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**SURFACE MODIFICATION OF STEELS AND ALUMINUM ALLOYS TO CONTROL CORROSION AND HYDROGEN EMBRITTLEMENT - PART I: CHEMICAL METHODS**

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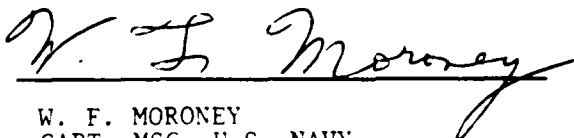
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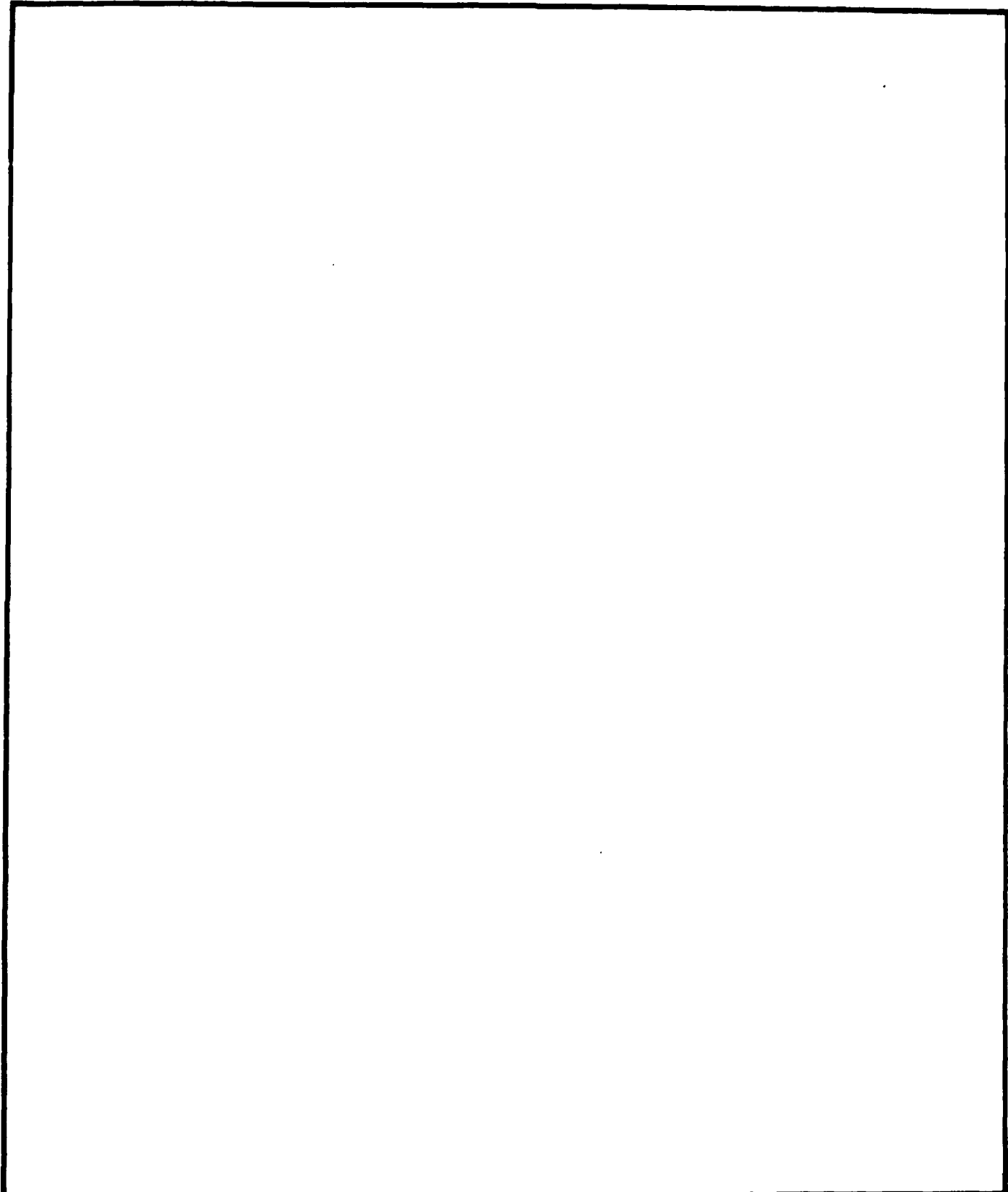
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<p>Surface modification to control corrosion and/or hydrogen embrittlement is approached in two ways: 1) treatment of the surface by chemicals, and 2) alteration of the electroplating process. This report describes the chemical modification of surfaces. Both a ferrocene derivative and a silane are used to prepare covalently bonded thin films on steels and aluminum alloys. The ferrocene should act as an electron reservoir whereas the silane should act as a barrier. Electrochemical properties were measured using potentiodynamic polarization and electrochemical impedance spectroscopy techniques. It was shown that the steels and an aluminum alloy which have good oxide coatings were covered more completely with the ferrocene than were carbon steels. Changes in potentiodynamic polarization scans indicated corrosion protection by the ferrocene coating on 4340 steel but not on 1018 steel. Electrochemical impedance measurements showed corrosion protection by the ferrocene coating on 7075-T6 aluminum. The electrochemical tests indicated that the silane gave corrosion protection to both 4130 and 1018 steel as well as to 7075-T6 aluminum.</p>					
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INTRODUCTION

Corrosion is an insidious process. It can take place under coatings, and in crevices as well as in direct view. It is also possible that the formation and absorption of hydrogen, which can lead to hydrogen embrittlement, will accompany corrosion. This, combined with stress or fatigue, can lead to catastrophic failure. Hydrogen can also be introduced during processing, such as electroplating. As naval aircraft operate in very severe environments, and under extreme mechanical conditions, the danger of very serious corrosion and/or hydrogen embrittlement problems is ever present. For these reasons, there is a continual need for seeking new ways to prevent or reduce corrosion and hydrogen embrittlement.

Because both corrosion and hydrogen entry take place at a metal's surface, modification of the surface is the best approach to alter these two processes. Surface modification can be either mechanical or chemical. Mechanical modification also has a chemical aspect, such as removal of oxides, before any type of coating or finishing is applied. Chemical conversion coatings, and inhibitors in general, all are forms of chemical modification. Specifically, in this work, chemical modification means the formation of thin films of large molecules, possibly polymers which have the ability to alter corrosion and hydrogen processes.

Conventional organic coatings used for corrosion protection can leave the underlying metal exposed to the environment when they are scratched. A modifying layer between the conventional coating and the metal can screen the metal's surface from direct contact with the environment. In recent years, there has been much activity in using thin films of electroactive substances to modify electrodes in order to enhance electron transfer<sup>1,2</sup>. As corrosion processes are electrochemical in nature, the principles of surface modification should be applicable to structural materials. Therefore, the objective of this research is to investigate the application of the technique of chemically modified electrodes to steels and aluminum alloys with the aim of inhibition of corrosion and hydrogen embrittlement.

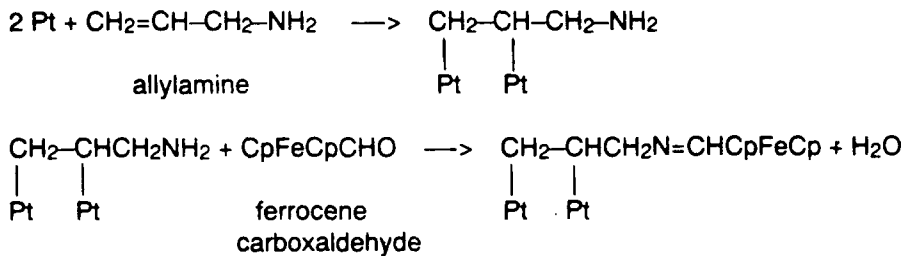
Chemical modification can be accomplished in various ways, such as, by attaching a thin film to a metal by adsorption or formation of a covalent bond. Various types of substances can be attached<sup>1,3</sup>. Some can act as barriers; others can have functional groups which can react with the environment. In either case, the underlying metal can be protected. These thin films, by themselves, would not have the capacity for protection in, say, a marine environment. They would, however, be useful under the thick organic coatings presently used, in the event of failure of the coating.

Two types of systems seem especially attractive from a corrosion/hydrogen viewpoint: one is an organic compound which can attach itself covalently, and possibly polymerize, thus covering the metal's surface, and which also has the potential to undergo oxidation-reduction; the other is a compound which can act as a barrier upon bonding covalently.

Corrosion is electrochemical by nature, i.e., it involves electron transfer. By attaching certain types of organic molecules to a metal, one can obtain systems in which electron transfer can be achieved through the organic chain, across organic chains, or between the organic chain and the metal. Systems of this type are reported to have very fast kinetics, leading to reversible oxidation-reduction systems<sup>1-4</sup>. This is due to the intimate contact between the organic molecule and the metal which eliminates the need for diffusional transport, thus giving a very high apparent concentration of the organic substance. In this way, it should be possible to produce systems which will resist metallic corrosion, using small quantities of the active agent.

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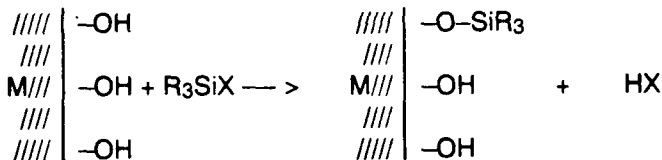
One such system is a ferrocene derivative attached to a metal. It has been shown that allylamine can be attached to platinum, and that ferrocene carboxaldehyde can react with this to form a ferrocene-metal complex<sup>4</sup>.



The expected surface structure is shown in Figure 1.

The ferrocene has a high electron density in the cyclopentadienyl rings which can act as an electron reservoir<sup>5</sup>. A typical current-potential curve is shown in Figure 2. The oxidation and reduction current peaks (upper and lower, respectively) are at essentially the same potential, indicating reversibility between the ferrocene and ferricenium states<sup>4</sup>. It is reasonable to assume that these reactions will proceed on steels as well as on platinum, thereby producing a system which should be able to offer corrosion protection by the above mechanism.

Silanes are good candidates as barriers toward corrosion of metals. All metals contain oxide layers which can be used as a bridge to the silane. If the metal is treated with acid, its surface becomes covered with hydroxyl groups which will react with halo- or alkoxy-silanes, such as



where X is a reactive group such as halo (e.g. Cl<sup>-</sup>) or methoxy (-OCH<sub>3</sub>). By choosing silanes having di- or tri-functionality, and by varying reaction conditions, multiple bonds can be formed to the metal. Also, cross linking through Si-O-Si bonds can be obtained<sup>2,6</sup>.

It has also been shown<sup>7</sup> that silanes not only improved corrosion resistance of steels, but also improved bonding of a polybutadiene coating. The latter is attributed to pi-bonding between alkoxy oxygens or ring systems in the silane and the double bonds in the coating. Bonding of this type can also be anticipated with the cyclopentadienyl groups in ferrocene. Also, by choosing appropriate derivatives of the silane, it should be possible to obtain both the barrier and electron transfer properties.

The properties of these films were investigated by various electrochemical techniques, such as potentiodynamic polarization and the state-of-the art method of electrochemical impedance spectroscopy (EIS). In the EIS method, the potential is varied in a sine wave, and the current response is recorded. The AC impedance, |Z|, which measures the resistance and capacitance components of the film under study, is plotted as a function of the frequency, f. It differs from DC measurements in that it provides additional information for time-dependent behavior of the interface in terms of, e.g., corrosion rate, which is indicated by the resistance at very low frequencies, the conductive nature of the film, and the ultra-fast reactions, such as obtained during electrochemical discharge and breakdown due to porosity of the film. The simplified electrical analog of the interface is shown in Figure 3. It has a double layer capacitance,

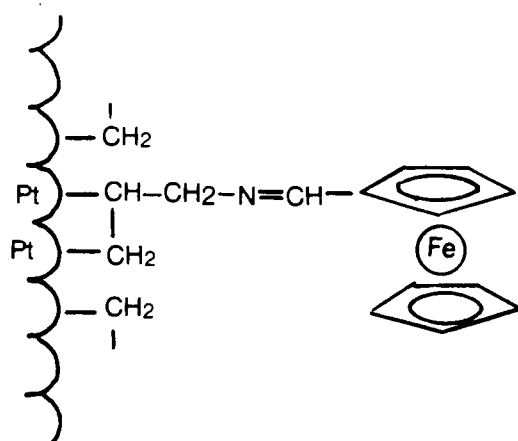


Figure 1. Structural configuration of Platinum-Ferrocene surface<sup>4</sup>.

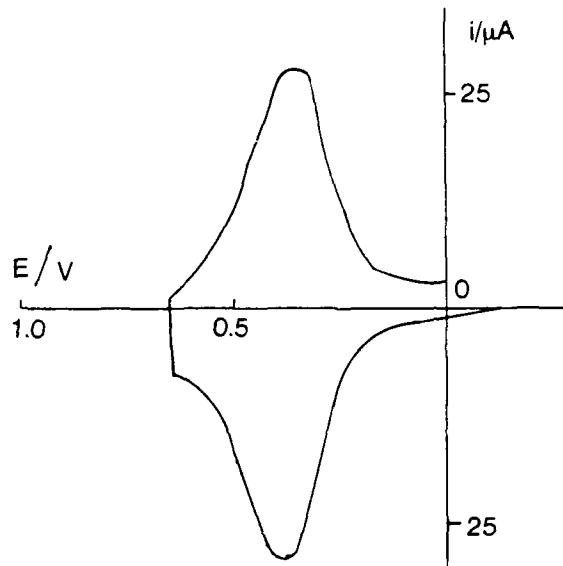


Figure 2. Current-potential curve for the Platinum-Ferrocene system<sup>4</sup>.

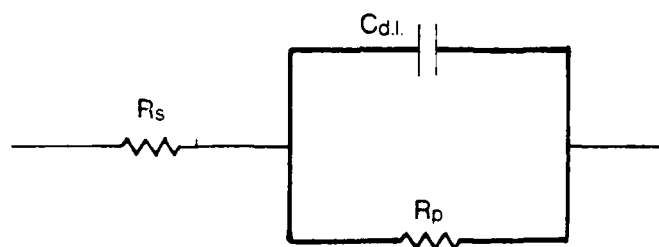


Figure 3. Equivalent circuit for a simple electrochemical cell.

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$C_{dl}$ , a polarization resistance,  $R_p$ , and a solution resistance,  $R_s$ ,<sup>8-10</sup>. An idealized Bode plot ( $\log |Z|$  versus  $\log f$ ) of this system is shown in Figure 4. This curve is essentially composed of three straight lines which can be used to determine the capacitance and resistance values. Extrapolation of the sloped line to 1 radian per second ( $\log \omega = 0$ ;  $\omega = 2 \pi f$ )

$$\text{gives } Z = 1/C_{dl}.$$

The upper horizontal line

$$\text{gives } Z = R_p + R_s.$$

The lower line

$$\text{give } Z = R_s.$$

The  $R_p$  is related to the protective coverage of a barrier coating; a high value means that coverage is good. The  $C_{dl}$  is related to the exposed electrochemical active area; a high value means that there is a large exposed area.

### EXPERIMENTAL

Several different types of specimens were used in these studies: Ferrovac iron and 1018 steel cylinders, 4130 and 4340 steel coupons, and 7075-T6 aluminum coupons. They were polished to 600 mesh using conventional methods, and degreased with methyl alcohol or acetone. The cylinders were attached to an electrode holder through a Makrides gasket for the electrochemical measurements; measurements were made on the coupons using clamp-on cells.

The specimens were treated with the modifying agent for measuring in the test solutions, or used in solutions of the modifying agent. All chemicals were of reagent grade quality. The silane was Union Carbide, Silane A-174, a tri-methoxysilane.

The allylamine-ferrocene was applied by dipping a clean specimen into 0.3M allylamine solution for five minutes, rinsing with methyl alcohol and air drying; then dipping into a 0.2 mM solution of ferrocene carboxaldehyde in ethyl alcohol at 60° C for 15 min, rinsing with methyl alcohol and air drying.

The silane was applied by dipping the specimen into a solution made up of equal volumes of silane, water and glacial acetic acid for 5 min, drying for 1 h at 60° C, and rinsing with water in an ultrasonic bath for 10 min.

A variety of electrochemical measurements were made on the treated and untreated specimens in different test solutions: potentiodynamic scans using the EG&G PAR 350 System; polarization scans using the Bell PEC-1/Scan 4 system; and electrochemical impedance spectroscopy (EIS) using the EG&G PAR 368-2 EIS software utilizing the models 273 potentiostat/galvanostat, 5208 lock-in analyzer, and Apple IIe computer. All electrochemical measurements were made using a saturated calomel reference electrode (SCE), where required, and all potentials are given versus the SCE.

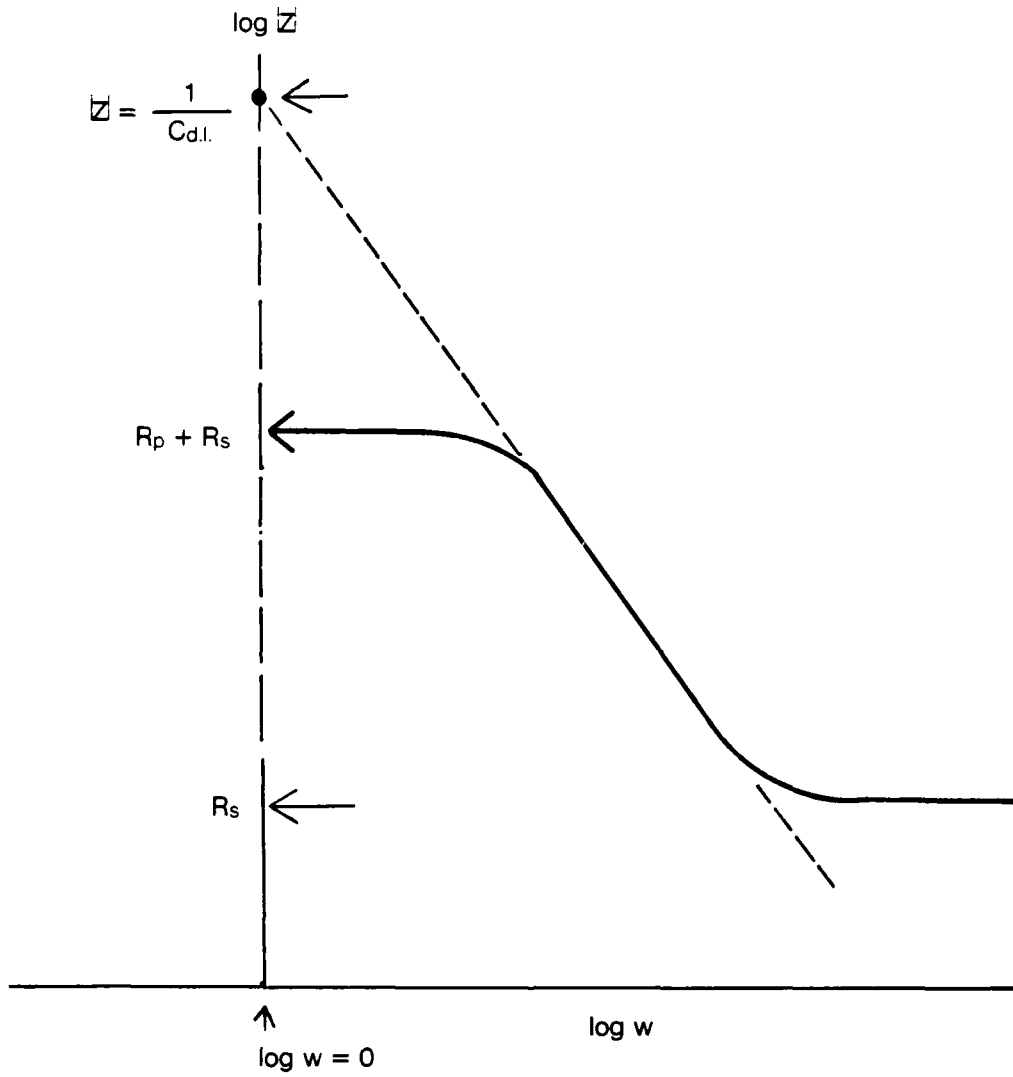


Figure 4. Idealized Bode plot.

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## RESULTS AND DISCUSSION

## POTENTIODYNAMIC POLARIZATION

Potentiodynamic polarization scans were run with steels in allylamine and ferrocene solutions. The scans were made from the open circuit potential in the cathodic direction, after which the electrode was allowed to recover before scanning in the anodic direction. Scanning rates were 0.5 mV/s. The results for 4340 steel in pH 10 NaOH solution as well as in 1 mM allylamine and 1 mM allylamine + 0.5 mM ferrocene carboxaldehyde are shown in Figure 5. The latter two systems were adjusted to pH 10 with NaOH. It can be seen that the allylamine not only causes a shift to a more noble potential, but also imparts passivity to the steel, which was not present with the NaOH alone. The addition of the ferrocene reduces the passivity region, however. Similar results were obtained with Ferrovac iron and 1018 steel.

These results show that the allylamine itself does have a beneficial effect, i.e., that of passivation. The addition of the ferrocene lessens the passive effect. The ferrocene solution by itself (at pH 10) gives the same results (not shown in Figure 5) as the NaOH. This experiment in an alkaline solution is not the same, however, as one with the ferrocene bonded directly to the metal-allylamine.

Potentiodynamic polarization scans were then run on steels with the bonded film. These scans were made from the cathodic to the anodic direction, at scan rates of 0.166 mV/s. Typical scans of 1018 steel, with and without an allylamine/ferrocene film, in a 1%, pH 6, NaCl solution are shown in Figure 6, and potential data are given in Table 1. As can be seen, the ferrocene coating results in a shift in the open circuit potential in the more active direction, and an increase in anodic currents. There is, however, a decrease in cathodic currents. During the cathodic polarization, the oxide layer on the bare metal is removed, thus making the surface more active. This can be seen in the more negative value of the potential at  $I = 0$  compared to that at open circuit (see Table 1). In the case of the ferrocene-coated specimen, the ferrocene is reduced during cathodic polarization, resulting in a more oxidizable species, thus having a more active potential after polarization (see Table 1). Thus, even though this system is more active than the bare metal, there may be protection by virtue of having an oxidizable coating.

Potentiodynamic scans were also made on bare 4130 steel and coated with allylamine/ferrocene and the silane. Typical scans of the steel in 1%, pH 6, NaCl solution are shown in Figure 7. Potential data are given in Table 1. Here also, as with the 1018 steel, the ferrocene-coated 4130 steel exhibits a more active potential after cathodic polarization (see Table 1). The potential of the bare metal, however, did not change, as the oxide coating is not easily reduced by cathodic polarization. The silane-coated steel, likewise did not exhibit a potential difference after cathodic polarization, as the coating is not electroactive.

The biggest difference in the results between the two steels is shown by the shift in the curves of the ferrocene-coated steels (see Figures 6 and 7). DeBerry<sup>11</sup> found that Polypyrrole could not be deposited onto iron or carbon steels, but could be deposited on stainless steels because of the need of an oxide film. A similar result is seen here. It is postulated that the allylamine-ferrocene is more tightly bonded to the 4130 steel than to the 1018 steel. The ferrocene-4130 steel system, though electroactive, is reversible, and thus exhibits a more noble open circuit potential than the less complete ferrocene-1018 steel system (see Table 1).

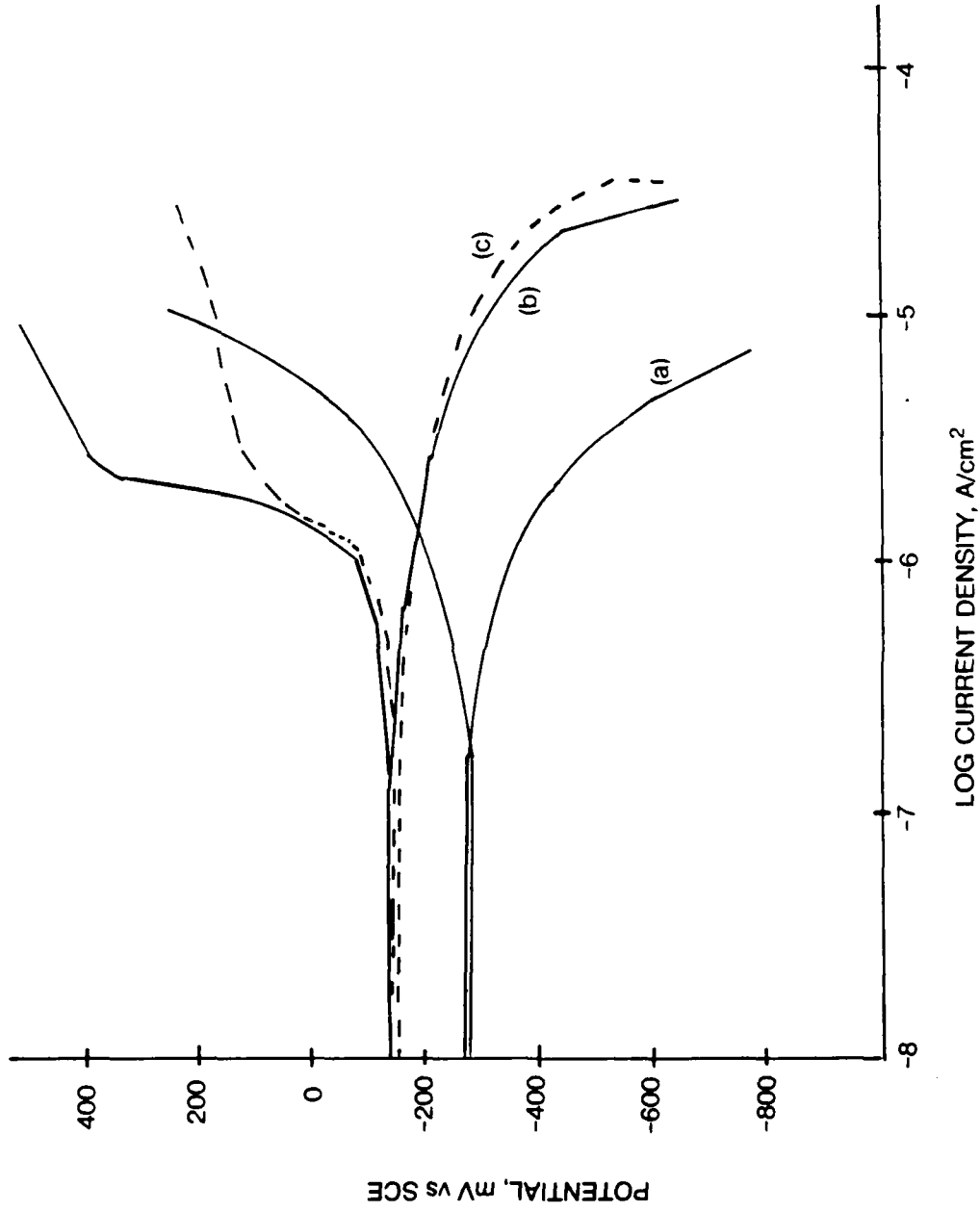


Figure 5. Potentiodynamic polarization scans of 4340 steel in a) pH 10 NaOH, b) 1 mM allylamine, and c) 1 mM allylamine + 0.5 mM ferrocene carboxaldehyde.

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Table 1. Polarization data for 1018 and 4130 steels, with and without coatings of ferrocene and silane, in 1% sodium chloride solution.

	Bare steel	Ferrocene-coated	Silane-coated
<u>1018 steel</u>			
Open circuit potential, mV	-555	-720	—
Potential at I = 0, mV	-750	-840	—
<u>4130 steel</u>			
Open circuit potential, mV	-570	-245	-470
Potential at I = 0, mV	-570	-375	-460

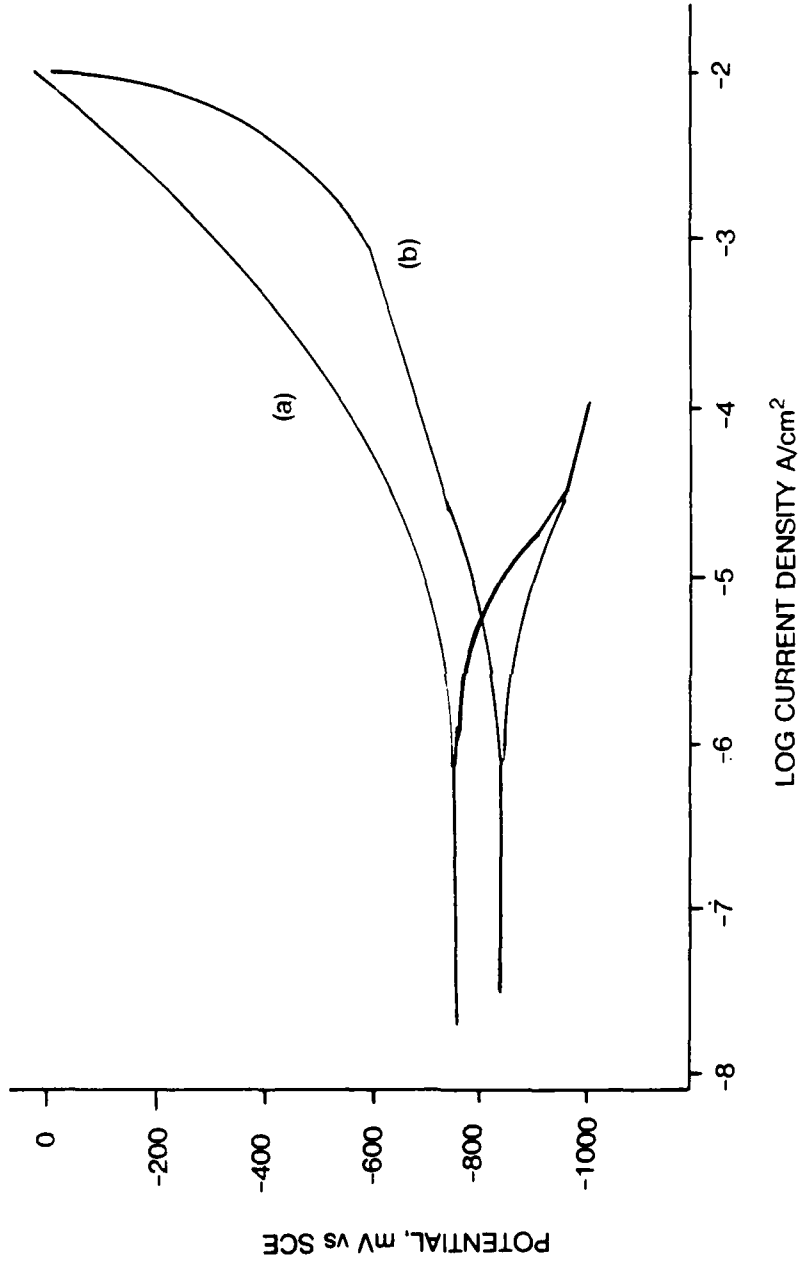


Figure 6. Potentiodynamic polarization scans of 1018 steel in 1% NaCl solution; a) bare steel and b) ferrocene-coated

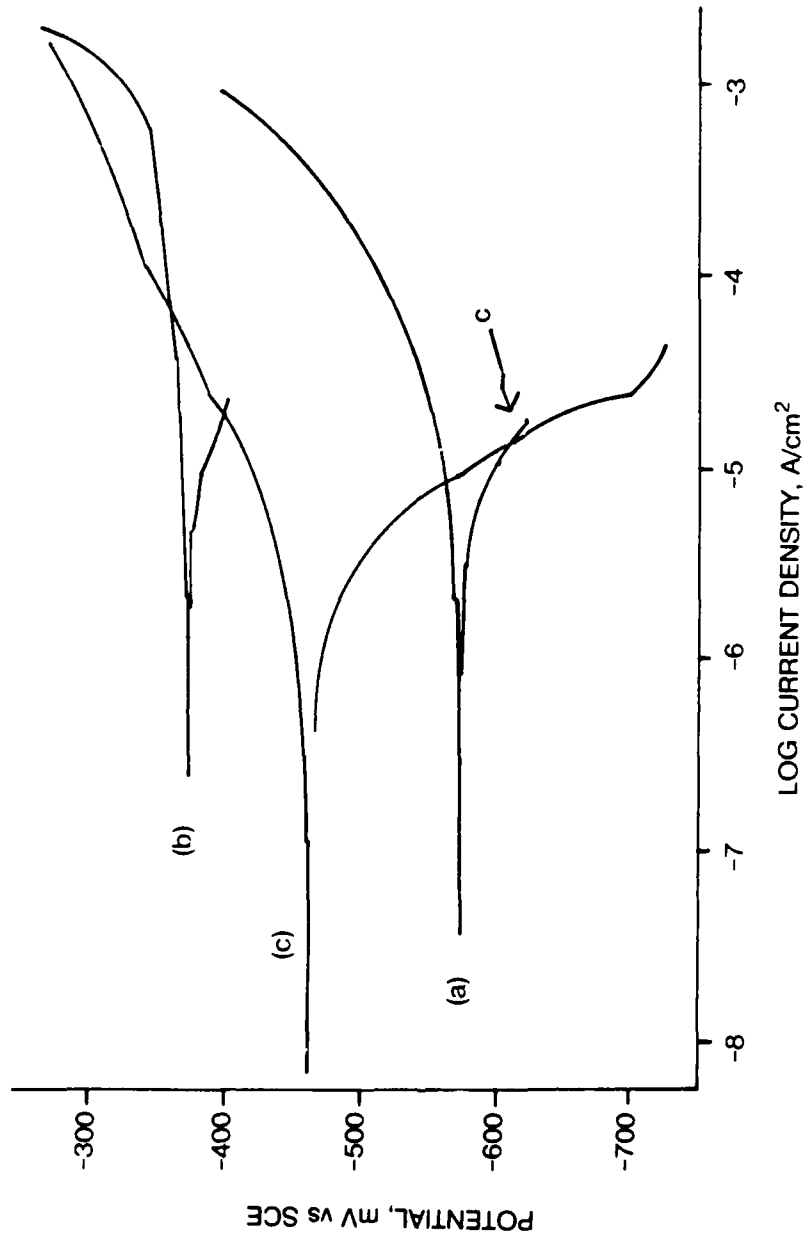


Figure 7. Potentiodynamic polarization scans of 4130 steel in 1% NaCl solution; a) bare steel, b) ferrocene-coated, and c) silane-coated.

## ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Because the potentiodynamic polarization method is damaging to the very thin films due to the large change in potential during testing, the less aggressive method of electrochemical impedance spectroscopy (EIS) was used. In EIS, the surface potential of the specimen is changed only 10 mv on either side of the open circuit potential. The EIS software uses the fast fourier transform technique (FFT) to generate a pseudorandom white noise waveform consisting of 20 frequencies from 0.01 to 1 Hz. Thus low frequency data can be obtained rapidly. The remaining data (6 Hz to 100 kHz) is obtained using the lock-in amplifier<sup>9</sup>.

EIS tests were performed on 1018 steel and 7075-T6 aluminum in 0.01M sodium sulfate, and in 3.5%, pH 2, sodium chloride solutions.

Figures 8 and 9 show typical Bode plots for the thin films on 1018 steel in 0.01M sodium sulfate and 3.5%, pH 2 sodium chloride, respectively. The curves for the ferrocene coated steel show little, if any, improvement over the uncoated steel. The silane coating shows marked improvement in both cases. Table 2 summarizes the polarization resistance and capacitance values obtained from these curves. The high  $R_p$  and low  $C_{dl}$  indicate good corrosion protection and good coverage with the silane. The ferrocene shows only slight improvement over the bare metal. As in the case of the polarization results discussed above, this is due to the electroactive nature of the ferrocene or the poor bonding to the 1018 steel.

Figures 10 and 11 show typical Bode plots for the thin films on 7075-T6 aluminum in 0.01M sodium sulfate and 3.5%, pH 2 sodium chloride, respectively. In the neutral sulfate solution, little difference is seen between the coated and uncoated specimens because of the good barrier effect of the natural oxide coating on the aluminum. (Note that the resistance values are in megohms.) In the aggressive acid-chloride, however, there is a marked difference. Table 2 summarizes the polarization resistance and capacitance values obtained from these curves. Improvements in both  $R_p$  and  $C_{dl}$  is seen in the acid-chloride environment. It was also noted that the aluminum alloy pitted, as expected, in the chloride solution, but both the coated specimens did not.

## CONCLUSIONS

When a well-adhering oxide exists on a metal (e.g. 4130 steel or 7075-T6 aluminum), the allylamine/ferrocene system bonds well; whereas if there is not a good oxide (e.g. 1018 steel), there is poor bonding. This was shown by: 1) coated 1018 steel exhibited more active behavior in potentiodynamic polarization tests than uncoated, whereas coated 4340 steel showed more noble behavior; 2) coated 1018 steel showed no change in electrochemical impedance measurements than uncoated; and 3) coated 7075-T6 aluminum exhibited greatly higher  $R_p$  and lower  $C_{dl}$  values than uncoated.

Silane acts as a barrier and improves the anti-corrosion properties of the steels and aluminum alloy. This was shown by: 1) coated 4130 steel exhibited a much more noble behavior in potentiodynamic polarization scans than uncoated; 2) coated 1018 steel showed greatly larger  $R_p$  and smaller  $C_{dl}$  values than uncoated; and 3) coated 7075-T6 aluminum also showed similar greatly improved  $R_p$  and  $C_{dl}$  values.

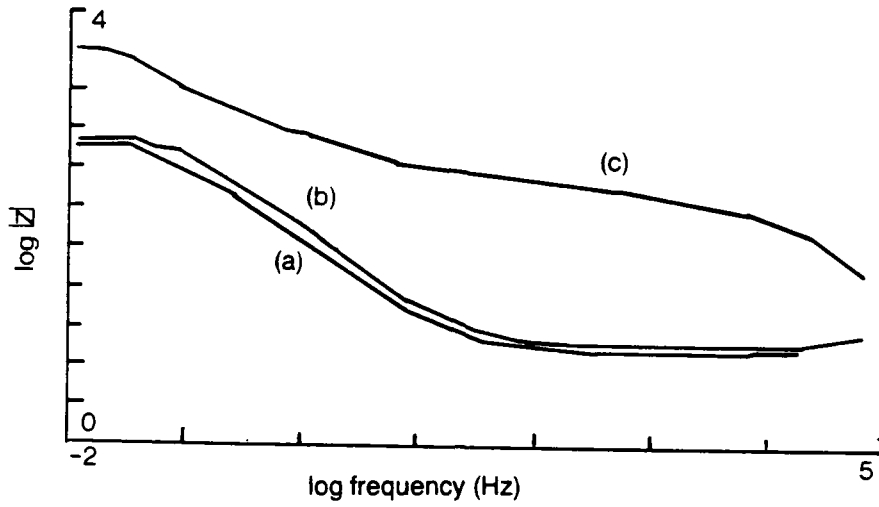


Figure 8. Bode plot of 1018 steel in 0.01M sodium sulfate solution; a) bare steel, b) ferrocene-coated, and c) silane-coated.

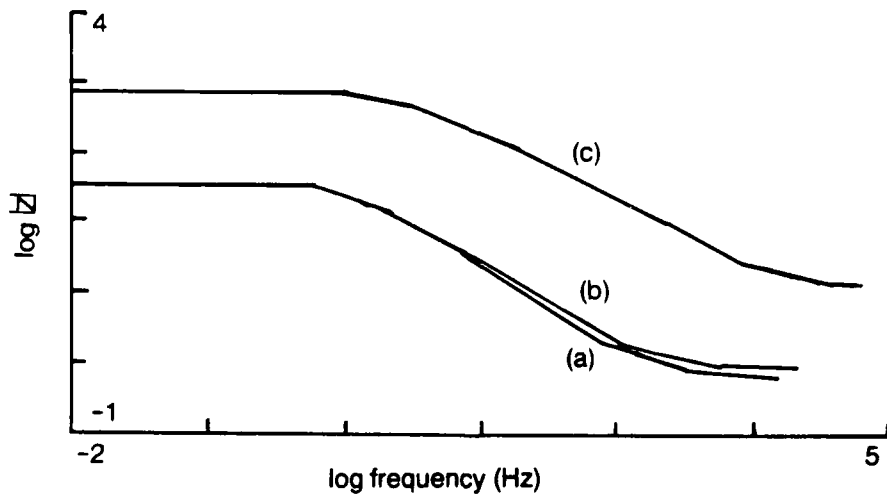


Figure 9. Bode plot of 1018 steel in pH 2, 3.5% sodium chloride solution; a) bare steel, b) ferrocene-coated, and c) silane-coated.

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Table 2. Effect of thin films on resistance and capacitance of 1018 steel and 7075-T6 aluminum.

<u>1018 steel</u>	Bare steel	Ferrocene-coated	Silane-coated
<u>In 0.01M Na<sub>2</sub>SO<sub>4</sub></u>			
Polarization resistance, Ohm	560	630	5,000
Capacitance, uF	3,700	2,800	660
<u>In 3.5%, pH 2 NaCl</u>			
Polarization resistance, Ohm	85	100	1,100
Capacitance, uF	1,000	890	32
<hr/>			
<u>7075-T6 aluminum</u>	Bare aluminum	Ferrocene-coated	Silane-coated
<u>In 0.01M Na<sub>2</sub>SO<sub>4</sub></u>			
Polarization resistance, M Ohm	4.0	0.89	5.5
Capacitance, uF	2.5	6.2	2.7
<u>In 3.5%, pH 2 NaCl</u>			
Polarization resistance, Ohm	96	7,400	6,000
Capacitance, uF	2,800	12	13

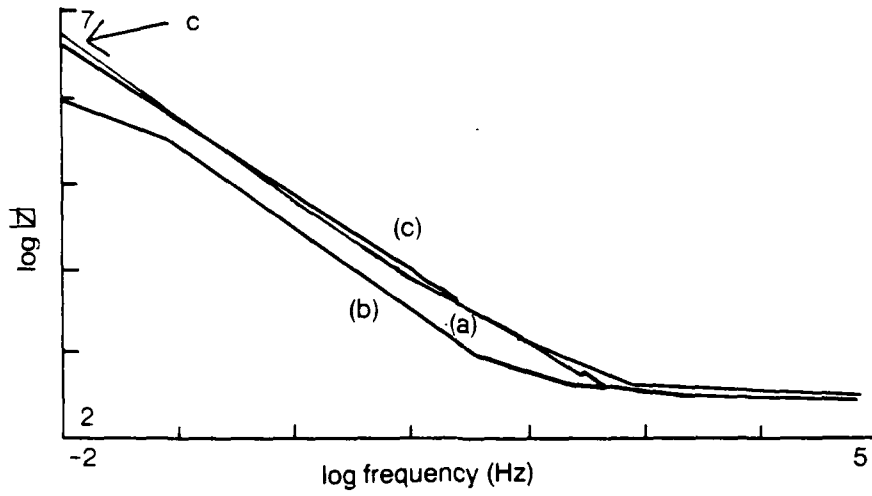


Figure 10. Bode plot of 7075-T6 aluminum in 0.01M sodium sulfate solution; a) bare aluminum, b) ferrocene-coated, and c) silane-coated.

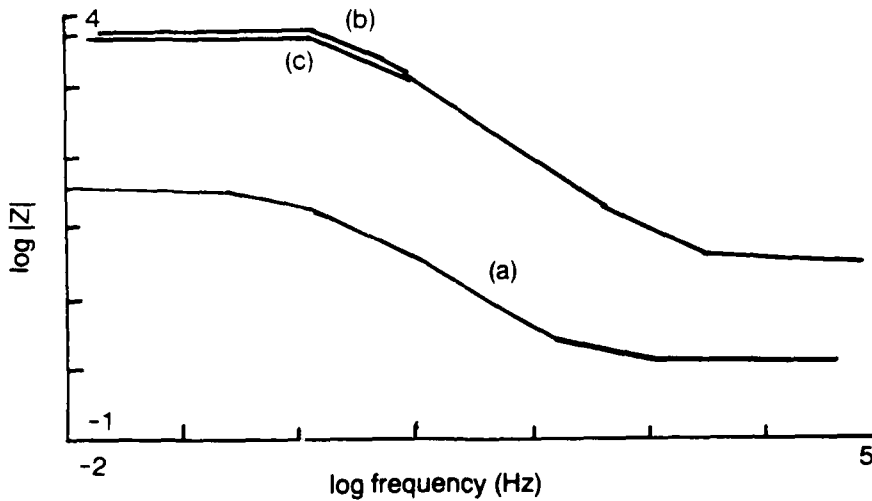


Figure 11. Bode plot of 7075-T6 aluminum in pH 2, 3.5% sodium chloride solution; a) bare aluminum, b) ferrocene-coated, and c) silane-coated.

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