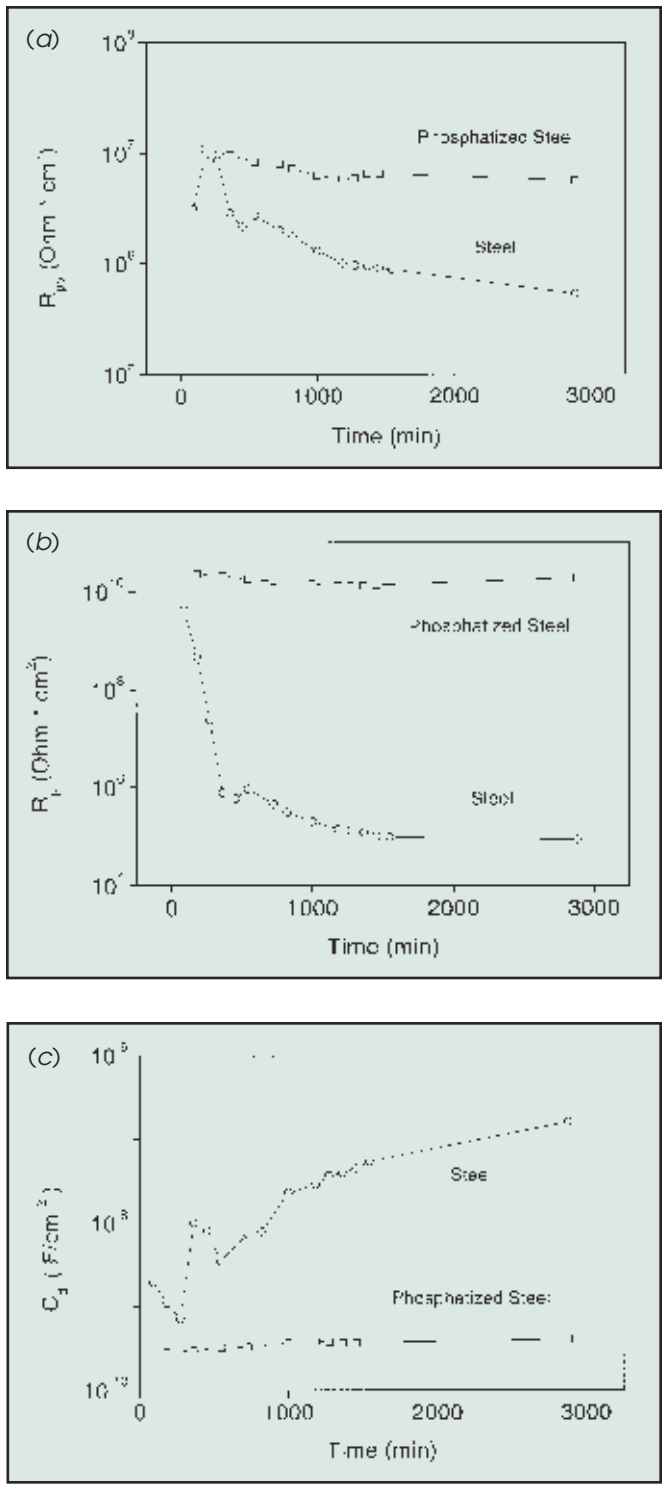
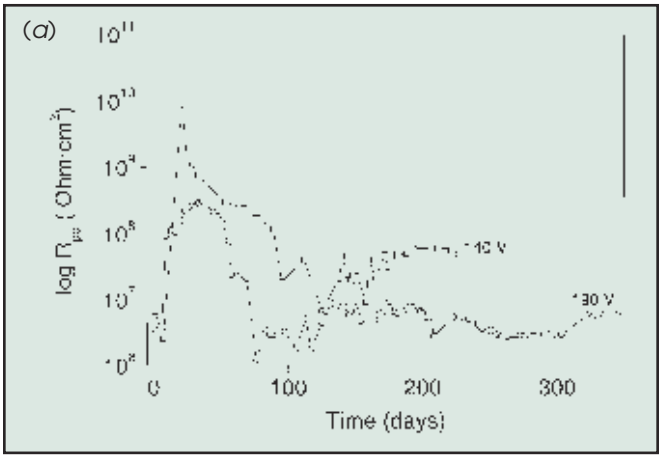
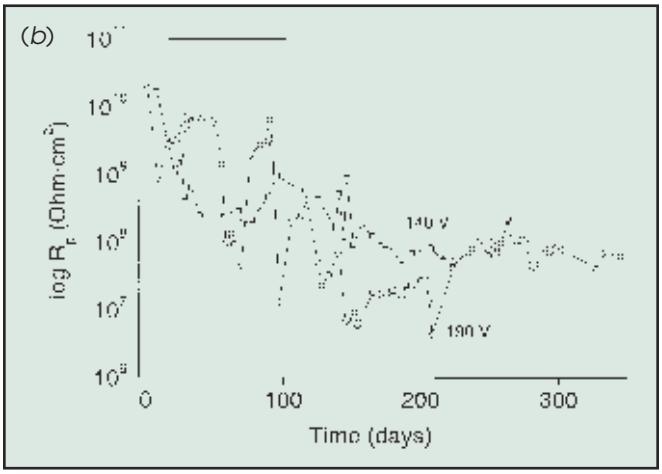


Figure 9—Effect of type M (steel) vs. Q (phosphatized steel) substrate. Parameters of the equivalent circuit from AC/DC/AC tests: (a) pore resistance R_{po}, (b) polarization resistance R_p, and (c) double layer capacitance C_{dl}.





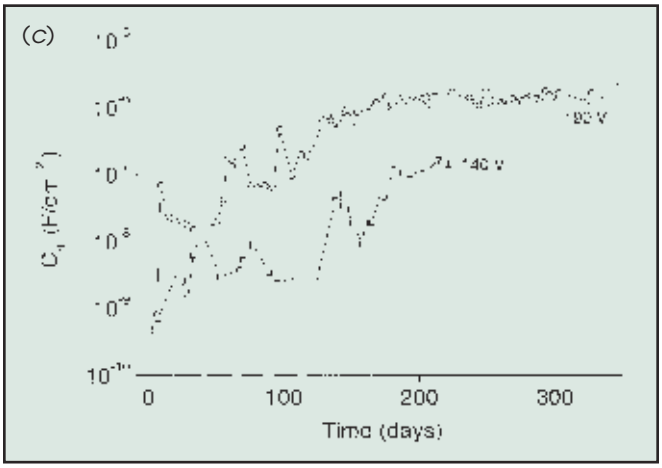
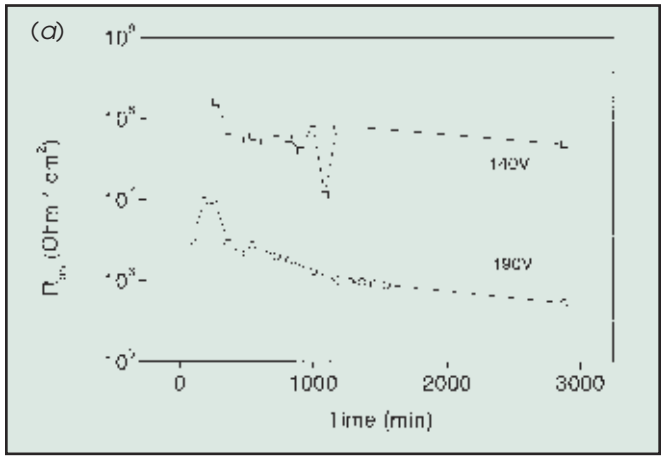
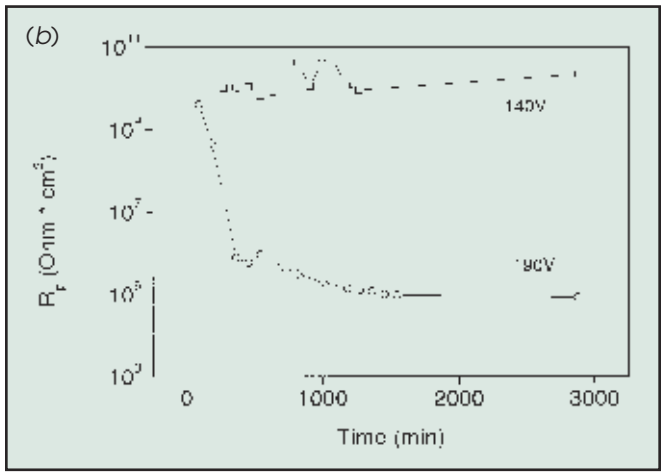


Figure 10—Effect of the application potential M (190 V) vs. P (140 V). Parameters of the equivalent circuit from EIS tests: (a) pore resistance R_{po}, (b) polarization resistance R_p, and (c) double layer capacitance C_{dl}.





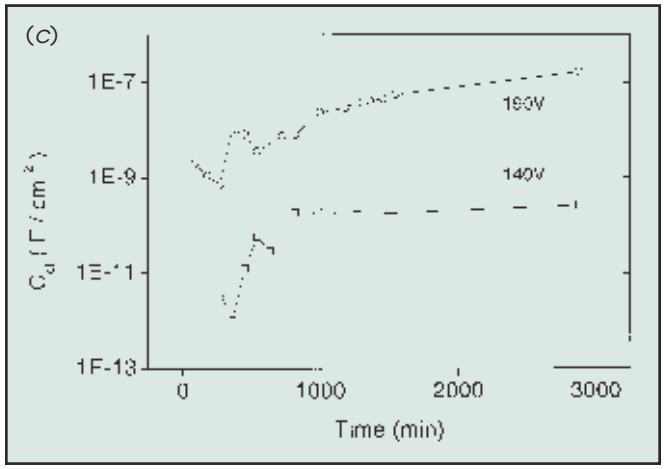


Figure 11—Effect of the application potential M (190 V) vs. P (140 V). Parameters of the equivalent circuit from AC/DC/AC tests: (a) pore resistance R_{po}, (b) polarization resistance R_p, and (c) double layer capacitance C_{dl}.

The cathodic disbonding test shows how the primer of the phosphatized steel substrate, sample Q, offers maximum adherence to the metallic substrate, while the primer applied to sample M (steel) has much lower adherence. This effect may be due to a good clamping process between the primer and the irregular surface caused by the phosphate process over the steel.

Accelerated cyclic tests show the excellent behavior of sample Q and much lower anticorrosion properties of sample M. Forty cycles do not affect the primer of sample Q (phosphatized), while delamination and blistering increase significantly in sample M (steel).

Primer quality seems to be increased to a significant extent when phosphatized steel was used, due to much lower primer permeability, much more stability at the interface, and greater adherence to the substrate.

Application Potential

Figures 10 a-c show the evolution of R_{po}, R_p, and C_{dl} versus time for samples M (190 V) and P (140 V) obtained by EIS after different exposure times to electrolyte. *Figures* 11 a-c show the evolution of the same parameters versus time obtained by the AC/DC/AC technique. The results presented in both figures show that sample P, with a primer that had been cataphoretically deposited at low potential, had greater resistances (R_{po} and R_p) but lower capacitances (C_{dl}) than sample M, where higher deposition potentials were used. The trend of these parameters is more stable in the case of sample P.

Sample P, where the primer was applied cataphoretically at low potential (140 V), showed greater resistance to pore formation and to the degradation process, due to electrolyte exposure, than sample M (190 V). As the time of exposure to electrolyte increases, there was a delamination process in both types of samples, especially at initial times. This process was more significant in sample M (190 V).

The cathodic disbonding test showed that when the primer is applied to the substrate cataphoretically with lower potentials, adherence is enhanced (sample P had better adherence than sample M).

Accelerated cyclic tests were able to confirm (results observed in blistering values at 20 and 40 cycles) that the quality of sample P is higher than that in sample M.

Primer quality was significantly increased when lower deposition potentials were used due to lower primer permeability, more stability in the interface, and greater adherence to the substrate. Higher deposition potentials in the cataphoretic process can produce an increase in hydrogen production at the metallic surface, which may be responsible for the lower quality of the primer.

CONCLUSIONS

An automotive epoxy primer was applied cataphoretically (using different times and potentials) and was studied by means of various electrochemical methods (EIS, AC/DC/AC, and cathodic disbonding) and by accelerated cyclic tests.

Primer quality results obtained with these four techniques coincided, although the AC/DC/AC and cathodic disbonding tests offered results in a shorter time (24 hr).

The best performance properties of the primer we studied were obtained when it was applied on phosphatized steel, deposited at low potential (140 V), and with the greatest thickness (25 µm). These substrates and deposition parameters produced minimum permeability in the primer, resistance to pore formation and to blistering, high adhesion, and a more stable coating-metal interface.

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