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THE CORROSION BEHAVIOR OF OILY FILM CORROSION
PREVENTATIVE COMPOUNDS APPLIED TO 1018 STEEL

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by
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ABSTRACT

Many corrosion problems for Army transport vehicles initiate when the vehicles are transported through seawater environments for eventual active use. Exposure to highly-corrosive salt ions, namely chloride, that are abundant in these environments is nearly unavoidable during vehicle transport, and the resulting corrosion is often initiated on these vehicles before they are used in their intended application. Corrosion Preventative Compounds, referred to as CPCs, are a strategy used commonly as a temporary and outermost line of defense against corrosion during transportation and active use in the field. The protection that a CPC provides to the uncoated steel components is of interest because bare metal exposure is the most vulnerable path for the onset of corrosion in this corrosion system. Should the uncoated steel become subjected to seawater environments, the formation of corrosion product is quite rapid.

This study focused on using surface-based characterization techniques to examine the role that three commercially-available oil-based CPC types played in protecting 1018 steel surfaces from corrosion initiation in artificial seawater environments. The CPCs used in this research were water-displacing oil-based liquids that cured to form nearly-dry films on the steel surfaces. Surface chemistry techniques, FT-IR and XPS, were used to examine the as-applied CPC films prior to and after exposure to the corrosive environment. Electrochemical and corrosion methods were used to monitor the stability and eventual degradation of the CPC films and the substrate as a function of time of exposure to the corrosive environment.

This study resolved some uncertainties that surround the mechanisms of oil-based corrosion preventative compounds on low carbon steel. In general after initial immersion, the oil-based CPC films, hydrophobic by nature, acted as a temporary barrier to protect the substrate from the aqueous-based corrosion environment. After longer immersion times, the CPC films appeared to intermix with the initially-forming corrosion products to form an intermediate type of protective film that prevented the underlying substrate from further corrosion. Eventually, the CPC films degraded such that they no longer inhibited further corrosion. While similar in composition and general behavior,
the three different CPC types provided varying degrees of protection from corrosion to the 1018 steel substrate in the artificial seawater environment.
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**Figure 79.** Plots of a) corrosion potential and b) corrosion rate for the two different CPC application techniques, spraying and dipping, using the Blue CPC type. While the lines are shown as continuous, the measurements were not. Measurements were made each 24 hours and are labeled by immersion day. The control results are included for comparison. The solid straight line for b) indicates the failure criteria.

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LIST OF SYMBOLS AND ABBREVIATIONS

\( \theta_c \) receding contact angle degrees or °
\( \theta_a \) advancing contact angle degrees or °
\( \gamma_{lv} \) surface tension of water mN/m
\( b_a \) anodic Tafel slope
\( b_c \) cathodic Tafel slope
\( C \) capacitance of electrical circuit Ohms\(^{-1}\)
\( C_{dl} \) double layer capacitance Ohms\(^{-1}\)
\( E \) potential mV
\( E_{CORR} \) corrosion potential Volts
\( E_{OC} \) open circuit potential Volts
\( F \) force mN
\( I \) current Amps
\( i_{CORR} \) corrosion current Amps
\( i \) current density Amps/cm\(^2\)
\( i_{CORR} \) corrosion current density Amps/cm\(^2\)
\( i_{PASS} \) Passive current density (A/cm\(^2\))
\( P \) Perimeter of wetted plate length mm
\( R \) resistance of electrical circuit Ohms
\( R_P \) polarization resistance Ohms cm\(^2\)
\( V \) voltage Volts

AFM Atomic Force Microscopy
CE counter electrode
CPC Corrosion Preventative Compound
EIS electrochemical impedance spectroscopy
FT-IR Fourier Transform-Infrared Spectroscopy
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP</td>
<td>optical profilometry</td>
</tr>
<tr>
<td>RE</td>
<td>reference electrode</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>WE</td>
<td>working electrode</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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Chapter 1

1.0 Introduction

Corrosion commonly initiates on Army transport vehicles when they are transported through seawater-based environments to destinations for active use. If left unattended, corrosion of the vehicles can be detrimental to both budgets and personnel. The Army spends an estimated 2.5 billion dollars a year to mitigate wheeled-vehicle corrosion\[^1\]. Various strategies are in place to prevent corrosion of Army transport vehicles, including the use of specially formulated primers and paints. Corrosion Preventative Compounds (CPCs) are another type of strategy used commonly as a temporary line of defense against corrosion. In this case, CPC is a broad term that generally describes a hard or soft film that is applied to the vehicle’s steel and aluminum components to create an outermost barrier of protection against corrosive environments. The CPC approach chosen for this research uses a water-displacing oil-based liquid that is dispersed onto the vehicles prior to transport and also in the field via spray nozzles in the same manner and facility that the vehicles are washed. The CPCs included in this research are composed of a blend of light oils that are intermixed with corrosion inhibitor components. In cured form, a CPC layer is a nearly-dry oily-film that is dispersed across the entire surface of the transport vehicle.

This research focuses on the use of three different commercially-produced corrosion preventative compounds on unpainted 1018 steel substrates, the primary structural material used in Army vehicles. The protection that the CPC provides to the uncoated steel is of interest at this time because bare metal exposure is the most vulnerable path for the initiation of corrosion in this corrosion system. Should the uncoated steel become subjected to seawater environments (neutral, oxygenated, and chloride-containing aqueous solutions), the formation of corrosion products that lead to further substrate degradation is quite rapid. The unpainted substrates were also chosen because of the high complexity of the current CPC protection system. In order to understand the CPC, it is
first necessary to begin with the least complicated substrate system (bare metal), with continuing work using painted surfaces and creviced areas occurring at a later time.

The corrosion preventative compounds described in this research are organic-based and form a hydrophobic barrier on the metal surface similar to a free-standing barrier film formed by a self-assembled monolayer. The CPC layer that forms on the surface is thicker than a typical self-assembled monolayer (SAM); the manner in which the CPC layer forms on the metal surface (by self-assembly) and the function that the CPC serves (as a barrier to the metal applied prior to immersion in electrolyte) causes the CPC to favor characteristics of a SAM rather than a typical corrosion inhibitor. A typical corrosion inhibitor is adsorbed onto the metal surface after introduction into the electrolyte and remains on the surface by competing with aggressive ions in the electrolyte for metal adsorption sites. Previous research\(^2\) involving the CPCs in this research on 1018 steel showed that the CPCs do prevent corrosion, at least temporarily, by forming a barrier on the metal surface. Bulk chemical analysis of the CPCs suggested the presence of barium and calcium sulfonate corrosion inhibitor types. The ability of the film to prevent corrosion was monitored via comparative electrochemical techniques\(^2\). No information was obtained in previous research\(^2\) regarding how the CPCs actually function as a barrier at the metal interface before and after corrosion initiation.

Some uncertainties existed in understanding how the CPCs mitigate corrosion of low carbon steel in aggressive chloride-containing environments, such as seawater. This research focused on characterizing the CPC films after application to the 1018 steel substrate and their ability to provide corrosion protection against seawater. Although all three of the commercially-produced CPCs included in this work were similar in composition and function, they could be differentiated by their success in preventing corrosion initiation. The primary focus of this research was to obtain information about each CPC type by determining:

- The chemical composition of the as-applied CPC barrier film – using surface chemistry-based methods (FT-IR and XPS).
- Physical characteristics of the film on the substrate such as degree of hydrophobicity, continuity across the substrate, and thickness – using tensiometry and profilometry.
• The effectiveness of the CPC film in mitigating corrosion of the substrate when exposed to neutral seawater solutions – using surface chemistry-based methods (FT-IR and XPS) and electrochemical methods (corrosion potential monitoring, polarization resistance, and EIS).

• The differentiation of the two techniques, dipping and spraying, used to initially apply the CPC to the substrate in terms of their effectiveness in inhibiting corrosion.
Chapter 2

2.0 Background

2.1 Composition of 1018 Steel and Its Use

When considering the function of 1018 steel for the breadth of this work, it is used as a primary structural material for Army transport vehicles. In general, 1018 steel is a low carbon steel and is comprised of 0.15 – 0.20% carbon, 0.6 – 0.9% manganese, 0.04% phosphorous, and 0.05% sulfur, with the balance as iron. The vehicle, when completely constructed, is coated with a water or solvent-based paint and then an oily liquid termed a Corrosion Preventative Compound (CPC) to create outer layers of defense against corrosive environments. In general, 1018 steel and other low carbon steels corrode via uniform corrosion, although localized corrosion is common in regions where crevices are present. This study focuses on the onset of uniform corrosion only, as the incorporation of crevice corrosion problems is out of the realm of this research.

2.2 Corrosion of Low Carbon Steel in Seawater

Low carbon steel is known to readily corrode when exposed to moisture, whether in air or liquid form. Corrosion of iron begins with the presence of water and can be described in terms of the reactions taking place at the solution interface. Figure 1 depicts the general electrochemical reactions, both anodic and cathodic, taking place at these sites. For general corrosion, such as is the case for low carbon steel, the anodic and cathodic sites are said to be indistinguishably close and also change with time. The chemical reactions that take place when iron corrodes in neutral and aerated aqueous solutions can be represented as half cell reactions:
Anodic: Iron is oxidized to a ferrous ion as: Fe(s) → Fe^{2+}(aq) + 2e^− \quad (1)

Cathodic: Dissolved oxygen from the aqueous solution is reduced at the cathodic sites as:
H_2O(aq) + 1/2O_2(g) + 2e^- → 2OH^- \quad (2)

Cathodic: Hydrogen is reduced as:
H_2O(aq) + e^- → OH^- + 1/2H_2 \quad (3)

The cations react with the OH^- ions and dissolved oxygen in solution to form a variety of compounds that are termed “rust”\[^{[5,6]}\]:

Fe^{2+}(aq) + 2OH^-(aq) → Fe(OH)_2(s) (ferrous oxide) \quad (4)

Fe^{3+}(aq) + 3OH^-(aq) → Fe(OH)_3(s) (ferric hydroxide) \quad (5)

The most common form of rust is formed after liberation of water:
2Fe(OH)_3(s) → Fe_2O_3•H_2O(s) + 2H_2O(l) \quad (6)

Corrosion of carbon steel in seawater environments is more aggressive than in water environments. A seawater solution is high in chloride-based dissolved salts, which cause the solution to have a higher conductivity than water. It has been suggested that this increase in conductivity increases the rate of corrosion of iron\[^{[5-7]}\]. The increased conductivity (decrease in electrical resistance) allows the electrical current, I_{CORR}, between the anodes and cathodes to proceed faster and over longer distances following Ohm’s Law (V = IR). More anodic and cathodic reactions sites are thereby available to participate in the above corrosion reactions.
2.3 Corrosion Preventative Compounds and Corrosion Inhibitors to Mitigate Corrosion

The use of oils in combination with organic-based corrosion inhibitors has been cited in early corrosion handbooks\(^6,8\) as a means to temporarily protect steel surfaces from corrosion, especially during shipment and/or storage. Previous literature termed these compounds as “slushing compounds”, and current terminology refers to more advanced formulas as “Corrosion Preventing Compounds”, though indeed both compounds serve the same purpose and can be referred to interchangeably. The organic corrosion inhibitor components in the oil-based mixtures have been cited to include “organic amines, zinc naphthenate, various oxidation products of petroleum, and alkali and alkaline earth metal salts of sulfonated oils”\(^6,8\).

Corrosion preventative compounds are used to protect metals from potentially corrosive environments by acting as a barrier between the environment and metal surface. CPCs are also known to displace the corroding environment, such as an aqueous solution, from the metal surface by replacing the water-based environment with a hydrophobic surface film\(^9\). These CPCs are typically comprised of corrosion inhibitors and a material to transport the inhibitor to the metal surface, such as paint or oil\(^8,10\). The CPC, and thus inhibitor component, is always applied to the metal surface prior to immersion in aqueous solution. CPC’s can be a water-displacing soft or semi-solid film, or a water-displacing to non-water-displacing hard (solid) film. In most cases the composition of CPCs are proprietary\(^11\). Basic and limited composition information can be found in the Materials Safety Data Sheets (MSDS) and may include (i) an oil, grease or resin-based film former, (ii) a volatile, low surface tension carrier solvent, (iii) a non volatile hydrophobic additive and (iv) various corrosion inhibitors or surface active agents\(^12\). Water-displacing CPCs spread across the metal and leave a residue that acts as a barrier after the carrier solvent in the CPC has evaporated. In this research, only oily-film water-displacing CPCs are considered.

Organic inhibitors or CPCs that are attached to steel, or any metal substrate, prior to immersion into an aqueous solution are seldom mentioned in literature. CPCs act as a barrier to prevent corrosive environments from damaging the protective metal oxide
barrier. The CPCs referred to in this research are applied to the metal surface, allowed to ‘cure’ in the sense that the solvent within the CPC solution evaporates, and dried to form a nearly-dry oily film residue. Although these CPC materials are commonly used in practice, specific published studies focusing on the ability of a CPC-type barrier to slow the formation of corrosion products on metals are nearly nonexistent. Two studies, by Purry[10] and Shankar[13], refer to the use of CPCs on aluminum surfaces. In these studies the CPCs were investigated in terms of their effect on fatigue behavior and no electrochemical or corrosion properties were addressed.

The application of inhibitors to protect metals from corrosion in aqueous environments has been recognized for a long time[8, 14, 15]. A general definition of a corrosion inhibitor describes an inhibitor as “a chemical compound or their mixture, which when present in a corrosive system at a sufficient concentration, decrease the corrosion rate of metals without changing significantly the concentration of any of the corrosive reagents”[14-34]. The method in which the inhibitor controls corrosion is generally by changing the anodic or cathodic polarization behavior of the system, reducing the diffusion of corrosive ions to the metallic surface, and/or increasing the electrical resistance of the metallic surface. The effect of corrosion inhibitors is always caused by changes in the state of the metal surface being protected. These surface changes occur due to the adsorption of hardly soluble compounds formed with metal cations[14]. Corrosion inhibitors reduce the active surface area of a metal and/or change the activation energy of the corrosion process. The ability of the inhibitor to form complexes with dissolved metal ions plays a key role in the inhibition mechanism[35]. Inhibitors may decrease the anodic dissolution rate of metal by facilitating the formation and retention of a passive oxide film. Traditional, or “pickling”, inhibitors are added to the corrosive aqueous environment in small concentrations that then adsorb to a metal surface to replace aggressive ions and block the discharge of H⁺ and metal ions into the solution. CPCs differ in that they are a pre-treatment that adsorbs onto the metal substrate prior to immersion into the aqueous service environment. The corrosion preventing barrier is established independently from the aqueous solutions.
2.4 Corrosion Preventative Compound as a Self-Assembled Multilayer

The CPCs chosen for review in this study are all hydrocarbon-based and form a slightly-tacky oily film on the substrate surface after curing. The function and formation of the film on the metal surface can be likened to that of a self-assembled monolayer (SAM), but the CPC film is much thicker and considered to be a multilayer. SAMs of corrosion inhibitors have been previously studied on iron and iron alloys\[^{36-42}\]. The formation of SAMs is a spontaneous process that takes place by immersion of a substrate into a solution of surfactant molecules, where the molecules adsorb and self-organize onto the substrate surface to form a highly-ordered monolayer\[^{37, 43}\]. The SAM molecule typically consists of one functional group that attaches to the metal via chemisorption, connected to a long alkyl-chain backbone via van der Waals forces that assures the dense and ordered structure of the SAM, and then possibly one terminal functional group that determines the characteristics of the modified surface\[^{39}\]. The alkyl chain also can be in direct contact with the atmosphere via their CH\(_3\) terminal groups to provide a hydrophobic and often corrosion-resistant barrier\[^{37, 39, 44}\]. Results from previous bulk chemical analysis of the CPCs included in this research showed that the CPCs consist of branched-chain alkane molecules that adhere to the metal substrate via their functional groups\[^{2}\]. Since the CPC structure, and some corrosion inhibitor structures, is likened to that of a SAM, similar methods used for surface analysis of SAMs will be used to characterize the CPCs in this research.

2.5 SAMs to Inhibit Corrosion of Steel in Neutral Chloride-Containing Environments

Some work has previously been reported in literature for SAMs used as corrosion inhibitors on steel alloys in neutral chloride-containing environments, along with their corresponding electrochemical behaviors in solution. Felhosi performed several studies using alkane mono- and diphosphonates as self-assembled layers on iron\[^{37-39}\]. The major difference in behavior between the mono- and diphosphonates related to the surface film
structure formed. The monophosphonates formed a monomolecular layer that provided a hydrophobic surface. The diphosphonates formed a thin multi-molecular layer via intermolecular interactions between the phosphono groups. The multi-molecular layer was characterized as consisting of a first layer that was strongly bonded to the metal surface, while the other layers bonded more weakly via the attractive interaction between additional phosphonate groups. The first layer was of most interest, as it was the layer that determined both bond strength and structure via the metal/phosphonate interaction and the degree of ordering via the Van der Waals interaction between alkane chains\[39\]. Felhosi’s study aimed to determine the possibilities and limitations of “practical applications of SAMS for corrosion protection” in that the SAMs were assembled in neutral chloride-containing solutions on Armco iron rather than a pure metal\[39\]. Variables, including chain-lengths of the inhibitor molecules, inhibitor concentration, and immersion times, were explored. In an earlier Felhosi study, the diphosphonates were discerned to be primarily anodic inhibitors (primarily affecting the anodic reaction), and the assembly of the SAMs provided the best corrosion protection when first immersed in a solution with the electrolyte\[39\]. The inhibitor only adsorbed onto the iron in the presence of water, namely the dissolved oxygen in the water. In a later Felhosi study, the kinetics of the same SAM on the same metal substrate was studied. As the spontaneous adsorption of the phosphonate layers increased over time, the dissolution of iron correspondingly decreased. As the iron substrate remained immersed for longer periods of time, up to 3 days, the areas where iron was exposed to electrolyte decreased and the electrochemical results showed passivation of the surface\[37\]. A more recent study by Felhosi again addressed the same system, but this time focused on optimizing the pre-treatment of iron in the absence of the supporting electrolyte solution and addressed the self-healing properties of the formed SAM\[38\]. After formation of the SAM, the surface was scratched and the corrosion potential and impedance of the surface were monitored as the film reformed at the defect. The SAM did protect the iron from corrosion, if only temporarily for about 6 hours, after its immersion into sodium perchlorate solution\[38\].

The study of another SAM, alkanethiols, on pure iron in 0.5M NaCl was completed to characterize the suppression of the cathodic reaction of oxygen diffusion to
the metal surface\cite{40}. Nozawa formed the SAM on the surface of the iron using solvents and deaerated aqueous solutions after the oxide layer was removed from the metal surface. Thiols are known to adsorb to oxide-free metal surfaces, rather than adhering to the metal by adsorbing to the oxide layer as for silanes and phosphonates\cite{43}. The SAM was formed as a free-standing/as-applied protective film without the need for adsorption in an aqueous solution. While the alkanethiol-type SAMs were confirmed to be close-packed continuous monolayers via surface chemistry techniques, the monolayers did not withstand the aggressive NaCl environment\cite{40}. The effectiveness of the SAM barrier was directly related to the thickness of the monolayer, but ultimately all of the SAMs desorbed from the iron surface after immersion into the electrolyte. Electrochemically, the alkanethiol SAMs hindered the cathodic reaction, but actually stimulated the anodic reaction\cite{40}. Ultimately, the use of alkanethiols as a SAM in an aqueous environment is not realistic because the thiols require an oxygen-free environment to assemble and maintain their barrier properties.

A series of work by Aramaki and Shimura\cite{45-55} has long focused on the protection of iron in NaCl-containing aqueous environments, first with the use of traditional corrosion inhibitors\cite{53-55}. Self-assembled monolayer use, namely via carboxylate and hexadecanoate ions, then replaced traditional corrosion inhibitors in their research to protect iron\cite{45,51}. Most recently, they used the same carboxylate and hexadecanoate SAMs that were modified for conversion into polymer films to provide more permanent protection for the iron substrates against corrosion via chloride ions\cite{47-50}. Aramaki’s series of work, although ongoing, is an example of the evolution of methods of protection: from traditional corrosion inhibitors to SAM-based polymer films, for vulnerable iron substrates exposed to highly corrosive neutral chloride-containing environments.
2.6 Corrosion Preventative Compound Characterization using Techniques Employed for SAMs and Traditional Corrosion Inhibitors

Because the application and use of CPCs is more similar to a self-assembled monolayer than a traditional corrosion inhibitor, techniques to characterize the substrate/CPC interface can be borrowed from those used for traditional SAMs. Because many SAMs are often used to prevent corrosion, electrochemical techniques similar to those used to characterize traditional inhibitors are readily used for determining the degree of a SAM’s corrosion protection\(^{[37-40, 44]}\). With the same idea, the substrate/CPC/solution interface can also be characterized by electrochemical methods similar to those used for traditional corrosion inhibitors. In previous literature, CPCs have been examined exclusively as traditional corrosion inhibitors\(^{[11]}\), leaving a rather large gap in information regarding the condition of the protective layer prior to immersion into any corrosive environment. The characterization of the CPC film prior to and after immersion has not yet been considered in terms of its interfacial interactions, namely the chemical composition of the film prior to and after immersion. Special attention was made, in this body of work, to consider the behavior of the CPC film on the substrate both prior to immersion (as-applied) and after immersion and during subsequent degradation over time.

2.6.1 Electrochemical/Corrosion Perspective

The CPC film’s sole function is to protect a metal substrate from the onset of corrosion. Regardless of how the film is adhered to the metal, the measure of its degree of corrosion protection can be determined using electrochemical techniques. Various electrochemical techniques, as will be explored in this section, are used to determine different characteristics of the protecting film. The electrochemical techniques will all collectively provide information regarding the CPC’s ability to mitigate corrosion.
2.6.1.1 Open Circuit (or Corrosion) Potential

Open circuit potential ($E_{OC}$), also interchangeably termed corrosion potential ($E_{CORR}$), is a simple and essential technique for monitoring the state of a metal surface in an electrolyte solution. This method measures the overall potential value of the system at open circuit conditions (no external potential or current is applied prior to measurements)\cite{56}. For the general corrosion of a metal electrode, a more noble potential value compared to the corrosion potential of the control implies that the electrode is protected or corroding at a lower rate. Figure 2 illustrates the dependency that the overall corrosion reaction of a system has on the polarization of the cathodic and anodic reactions. Figure 2 is based on plots originated from Evans\cite{57,58} and Wagner and Traud\cite{59}. Shown in Figure 2, $E_{CORR}$ values correspond to where the anodic and cathodic current densities, $i_a$ and $i_b$, are equal. The shift to a more noble potential value is directly related to cases when the anodic reaction is more dominant and controlling of the corrosion rate, $I_{CORR}$.

Corrosion potential measurements accurately provide information that can be translated to the condition of the substrate, such as whether passivation or corrosion is occurring at the surface of the metal. Figures 3a and 3b depict the basic regions on a potential, $E$, versus time plot that are used to determine the state of the metal substrate immersed in electrolyte solution. This system used 1018 steel with and without a CPC film in a $\frac{1}{4}$-strength neutral artificial seawater solution. The identification of the CPC film in this plot is unnecessary for the technique explanation, as the general trend is the same for all CPCs within this current body of work. Figure 3a shows that after initial immersion, the metal electrode typically approaches steady-state...
potential values. In the case of the CPC-coated electrode, an initial steady-state potential value is reached when the protective film becomes stable at the solution interface. Shown in Figure 3b, once the film begins to degrade and corrosion products form on the electrode, the slope of the potential vs. time curve becomes negative. The potential approaches a more negative potential value similar to the potential of an electrode with no protective film. A second steady-state potential occurs when the CPC-coated electrode has been corroded (cathodic reaction controlled) and reached a correspondingly more negative corrosion potential value. As shown in Figure 3b, the final corrosion potential of the electrode with the CPC film approaches the less noble corrosion potential values of the control electrode (shown in Figures 3a and 3b), having no CPC film.

$E_{\text{CORR}}$ values are important to note prior to most other electrochemical measurements, mainly because understanding the state of the electrode (whether anodic or cathodic reactions are controlling or steady state conditions are occurring) prior to the other measurements is necessary in interpreting other subsequent measurements (such as EIS and polarization resistance). One distinct example of using potential measurements in tandem with other electrochemical techniques was Felhosi’s comparison of $E_{\text{OC}}$ values on different days as a means to compare corresponding impedance plots for corrosion behavior of the diphosphono-alkane SAM on iron\textsuperscript{[38]}. This comparison is depicted in Figure 4, where the values for $E_{\text{CORR}}$ and impedance (Z) on the Nyquist plots correspond to different days and corrosion behaviors. In this case the potential value increase was
caused by the adsorption of a SAM inhibitor to the iron surface and corresponding anodic reaction control. The potential results also showed that steady-state conditions existed at the time when the EIS measurements were made, thereby also verifying that the corresponding impedance measurements were not made during corrosion or another active disturbance in the corrosion cell. Two other studies by Felhosi also consistently used the measurement of corrosion potential to verify the other electrochemical results, namely changes in anodic polarization curves, polarization resistance values, and various EIS-based plots as a function of immersion time\[37, 39\]. A study by Stefenel examined the corrosion potential behavior of aluminum in the presence of phosphonic inhibitor types over short and long immersion times\[60\]. After short immersion times the $E_{\text{CORR}}$ became controlled by the anodic reaction (shift to a more positive value) because of oxide film growth, and while under longer immersion times $E_{\text{CORR}}$ values decreased (now more controlled by the cathodic reactions) due to competitive adsorption between the inhibitor and aggressive anion\[60\]. This trend is common for forms of general corrosion, especially low carbon steel types.

Figure 4. Example of using corrosion potential results in tandem with other electrochemical measurements. This comparison shows an increase in protective film as a function of time via an increase in corrosion potential (shown as “a” in the figure) and impedance on a Nyquist plot (shown as “b” in the figure)\[38\].
2.6.1.2 Polarization Resistance

Polarization resistance techniques using the dc linear polarization analysis method are commonly used to measure the corrosion rate of an inhibitor/metal system submerged in an aqueous solution as a function of immersion time. Potential is scanned (commonly ±10-20 millivolts vs. EOC) and the corresponding current is measured. This method is used to measure polarization resistance, $R_P$, (which is often converted to a corrosion rate) at a potential range that is close to the corrosion potential, therefore the measured currents are generally smaller than the corrosion current and the reactions proceed as they would naturally occur during the corrosion process. Because $R_P$ is the slope of the potential vs. current at the corrosion potential, it can be related to the corrosion current, $I_{CORR}$, by the Stern-Geary equation:\[^{[61, 62]}\]:

$$R_P = B/I_{CORR} = \frac{\Delta E}{\Delta I} \mid_{I \to 0} , \text{where} \quad B = \frac{b_a b_c}{2.3(b_a + b_c)}$$

Note that $b_a$ and $b_c$ are obtained from the Tafel slopes or estimated, as often in the case for inhibitor systems\[^{[7]}\]. The corrosion currents can be converted to current density, $i_{CORR}$, and also penetration rates, mm/yr, (using Faraday’s law).

This method for obtaining polarization resistance and corrosion rate has been used in various inhibitor and corrosion-inhibiting SAM studies. Polarization resistance via the linear dc method was used to quickly measure the effect that a solvent had on corrosion inhibition and the stability of the adsorbed SAM layer\[^{[39]}\]. The individual $R_P$ values were analyzed as a function of time, and the results were then related to corrosion potential results over the same time period. A study by El-Dahan used polarization resistance measurements in conjunction with both open circuit potential and potentiodynamic polarization techniques to determine the corrosion rate of aluminum with hexamine-halide inhibitor blends in HCl solution\[^{[63]}\]. This study concluded that the polarization resistance value, $R_p$, aided in the assessment of the ability of the material to resist corrosion. The polarization resistance value has also been recorded over time to understand the change in corrosion rate over a more extended substrate immersion.
time\textsuperscript{[22]}. Multiple other studies also utilized the polarization resistance method to determine corrosion rate of a material with different corrosion inhibitor concentrations in various solutions\textsuperscript{[31, 60, 64, 65]}.

### 2.6.1.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is an electrochemical method that can determine the dielectric properties of the surface film of an inhibitor. Measuring the electric response of the metal/CPC/solution interface to the applied AC signal over a frequency spectrum from \( \mu \text{Hz} \) to kHz reveals the surface film’s properties. The ‘Nyquist’ plot graphs imaginary and real components of impedance and is used to check for time constants (they are more obvious with this view) and monitor the overall behavior at the surface via the shape of the spectra. The ‘Bode’ plot graphs impedance and phase angle to understand the frequency dependence of the impedance data and the often the capacitance properties of the surface\textsuperscript{[66, 67]}. Previous work has shown that a high frequency capacitive loop on a Nyquist plot can be attributed to charge-transfer and properties of the oxide film. A low frequency loop relates to mass transport that occurs in the liquid phase as well as through the inhibitor layer on the metal surface, also related to hydrogen adsorption\textsuperscript{[23, 31, 34]}. Initial evaluation of time constants on impedance plots can be related to the nature of a surface film. For instance, the presence of only a charge transfer time constant relates to a fully-protective film, while the existence of both charge and mass transfer time constants can relate to diffusion of metal ions through the film and initiation of corrosion.

Values for charge transfer resistance and double layer capacitance can often be determined via EIS evaluation\textsuperscript{[66, 68]}. An equivalent circuit for the metal/inhibitor/solution interface is chosen, containing various R (resistance) and C (capacitance) elements corresponding to electrical circuit elements. The R and C elements can correspond to the polarization resistance, \( R_p \), and double layer capacity, \( C_{dl} \)\textsuperscript{[34]}. The \( R_p \) value is determined using data in the low frequency range of the
impedance magnitude, while \( C_{dl} \) is determined using data in the high frequency range. \( R_p \) is inversely proportional to the corrosion rate, and \( C_{dl} \) is considered proportional to the surface area not covered by the inhibitor\[^{34}\].

Examples of some equivalent circuits that have previously represented electrolyte/inhibitor/metal interfaces will be discussed. A study that measured the efficiency of an inhibitor, phosphono-alkane, that was applied prior to immersion into solution, \( \text{NaClO}_4 \), was performed by Felhosi\[^{38}\]. In the study, EIS methods were used to show the influence of inhibitor treatment time on the success of the phosphono-alkane inhibitor in preventing corrosion of iron. The longest treatment time, 4 days, exhibited the highest protection of the metal, likely due to the denser structure of the protective layer that formed over the longer period of time\[^{38}\]. Figure 5 displays Nyquist plots and corresponding equivalent circuits, where Felhosi looked at long-term corrosion behavior of the most successful inhibitor treatment.

Fig. 4. Equivalent circuit proposed to model the impedance response of SAM-covered metals. (a) Model of SAM-coated metal with structural disorders without charge transfer reaction and (b, c) model of SAM-coated metal with structural disorders in the presence of charge transfer reaction. \( R_s \): solution resistance, \( R_{SAM} \): layer resistance; \( Q_{SAM} \): frequency-dependent capacitance (CPE) of layer; \( R_{ct} \): charge transfer resistance, and \( Q_{dl} \): frequency-dependent capacitance (CPE) of the double layer.

Figure 5. Equivalent circuits and impedance data for inhibitor-coated iron immersed in \( \text{NaClO}_4 \) solution. The Nyquist plot represented the corrosion behavior of untreated and treated iron and compared the influence of inhibitor treatment time\[^{38}\].
Other studies used EIS to determine the condition of the metal surface. A study by Selvi concluded that an increase in inhibitor concentration decreased the capacitance of the double layer, suggesting that the inhibitor functioned by adsorption at the metal-solution interface\(^{[69]}\). This decrease in \(C_{dl}\) was noted to be a result from a decrease in local dielectric constant and/or increase in the thickness of the electrical double layer i.e. adsorption of inhibitor. The corrosion resistance of inhibitors as a function of immersion time in NaCl solution has been studied using EIS\(^{[23, 32, 66, 70]}\). In Montincelli’s study\(^{[70]}\) several inhibitors were compared and multiple equivalent circuits were used. In some of the above mentioned studies\(^{[69, 70]}\), the inhibitor was added to a solution and adsorption of the inhibitor to the metal substrate was shown to increase with time. In the case of the CPCs included in this body of research, the corrosion inhibiting components are adsorbed to the metal surface prior to immersion. The corresponding data should reflect a decrease in adsorption to the metal surface over time due to breakdown of the protective layer and onset of corrosion. Accurate equivalent circuit models are often difficult to define due to the changing nature of the CPC film and fact that the reactions do not occur homogeneously across the surface of the measured film, but rather the sum of the reactions is measured. In the case for the CPCs studied in this body of work, analysis of EIS methods will likely be more comparative and qualitative than quantifiable using models.

### 2.6.1.4 Potentiodynamic Polarization

Potentiodynamic polarization can be used to determine the electrochemical behavior of the adsorbed corrosion inhibitor-laden CPC film in regards to its effect on the anodic or cathodic reactions occurring at the metal surface. Corrosion inhibitors can be termed anodic or cathodic, in that they suppress either the anodic and cathodic reactions more dominantly. Potentiodynamic scanning involves applying a potential, usually either much more or less noble than the corrosion potential, to then measure the corresponding anodic or cathodic current reactions. Potentiodynamic scanning is destructive, as a higher or lower potential vs. open circuit potential is applied to the metal than in the dc
linear polarization resistance method such that the metal surface purposely becomes degraded. The potentiodynamic method is, therefore, not used for continuously measuring a single coupon’s corrosion behavior over subsequent immersion times in an aqueous solution, however measuring the potentiodynamic parameters as a function of immersion time is common.

For a CPC on a metal in neutral electrolyte environments, often qualitative information, rather than quantitative, is found suitable for system analysis. Tafel slope information can, in some cases, be extrapolated from the potentiodynamic curves to determine the corrosion rate of the metal system. In many cases, with corrosion inhibitors in neutral solutions containing oxygen, the criteria for obtaining useful Tafel slopes cannot be met and only qualitative comparisons can be made from the analysis\[^{71-73}\]. Scanning a system in the anodic direction relative to its corrosion potential provides information regarding oxygen evolution and active and passive corrosion stages of the metal. Typically the anodic Tafel slope value can be easily determined. Cathodic scanning would ideally provide separate hydrogen evolution and oxygen reduction reaction information; however, these two reactions are rarely able to be separated for neutral solutions containing oxygen. Due to the fact that the potential for 1018 steel in seawater solution is within the potential for oxygen reduction and hydrogen evolution, the effects of oxygen greatly overshadow the effects of hydrogen evolution\[^{74}\] and the cathodic Tafel slope value is difficult to legitimately determine.

Potentiodynamic polarization is a common criteria sought for evaluating both traditional and SAM-based corrosion inhibitors. Several studies\[^{37-39}\] used both anodic and cathodic potentiodynamic methods to better understand the effects of phosphonoalkane inhibitors as they adsorbed to iron in a neutral solution of NaClO\(_4\). Figure 6 displays the potential vs. current density (in log notation) plot for anodic and cathodic polarization measurements for the corrosion cell above. The more noble shift in corrosion potential, as compared to the control system without an inhibitor film, depicted a surface where the anodic reaction is suppressed (corrosion is not occurring or slow to occur)\[^{39}\]. In this example in Figure 6, the cathodic reaction did not change with the addition of a self-assembling corrosion inhibitor layer largely due to the overwhelming
affects of the oxygen reduction reaction. In this example, the corrosion reaction is controlled by a more dominant anodic reaction.

Other research that involved fully assembling a corrosion inhibiting film on a metal surface prior to immersion into a corrosive environment has used potentiodynamic scanning as a tool to determine the quality of the SAM. In Nozawa’s work, an alkanethiol SAM was assembled onto iron and measured for its protection from corrosion via both anodic and cathodic potentiodynamic scanning\(^4\). Nozawa concluded that the cathodic reaction was actually somewhat suppressed, but the anodic reaction became more active and corrosion readily ensued. Ultimately the alkanethiol SAM, as assembled by Nozawa, needed to be further modified if it was to provide adequate protection from corrosion. A recent study by Shimura and Aramaki used SAMs of \(p\)-toluene and \(p\)-hydroxymethylbenzene moieties on iron with and without an oxide layer to examine their protective properties in oxygenated NaCl solutions\(^7\).

Shimura’s work noted that the polarization curves lent favor for extrapolating Tafel slopes, shown in Figure 7 with the \(-90^\circ\) angle lines connecting the anodic and cathodic reactions. Both the anodic iron

Figure 6. Polarization curves of iron in solution of 0.1 M NaClO\(_4\), 1) without and 2) with \(5 \times 10^{-4}\) M 1,7-DPH after 1-hr immersion\(^3\).

Figure 7. Anodic and cathodic potentiodynamic polarization scans of \(p\)-toluene and \(p\)-hydroxymethylbenzene-based SAMs on iron, where the Tafel slopes were extrapolated to obtain the corrosion current density, \(i_{CORR}\)\(^7\).
dissolution reaction and oxygen reduction cathodic reaction were claimed to be suppressed. Further examination of the plot in Figure 7 leads to the conclusion that the conclusions regarding the cathodic reaction could not have been made since all of the cathodic reactions were basically the same and followed the general path of the oxygen reduction reaction. In this case, the Tafel slope information for the cathodic reactions was not actually legitimate.

2.6.2 Surface Chemistry Perspective

A CPC’s ability to mitigate corrosion depends heavily on how the CPC is adsorbed onto the 1018 steel surface. Characterization of the intact surface film, as well as the morphology or degradation of the film after initial immersion into artificial seawater solutions and after corrosion is initiated, will be performed using surface chemistry techniques.

2.6.2.1 Fourier Transform-Infrared Spectroscopy

In general, FT-IR is used to identify the composition of materials in solid, liquid, or gas form, specifically the strength of the bonds between atoms and the structure of the molecule. As explained by Bray and Sibilia, FTIR analysis is “based on the fact that molecules have specific frequencies associated with internal vibrations of groups of atoms...When a sample is placed in a beam of IR radiation, the sample absorbs radiation at frequencies corresponding to molecular vibrational frequencies, but transmits all other frequencies. An IR spectrometer measures the frequencies of absorbed radiation, and the resulting plot of absorbed energy versus frequency is called the IR spectrum of the material.” Each chemical structure, including functional groups, has its own characteristic vibrations that act as ‘fingerprints’ in identification. Also, shifts in these characteristic band energies provide information regarding the compounds formed on a
material surface\textsuperscript{[32]}, namely the presence of an organic corrosion inhibitor film on a metal substrate for this research.

FT-IR, in adsorption mode, is commonly used to characterize the adsorption of SAMs on a metal surface. Much research has been completed for SAMs on pure metal surfaces, such as gold, platinum, and aluminum\textsuperscript{[42, 77, 78]}. More recently, SAMs have been assembled onto metal alloys for corrosion inhibition purposes and have been evaluated using FT-IR. Several studies have used FT-IR to examine the inhibitor/metal interface prior to and after immersion in electrolyte. Most notably are the following that will be discussed. Monticelli studied the corrosion inhibition of steel in chloride-containing solutions via sodium $\beta$-glycerophosphate (GPH)\textsuperscript{[70]}. Ultimately Monticelli concluded using IR spectra that the GPH anion bridged two surface cations and “produced a surface polymeric complex”\textsuperscript{[70]}. Figure 8 displays the molecular structure of this inhibitor and the attachment of it to the metal surface, where the metal cations are bound to a single P atom via O atoms. IR analysis also showed that the GPH was found to adsorb in

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig8.png}
\caption{Structure of the surface chelating complexes formed by chemisorption of GPH\textsuperscript{[70]}.}
\end{figure}

the presence of CaOH solution and not NaOH, suggesting that GPH is chemisorbed on steel as a surface calcium complex\textsuperscript{[70]}. In another previous study, Sherif identified the adsorption of 1,5-naphthalenedion (ND) on aluminum via FT-IR\textsuperscript{[79]}. After immersion of the aluminum substrate into NaCl and ND, FT-IR results showed that the hydroxide groups on the ND interacted with O atoms of the aluminum oxide via hydrogen bonding\textsuperscript{[79]}. One study, by Manov, was the only study found to compare IR spectra of the bulk SAM molecule and then the corresponding metal treated with the corrosion inhibiting SAM, in this case zinc and 2-hydrazono-3-bornanemethylenedithion disodium salt (MDS)\textsuperscript{[30]}. In the IR spectra, shown in Figure 9, characteristic bands could be compared for the bulk material and then the metal after the bulk was assembled to the metal. Manov suggested that since the treated zinc did not exhibit the characteristic band
for ZnO, the protective film consisted of an organometallic compound (adsorbed inhibitor attached to the metal). Manov could not determine if the C=N- or –NH₂ groups on the MDS, shown in Figure 9, functioned as chelating bonds³⁰.

![Figure 9. IR spectra of the organic molecule MDS (structure shown to the right) in aqueous solution and of the treated zinc (1.35×10⁻² M MDS, 2 h, 60°C)³⁰.](image)

### 2.6.2.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a technique used to detect the presence of different elements and their corresponding states on the surface of a material. When a material is exposed to x-ray-induced photons, element-specific photoelectrons that originate from an atom’s discrete electronic energy levels are emitted⁸⁰. Of the different energies emitted, the binding energy, Eᵱ, is used for diagnostics and is plotted against intensity. XPS determines the oxidation states of elements, which provides structural information of organic molecules⁶⁸. XPS instrumentation can detect all elements from lithium to uranium. The sensitivity of XPS is between 0.01 and 0.5 atomic percent, with a sampling depth of 0-10nm and lateral resolution of 15μm.
Several studies have used XPS to determine how corrosion inhibitor molecules are attached to a metal surface. In one study by Fang\textsuperscript{[81]}, amino-trimethylidene phosphonic acid (ATMP) was shown via both XPS and FTIR methods to attach to the Fe\textsuperscript{2+} atoms on the oxide layer on A3 mild steel via N and O atoms from the ATMP. This conclusion was made using changes in binding energy. When the Fe\textsuperscript{2+} atoms coordinated with the N and O atoms, the electron cloud of the N and O atoms in the ATMP molecule partially transferred to the Fe\textsuperscript{2+}[81]. This transfer directly related to a decrease in binding energy for Fe\textsuperscript{2+} and an increase in binding energy for N and O atoms. Thus, reasonable conclusions could be made regarding the attachment of the ATMP corrosion inhibitor to the steel via N and O atoms. Cicileo\textsuperscript{[32]} used XPS, in conjunction with FT-IR, to confirm that the composition of two corrosion inhibitors, salicylaldehyde and benzilin oxide, were the same after 1 day or 9 days of substrate immersion, while the thickness of the film did increase with time. In Cicileo’s study, XPS spectra was taken on the un-inhibited copper metal immersed in 0.1M NaCl and the substrate immersed in the inhibitor-loaded NaCl solutions. XPS showed that the inhibitor molecules prevented photo-electron emission from the copper surface due to the blocking effects of the surface-adsorbed layer\textsuperscript{[32]}. A study of alkylthiol and alkylamine-based SAMs on 316L stainless steel used XPS in conjunction with FT-IR to verify the attachment of thiols and amines\textsuperscript{[42]}. Ruan used XPS to target known elements, namely S-based peaks (S\textsubscript{2p3/2} and S\textsubscript{2p}), to identify the presence and oxidative stability of the sulfur-anchored film\textsuperscript{[42]}. Nozawa performed a similar study with an alkylthiol SAM on iron, in which XPS spectra was measured for targeted elements as a function of sputtering time\textsuperscript{[40]}. Figure 10 shows the resulting evolution of spectra vs sputtering time, where the Fe peaks increased and the O, C, and S peaks decreased as the ion beam penetrated through the SAM and into the bulk iron. The author concluded from this data and previous work that the SAM was adsorbed on the surface by the formation of iron thiolate.
XPS has been used to study the presence and composition of an inhibitor film on steel in neutral NaCl solutions\textsuperscript{15,35,40}. All of these studies analyzed the steel surfaces prior to and after immersion in NaCl solutions to try to identify how the inhibitors were attaching to the substrate. Welle\textsuperscript{15} compared intensities of the various signals, including Fe\textsuperscript{2p}, C\textsuperscript{1s}, Na\textsuperscript{1}, O\textsuperscript{1s}, and N\textsuperscript{1s}, on both bare and N, N'-dimethylethanolamine (DMEA)-treated steel prior to and after immersion in NaCl. In this case, conclusions were made that the Cl\textsuperscript{−} ions attacked the iron oxide and formed soluble ionic iron compounds\textsuperscript{15}. Using this previously well-known and confirmed information, further analysis of the addition of the corrosion inhibitor led to observations that the inhibitor adsorbed onto the iron oxide surface, reacting with hydroxyl groups and removing ionic species that cause corrosion and creating a passive film. Sastri\textsuperscript{35} performed a similar experiment using imidazole (C\textsubscript{3}H\textsubscript{4}N\textsubscript{2}) as the inhibitor on steel. By analyzing binding energies for treated and untreated steel coupons, the steel was thought to be “covered with a layer of iron sulfide or oxide which, in turn, was covered by a thin layer of Fe bonded to C\textsubscript{3}H\textsubscript{4}N\textsubscript{2} and bisulfide moieties”\textsuperscript{35}, as pictured in Figure 11. The inhibitor layer was therefore thought to prevent corrosion by preventing dissolution of the lower iron sulfide or oxide layer on the metal.
2.6.3 Physical Characteristics Perspective

Determining the physical nature of the film on the surface of the metal after curing can provide insight into other factors that may affect the success of a CPC in mitigating corrosion. For instance, the CPC film thickness could have related to the success of the CPC barrier and therefore could not be ignored. Also, the consistency of the CPC across the metal surface is likely strongly related to the onset of corrosion. Contact angle measurements determine the uniformity and hydrophobicity of the CPC film after curing. Microscopy techniques, namely using the optical microscope and CCD camera attachment prior to measuring FTIR spectrum, and photography recorded the visual CPC film appearance prior to and after the onset of corrosion. Although simple techniques, visual representations of the condition of the CPC film have proven to be as valuable as the other characterization techniques in the bulk chemistry and initial electrochemical study\textsuperscript{[2]}. 

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Figure 11. Schematic depicting the interface between iron and \( C_3H_7N_2 \) inhibitor\textsuperscript{[35]}. 

\[
\text{Fe (Metal)}
\]
2.6.3.1 Film Thickness – Optical Profilometry and Atomic Force Microscopy

The CPC films in this body of research, when cured on the metal surface, are not solid, but rather form a semi-tacky and oily film. Methods to measure the thickness of the CPC film must accordingly account for the liquidity of the film. Optical Profilometry (OP) uses the reflection of a light source on a substrate surface to determine its topography. This technique is useful if the apparatus is able to differentiate between the transparent CPC film and the bare metal surface, which is not possible for all optical profilometer types. Only one study was found that mentioned using OP for determining the thickness of an oil-based surface film[82].

Atomic Force Microscopy (AFM) can be used in intermittent contact mode (a dynamic imaging mode) to obtain the topographical information necessary to determine the film thickness. AFM uses a cantilever that holds a sharp probe tip to scan the surface laterally, while vertical movements of the tip are recorded simultaneously to produce a resulting 3-dimensional image of the surface[83]. In the case of the CPC film, AFM was used to measure step-height to obtain the film thickness. Several studies were found that used AFM to monitor film thickness and topography of lubricating oil films on metallic surfaces[84, 85]; however, none used AFM in the same manner as chosen to measure the CPC film thickness.

2.6.3.2 Film Homogeneity and Hydrophobicity - Contact Angle

Contact angle methods are well-known to provide information regarding the homogeneity and hydrophobicity of the outermost atomic layers of a surface[86-88]. This technique, specifically the Wilhelmy balance tensiometry (or plate) method, uses advancing and receding water contact angles to measure the hydrophobicity and overall homogeneity of a surface. As a general rule for SAMs, a high advancing angle, \( \theta_a \), of \(~70^\circ\) or greater equates to a hydrophobic surface[89], with values more commonly near \(~110^\circ\)[90, 91]. \( \theta_a \) values of \(0^\circ\) relate to a completely hydrophilic surface, while values between \(10^\circ\) - \(30^\circ\) are more common[89]. Hysteresis, defined as (\(\cos\theta_r - \cos\theta_a\)), relates to
the homogeneity of the surface. A small value of hysteresis equates to a homogenous surface, while a large hysteresis of about 1.0 relates to an incomplete surface layer\textsuperscript{[92]}. This criteria is used in nearly all surface characteristic SAM-based studies\textsuperscript{[42, 78, 90, 93]}, but rarely in SAM studies that also focus on the electrochemical nature of the SAM film\textsuperscript{[40]}.

Contact angle is relatively easily measured and often an initial indicator as to the success of a SAM in mitigating corrosion. For instance, if a SAM-coated surface is found to be discontinuous and generally hydrophilic, then the likelihood that the SAM will successfully suppress electrochemical reactions in later evaluations is much less. A study of organosilane-based SAMs on AA2024 began with unfavorable contact angle results; however, the study continued with electrochemical measurements although they were predicted to be also unfavorable, and rightly so\textsuperscript{[90]}. The author continued with the study to then study more about why the SAM failed, rather than continuing to prove its success. Ruan used contact angle measurements to first optimize the assembly method for the alkythiol and alklyamine SAMs on stainless steel\textsuperscript{[42]}. After a successful method was determined, contact angle measurements were used to verify the close-packed structure of the SAM in relation to carbon chain-length, surface roughness, and other selected variables. A study by Laibinis used contact angle measurements to compare the structural integrity of alkanethiol-based SAMs on copper after exposure to air\textsuperscript{[93]}. Over time, the advancing and receding angles decreased, and an increase in hysteresis occurred. The author suggested that the decreases were likely due to a decrease in homogeneity of the film, as part of the SAM was thought to convert from thiolates to sulfonates\textsuperscript{[93]}. The increase in hysteresis as a function of exposure time also reflected an increase in heterogeneity, thought to be due to the same conversion of thiolates.

**2.6.3.3 Visual Techniques**

Visual techniques, including microscopy and photography, are simple and imperative means to correlate electrochemical and surface chemistry analysis. Prior to FT-IR scanning, a photomicrograph can be taken using a CCD camera to record the condition of the point of interest being measured. After subsequent immersion into
electrolyte, the visual condition of the film on a metal substrate can be related to
electrochemical behaviors prior to, during, and after the onset of corrosion products.
Often in corrosion studies, the degree of corrosion on a metal surface dictates the criteria
for failure. Maximum values of corrosion rate and polarization resistance can be first
correlated to visual results to later use when measuring only electrochemical properties of
a metal. Studies involving SAMs and corrosion inhibitors have often used visual
techniques to enhance their arguments for success or failure against corrosion
mitigation[11, 36, 44, 94-97].
Chapter 3

3.0 Experimental

Various techniques were used to apply and characterize the CPC films on 1018 steel. Characterization of the CPC films consisted of using surface chemistry techniques for the as-applied films, and surface chemistry and electrochemical techniques for the immersed and degrading CPC films. The parameters used for each technique are described first, followed by a description of the experimental plan that used these techniques for characterization of the as-applied and immersed CPC film.

3.1 Materials

3.1.1 CPC Types

Three commercially-available CPC types were characterized in this research. Two of the CPC types, both known commercially as CP90 or T-32 depending on end-use application, originated from CarWell Inc. The third CPC type, Corrosion Block, originated from Lear Chemical Research Group. To simplify identification, the CPC types (shown in Figure 12) were described by their color, Red (CP90), Brown (CP90), and Blue (Corrosion Block), throughout this research. CPC types Red and Blue are approved for MIL PRF 81309F (Performance Specification: Corrosion Preventative Compounds, Water Displacing, Ultra-Thin Film)\(^98\). The MSDS for each CPC type merely listed the products as a proprietary blend of ultra pure synthetic and organic hydrocarbons, or a mixture of petroleum hydrocarbons\(^99, 100\). Bulk chemical analysis was previously completed to distinguish the CPC types\(^2\). Table 1 displays the

![Figure 12. CPC types in bulk form by color from left to right: Brown, Red, and Blue.](image)
basic compositional information that was previously obtained for further use in this body of work.

Table 1. Known\(^{[2]}\) compositional information for the CPC types studied in this research.

<table>
<thead>
<tr>
<th>CPC Type</th>
<th>Components</th>
<th>Viscosity (cStokes)*</th>
<th>Oxygen concentration</th>
<th>C-H chain length distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brown</td>
<td>C, O, Ca, Si, S, Na</td>
<td>67.5</td>
<td>~50% branched aromatic w/ oxygen and alcohol groups, branching of other elements</td>
<td>15-44, highest concentration: 15-20</td>
</tr>
<tr>
<td>Red</td>
<td>C, O, Ba, Si, S, Na</td>
<td>46.3</td>
<td>&lt;1% branched aromatic w/ no oxygen, oxygen groups on backbone, branching of other elements</td>
<td>48-66, highest concentration: 56-60</td>
</tr>
<tr>
<td>Blue</td>
<td>C, O, Ca, Si, S, Zn</td>
<td>32.1</td>
<td>~2% branched alcohol and aromatic groups w/ no oxygen, branching of other elements at MW ~38+</td>
<td>8-28, 38-54, and 56-72</td>
</tr>
</tbody>
</table>

* Viscosity was experimentally found not to significantly affect the corrosion inhibiting abilities of the CPCs, and details are included in Appendix 3.

3.1.2 Substrate

The 1018 steel (Type A Panels 1018 steel from KTA Tator, Inc.) is used with a 100-grit Al\(_2\)O\(_3\) surface finish in the end-use application to manufacture Army transportation vehicles, thus much of the electrochemical evaluations within this research use this surface finish. In some cases, especially for surface chemistry techniques that are surface roughness sensitive, FT-IR and XPS, the coupons were polished using up to a 1200 silicon carbide wet paper grit. Surface finish will be designated, but generally will be known to be the 100-grit finish for most electrochemistry measurements and the polished finish for surface characterization measurements. The 1018 steel coupon size for use in all experimental techniques was 38mm x 50mm x 3mm, unless otherwise noted.
3.1.3 Corrosion Test Cell

The same type of test cell and electrolyte solution were used for all open-to-air immersion-related techniques. Due to the non-solid nature and resulting contamination probabilities of the cured CPC films, a semi-disposable barnacle-type cell was produced. The cell consisted of a plexi-glass body with an outside diameter of 31.75mm and inside diameter of 25.4mm (McMaster Carr) for convenient visual examination. A 9.52mm thick plexi-glass coupon mounting plate (McMaster Carr), nitrile o-rings (with an outside diameter of 31.75mm and inside diameter of 25.4mm obtained from O-Rings West), and rubber bands (Kenner Rubber Co.) were used to apply enough pressure between the cell body to create a leak-proof seal. For electrochemical experiments, a graphite rod counter electrode, CE, (Alfa Aesar) was used, along with a saturated calomel electrode (SCE) as the reference electrode, RE (Gamry Instruments). Figure 13 displays a photograph of the test cell, where the counter and reference electrodes could be mounted easily between the rubber band gaps during electrochemical measurements. The electrolyte consisted of ¼-strength artificial seawater solution. The artificial sea-salt was mixed with deionized water in ratios according to the manufacturer’s instructions (ASTM D-1141-52, Formula A, Table 1, Section 4 from Lake Products Company, Inc.) to make full-strength artificial seawater solutions that were then diluted to ¼-strength solutions. Although the ¼-strength solution is not typically used, the dilution from full-strength solution functioned to slow down the inevitable corrosion of the coupons, both CPC treated and untreated, so that the corrosion reactions could be more carefully studied over time. The ¼-strength artificial seawater solution was an electrolyte concentration agreed upon by the sponsor of this research.

A paint cell type electrochemical cell was used for the polarization measurements performed in deaerated ¼-strength artificial seawater solution. The paint cell
configuration included a glass cell body that was 15cm high and had a test surface area of 69.4cm² (9.4cm diameter), a nitrile o-ring with 9.1cm inside diameter and 9.6cm outside diameter, a plastic base-plate, and a metal clamp. A rubber stopper (VWR) was modified to seal the bubbler for N₂, SCE reference electrode, and graphite counter electrode into the top of the glass test cell body. The working electrode (WE), 1018 steel treated or untreated, was located at the bottom of the test cell, sandwiched between the o-ring and the base plate. The N₂ source was from a N₂ tank that was attached through a pressure regulator directly to the N₂ bubbler via plastic tubing. Figure 14a displays the test set-up for the polarization experiments using deaerated ¼-strength artificial seawater, where the N₂ bubbler had been transferred from the bulk deaerated solution to the test cell. Figure 14b displays a closer image of the test cell, that includes the CE, RE, WE, and bubbler locations. Deaeration of the bulk ¼-strength artificial seawater solution was performed for approximately 45 minutes prior to addition to the paint cell. Deaeration of the solution in the paint cell continued during electrochemical measurements.

Figure 14. The test set-up for the electrochemical cell using deaerated ¼-strength artificial seawater electrolyte is shown in a). The set-up includes a N₂ tank that is connected to a bubbler and air outlet via hosing, and the electrochemical cell (paint cell type with glass cell, plastic base plate, and screw clamp). The paint cell set-up, shown in a close-up photograph in b), included a rubber stopper that was modified to seal the bubbler, CE, and RE to the top of the cell. The working electrode, WE (1018 steel coupon), was clamped to the bottom of the glass cell. The leads for the CE, RE, and WE, shown in b), are connected to the computer-controlled potentiostat.
3.2 Preparation and Application of CPCs to 1018 Steel

Three methods, dipping, spraying, and spin-coating were used to apply the CPC to the metal surface. The dipping method was originally used for CPC application in laboratory settings and was the method recommended by partners (Concurrent Technologies Corporation) initially involved in this research topic. For the dipping method, metal coupons were fully immersed into the bulk CPC for a limited time (1.5 minutes on each side), and then the coupons were hung vertically to allow excess CPC to drip from the substrate. The coupons were allowed to cure at ambient conditions for 48 hours. After curing, the coupons were rinsed with a stream of deionized water and allowed to dry. The specific procedure used for the dipping application method is described in Appendix 1. The dipping application method was used to apply CPCs for electrochemical evaluations in this research.

The spray method used a combination of pressurized air and bulk CPC to apply the CPC coating across the coupon surface. To apply the CPC to Army transport vehicles, the CPCs are typically sprayed onto the vehicle surfaces. The spray technique is used in an effort to conserve bulk CPC and due to its ease of application. The coupons were hung vertically during CPC application, then placed horizontally in containers for transport, and finally hung vertically to cure at ambient conditions for 48 hours. The coupons were then rinsed with deionized water and allowed to dry after curing. Figure 15 is a photograph of the spray gun used in this research (nozzle is part# 62240-60° from Spraying Systems Co.). A detailed procedure of the spray application method is described in Appendix 1. Spraying was used to apply CPCs for electrochemical, surface chemistry, film thickness, and hydrophobicity evaluations in this research.

Figure 15. Photograph of the spray gun system used to apply CPCs to the 1018 steel coupons.
Spin-coating was used to apply the CPCs for XPS measurements. In order to obtain interfacial elemental component information via XPS, a thin CPC film was required. For the spin-coating method, the substrate was rotated at 1200rpm and 2-3 drops of the CPC was released onto the substrate. The substrate was rotated for 60 seconds after the CPC was applied. The spin-coated metal coupons were hung vertically to cure at ambient conditions for 48 hours, rinsed in deionized water, and then dried prior to use.
3.3 Characterization Techniques

3.3.1 Fourier Transform-Infrared Spectroscopy (FT-IR)

FT-IR was used to obtain chemical information about the composition of the as-applied CPC films prior to and after immersion in electrolyte. FT-IR was performed at the Materials Research Institute at the Pennsylvania State University using a Bruker IFS 66/S FT-IR Spectrometer. The 15X reflection objective and absorption mode were found to be optimal for all FT-IR-based measurements of the CPCs investigated in the research. The resolution of the absorbance scan was 8cm⁻¹, with a scan time of 200 scans between 4000-600cm⁻¹ (mid-IR). The lateral resolution was defined as an 80µm² spot in all cases. To obtain adsorption units, background subtraction was performed using the reference spectra for a polished and untreated 1018 steel control coupon.

3.3.2 X-ray Photoelectron Spectroscopy (XPS)

XPS was used to obtain information about the elemental components and percent composition of the as-applied CPC films prior to and after immersion in electrolyte. XPS spectra were recorded at the Materials Research Institute at the Pennsylvania State University (Kratos Ultra XPS, Kratos Instruments) using an Al K-alpha x-ray source. Lateral resolution was 15µm and the sampling depth was up to 10nm. The survey scans were taken at a pass energy of 80eV with a step size of 1.0eV and at a binding energy range of 1350 - 0eV. High resolution scans used a pass energy of 20eV and step size of 0.25eV at binding energies typical for C, O, Zn, Ca, Ba, Na, Si, and S as indicated necessary by the survey scan. Spectra were referenced to the C1s peak using a binding energy of 285.0eV. High resolution results used linear background subtraction prior to peak synthesis using the instrument software. Sample size constraints and issues with
magnetization inside the measurement chamber for the XPS (the 1018 steel coupons are inherently magnetic and they physically shifted towards the magnetic field once it was activated during measurements) caused the coupons to be smaller in size than for the other evaluation methods: 10mm x 20mm x 3.2mm.

3.3.3 Wilhelmy Balance Tensiometry

The Wilhelmy balance tensiometry method was used to determine the homogeneity and hydrophobicity of each surface type. Measurements were performed for polished and grit-blasted 1018 steel coupons with and without CPC spray treatment. The coupons were immersed in the test solution of distilled-deionized (18.2MΩ-cm) water using the Wilhelmy balance, a computer-controlled instrument (Camtel CDCA 100, Royston, UK) at The Pennsylvania State University. The balance was calibrated with standard weights. The measurements were made at ambient laboratory conditions. Polystyrene beakers with 10ml of test solution were used. Advancing and receding contact angles were calculated from the last of three immersion and emersion force
measurements respectively to account for variability often shown in the first contact with the test solution. Contact angle and hysteresis information were extracted from the measured data using a force-balance equation corrected for buoyancy (by extrapolation to zero volume):

\[ F = P \gamma_{lv} \cos \theta \]

Where \( F \) is the force in mN (varies with each measurement), \( \gamma_{lv} \) is the surface tension of water at 71.9 mN/m at 25 °C, \( P \) is the perimeter (wetted length) of the metal plate (23.5 mm, for a thickness of 2.5 mm), and \( \theta \) is either the advancing (\( \theta_a \)) or receding (\( \theta_r \)) contact angle. Figure 16 displays a schematic of the Wilhelmy method, where hydrophobic and hydrophilic surfaces are shown as examples. Data manipulations were made using the instrument’s software.

### 3.3.4 Optical Profilometry and Atomic Force Microscopy

Optical profilometry (OP) using a light source and atomic force microscopy (AFM) were used to measure the thickness of the semi-tacky oily CPC films prior to immersion. In general, thickness was obtained by measuring the step height between the bare 1018 steel surface and the CPC film. A narrow piece of tape was adhered to the surface of the coupons prior to treatment in order to act as a resist from the CPC during application. A portion of the tape was removed to expose the bare metal when measurements were made.

For the OP technique, the treated coupon was scanned from the top to the bottom of the coupon with an 80μm optical probe (Micro Photonics, Inc). The coupon top refers to the end of the coupon that was at the top when the coupon was hung vertically during curing. The scan collected 2-dimensional data, height variations across the length of coupon, as one single and continuous line. During the testing, the optical profilometer suffered mechanical problems that rendered the apparatus useless; therefore this apparatus (although successful at obtaining CPC film thickness) had to be abandoned for
the remainder of this research. Prior to mechanical failure, thickness data was obtained for the Brown CPC type that was applied to the 1018 steel coupons (grit-blasted surface finish) using the dipping method.

For the AFM technique, in order to create a measurable surface (solid enough to withstand the intermittent contact of the AFM tip), a ~50Å thick Au coating was applied to the cured CPC film surfaces. The tape resist was taken off of the substrate prior to Au-coating so that the step-height between the untreated and treated surfaces could be directly compared. The CPC films tended to bleed at the interface between the tape and film, even after Au-coating, because the films remained in liquid form. Step heights were measured on areas that best represented the interface, although the conditions were not ideal (interface between the untreated and CPC-treated surfaces was not as sharp as desired). In most cases, contiguous areas were scanned via AFM and the difference between the substrate and CPC film were determined, excluding the interference of the less-than-ideal interfacial areas. While using the AFM, the oily CPC film did not remain under the Au-coating, and the liquid CPC wetted the cantilever and interrupted the measurements. Results for thickness using AFM were obtained for the Brown CPC type that was applied to the 1018 steel coupons (grit-blasted surface finish) using the spray method.

3.3.5 Electrochemical Methods

All electrochemical measurements were taken and recorded with Gamry PC4 and PCI4 type potentiostats and integrated computer systems and Echem Analyst software (Gamry Instruments). The electrochemical measurements were made at ambient laboratory conditions using ¼-strength artificial seawater electrolyte.
3.3.5.1 Corrosion Potential

The corrosion potential, $E_{\text{CORR}}$, was initially measured until the CPC/steel system reached a steady-state potential in $\frac{1}{4}$-strength artificial seawater electrolyte solution (approximately between 1500 seconds to 6000 seconds depending on CPC type). $E_{\text{CORR}}$ values were also measured each immersion day to verify steady-state conditions prior to making further electrochemical measurements.

3.3.5.2 Polarization Resistance

Polarization resistance measurements were made by scanning the potential from $\pm 0.015\text{V}$ vs $E_{\text{CORR}}$ immediately after a steady-state potential value was reached and measuring the corresponding current response. This method is considered non-destructive due to the low voltage applied. Data was analyzed by plotting potential, $E$ (versus SCE), against current density, $i$, and measuring the slope of the linear region approximately $\pm 0.010\text{V}$ from $E_{\text{CORR}}$. Figure 17 is an example of the region included in analysis. If the entire range of data was not linear, then the linear portion at zero current was used. The measured slope, $\Delta E / \Delta i$, was inserted into the Stern-Geary equation:

$$R_p = \frac{B}{i_{\text{CORR}}} = \frac{\Delta E}{\Delta i} \Big|_{i=0} , \text{ where } B = \frac{ba bc}{2.3(ba + bc)}$$

Values of 0.100 were chosen for $ba$ and $bc$. $i_{\text{CORR}}$ was converted to penetration rates (corrosion rates), in mm/yr, using Faraday’s law and the following equation:

$$\text{mm/yr} = K_1 \text{EW} \left( \frac{i_{\text{CORR}}}{\rho} \right)$$

Where $K_1 = 3.27 \times 10^{-3}\text{mm·g/μA·cm·yr}$, $\rho = 7.87\text{g/cm}^3$ for the iron, and EW = equivalent weight (W/n = molecular weight/# of electrons) at 27.92 for iron. The corrosion rate values were monitored as a function of immersion time. An increase in corrosion rate
related to an increase in corrosion product formation on the surface and decrease in protective nature of the CPC film. A corrosion rate of 0.040mm/yr was chosen as an upper limit for coupon failure; the reasons for it will be described later in this section.

![Polarization curve](image)

**Figure 17.** Example of a polarization curve where a potential, ±0.015V vs ECORR, is applied and only the linear region ±5-10mV vs. ECORR is used to measure the $\Delta E/\Delta i$ slope. The solid gray line represents the measured data, the line with the x-marks on either side is the region selected to calculate the slope, and the dashed line is the best fit line based on the selected slope. The $\Delta E/\Delta i$ slope is used to measure corrosion rate in mm/yr. The plot measured 1018 steel treated with a CPC and immersed in ¼-strength artificial seawater.

### 3.3.5.3 Electrochemical Impedance Spectroscopy

EIS was performed at ECORR as a function of immersion time. The amplitude of the applied signal was ±10mV (peak to peak), with frequency ranging from $10^4$ to $10^{-2}$Hz at a rate of 7 points/decade. The Bode plots (the modulus of impedance versus frequency) were used to measure the increase or decrease in impedance values as a function of immersion time. The decrease in impedance reflected the decrease in surface protection from the CPC film. Nyquist plots were used to determine the presence of the different time constants and monitor changes in them as a function of immersion time.
3.3.5.4 Potentiodynamic Polarization

Anodic and cathodic scans were performed by applying potentials to the metal electrode and measuring the resulting current response. The anodic scans applied potentials from -0.02V vs. $E_{OC}$ to 1.8V vs. SCE, while the cathodic scans applied potentials from 0.02V vs. $E_{OC}$ to -1.8V vs. SCE; both were measured at a scan rate of 0.2mV/s once an initial steady-state potential was reached for each CPC-treated 1018 steel coupon.

Initially the anodic polarization curves appeared to have regions of passivity, or semi-passivity, in aerated solutions. In order to determine the degree to which the anodic reactions were slowed, if at all, or rather the seemingly-passive regions could be attributed to effects of the oxygenated solution, anodic polarization scans were performed in deaerated ¼-strength artificial seawater solutions. Each anodic scan applied potentials from -0.02V vs. $E_{OC}$ to 1.2V vs. SCE at 0.2mV/s once an initial steady-state potential was reached for each CPC-treated 1018 steel coupon.

Polarization plots from scans of both the aerated and deaerated solutions were analyzed in the same manner. $E_{CORR}$ and $i_{CORR}$ values were obtained from plots, $E$ (versus SCE) versus log $i$, for each anodic and cathodic scan. The Tafel slopes were not obtained because the linear regions (over at least two orders of magnitude) required for their calculation did not exist on the scale\,[71, 73, 74, 101]\). Figure 18 is an example of a polarization plot, where $E_{CORR}$ and $i_{CORR}$ were measured. Qualitative information, such as a general shift in $E_{CORR}$ values, was obtained from the polarization plots, both anodic and cathodic. For example, a shift to more noble $E_{CORR}$ values compared to the control value relates to corrosion conditions where the anodic reactions are more dominant (occur at a slower rate) in controlling the overall corrosion reactions than the cathodic reactions. Detailed information regarding what a shift in potential or current means in relation to the corrosion reactions at a metal surface is included in the Background and Results sections within this body of work.
Figure 18. Example of anodic and cathodic polarization plots (solid lines), where both $E_{\text{CORR}}$ and $i_{\text{CORR}}$ are measured from the intersection of slopes chosen to best fit the anodic and cathodic Tafel regions. The measured slopes are shown as the dashed lines. The slope for the cathodic Tafel region is estimated, as the region for activation polarization does not extend long enough and concentration polarization (due to dominating influences from the oxygen reduction reaction) dominates most of the cathodic curve.
3.4 Experimental Plan

3.4.1 As-applied CPC Film Prior to Immersion

The CPC films, applied to 1018 steel substrates, were characterized in terms of their chemical composition and physical properties:

- FT-IR was used to identify the compounds comprising the different CPC types, applied by both the spray method and spin-coating of polished coupons. Several random points were measured on each prepared coupon to monitor composition consistency.

- XPS was used to identify the atomic percent and chemical state of the elemental components of the CPC types, applied via spin-coating on polished coupons. Several random points across the treated coupon surface were measured to determine consistency within the CPC compositions.

- OP was used to measure the thickness of the CPC films, applied via the dipping method on grit-blasted coupons.

- AFM was used to measure the thickness of the CPC films, applied via the spray method on grit-blasted coupons.

- Wilhelmy balance tensionmetry was used to measure the hysteresis and contact angle of the CPC films, applied via the spray method on grit-blasted and polished coupons. Three replicates of each CPC type on each surface finish were measured.
3.4.2 As-applied CPC Film After Immersion

The CPC films, applied to the 1018 steel substrates, were characterized in terms of the degree of film degradation and also the initiation of corrosion after immersion in ¼-strength artificial seawater solution. Two types of studies, one dedicated to electrochemical and corrosion properties, and the other dedicated to the composition of the surface film after immersion, were performed.

3.4.2.1 Electrochemical Corrosion Study as a Function of Immersion Time

Electrochemical measurements were made every 20-24 hours after an initial steady-state potential value was reached and until failure criteria were met for the final coupon in the replicate series. Failure was met when: 1) the corrosion rate was 0.04mm/yr or greater, calculated from polarization resistance method and; 2) the corrosion potential reached and sustained a value very close to or the same as the control coupon, -725mV vs. SCE. The failure criteria were originally determined to be when the corrosion product completely covered the coupon surface and the corrosion potential of the cell reached the same value as the control coupon. The corrosion rate value was later chosen as another primary failure criterion, as it corresponded to values obtained when the corrosion product coverage and potential criteria were met. The corrosion rate value, 0.04mm/yr, was used as the main measure of failure criteria thereafter. For each CPC treatment type (Brown, Red, and Blue), as well as for the untreated control, electrochemical measurements were carried out. Electrochemical measurements, described below, were taken up to day 20 for the control, Blue, and Red-treated CPC types, and up to day 23 for the Brown CPC type:

- Open circuit potential values were used to monitor the overall corrosion behavior, anodic or cathodic dominated, occurring at the metal surface as a function of immersion time.
• Polarization resistance was used to monitor the corrosion rate as a function of immersion time.

• Electrochemical impedance spectroscopy was used to monitor the presence of charge and/or mass transfer time constants and the impedance values as a function of immersion time.

• Photographs were taken after the coupons were taken out of the electrolyte and again after rinsing with deionized water and acetone. The photographs were used to visually compare the surfaces of the failed coupons by surface treatment type.

3.4.2.1 Electrochemical Corrosion Study as a Function of Applied Potential

Potentiodynamic polarization measurements were carried out to determine whether the anodic or cathodic reaction was dominant in the corrosion reaction and if the CPC films passivated the metal surface and mitigated corrosion:

• Potentiodynamic polarization was performed in both the anodic and cathodic directions for each surface treatment on steel: bare metal, Brown, Blue, and Red CPC types. The coupons were immersed in ¼-strength artificial seawater at ambient conditions using the barnacle cell configuration.

• Potentiodynamic polarization in deaerated solution was performed in the anodic direction for each surface treatment on 1018 steel: bare metal, Brown, Blue, and Red CPC types. The coupons were immersed in ¼-strength artificial seawater after N₂ was used to purge the solution of dissolved oxygen. The paint cell described previously in the section, was used for this experiment. The same experimental set up, minus deaeration of the electrolyte, was completed for a second set of coupons so that the deaerated and aerated measurements could be directly compared.
3.4.2.2 Study of the Chemical Composition of the CPC Film After Immersion

The degradation of the CPC films, applied via the spray method to 1018 steel coupons, were monitored using FT-IR and XPS as a function of the different stages of CPC film degradation after immersion and as a function of immersion time in ¼-strength artificial seawater.

FT-IR

The coupons used in the FT-IR study were all subjected to the same immersion schedule up to day 6. The Red CPC type was immersed until day 8 and the Brown CPC type was immersed until day 10. The immersion ended for each CPC type when the IR measurements were the same for two consecutive days, the coupons appeared corroded across the entire coupon surface, and no CPC was detected on the coupon surface via FT-IR. The immersion times varied between CPC types due to the fact that the CPCs offered different degrees of protection to the metal surfaces. After each immersion, the coupons were rinsed with a gentle stream of deionized water and dried at ambient laboratory conditions. The reference spectrum used for background subtraction was measured on an untreated and un-immersed 1018 steel coupon for tracking the morphology of the films from their original states. The procedure used in the FT-IR related portion of the CPC film chemical composition study after immersion in ¼-strength artificial seawater was as follows:

- Electrochemical measurements, corrosion potential and polarization resistance, were made prior to taking the coupons out of immersion to determine the overall corrosion-related state of the substrate surface.
- Digital photographs were taken after the coupon dried to record the visual changes across the surface as a function of immersion time. Figure 19a is an example of a photograph taken after immersion and drying.
- FT-IR measurements were made at the center point on each coupon to monitor chemical composition changes at one point on the substrate surface as a function
of immersion time. Figure 19b, point 1, is an example of the center point chosen for IR monitoring.

- FT-IR measurements were made at different points on the same coupon relating to the different film states that existed across the coupon surface on the same day. The different points were measured across the coupon surface to capture all of the different film degradation stages, because the surface of each coupon did not homogeneously degrade over time. In Figure 19b, points 2-5 are an example of the various points chosen for IR measurements across a coupon surface that represented different surface degradation stages. The degradation stages were categorized and are described in the Results section within this body of work.

- Digital photographs of each point measured by FT-IR were recorded using the apparatus’ CCD camera attachment. The photographs were used to match the IR spectra to the visual appearance of the surface. Figure 19c is an example of a CCD camera photograph, where the measured area in the box is 80μm x 80μm.

Figure 19. Example (shown as the Blue CPC type after 3 days of immersion in 1/4-strength artificial seawater) of the process for selecting and measuring various degradation stages on a treated coupon surface using FT-IR. A photograph of a coupon after immersion and drying is shown in a). An enlarged image, shown in b), of the immersed area shows marks denoted for IR measurements, with the center denoted by 1, and various other degradation stages denoted by points 2-5. The area (80μm x 80μm) scanned by the IR beam is shown in c) using a CCD camera. This photograph was used to match the IR measurements to the visual appearance of the substrate surface.
XPS

A separate set of coupons (not the same coupons used for the FT-IR measurements due to size constraints of the XPS) was used for XPS surface characterization. The coupons for the XPS-based study were immersed in ¼-strength artificial seawater solution until a sampling of CPC film degradation stages similar to those found in the FT-IR study were obtained on the coupon surfaces. The degradation stages were defined during the FT-IR work and are detailed in the Results section of this body of work. After the degradation stages formed on the immersed coupons, the coupons were taken out of immersion, gently rinsed in deionized water, and dried under ambient laboratory conditions. The procedure for the XPS-based study is as follows:

- For each CPC type, FT-IR measurements were made at multiple points on each coupon used in the XPS-based study. Several points were then selected based on their similarity both visually and spectrally to degradation stages already established during the FT-IR-based study.

- XPS was used to determine what elemental components existed on the coupon surfaces for the different degradation stages. Figure 20 displays all of the points, circled in black on each coupon, where XPS measurements were made for each CPC type. The points in Figure 20 were chosen based on their similarity to degradation stages determined in the FT-IR-based study. Two separate coupons were used in the XPS study of the Blue and Brown CPC types, while one coupon was used for the Red CPC type. The number of coupons chosen to make XPS measurements was dictated by the number and different types of degradation stages found on each coupon. For instance, only one coupon was chosen for the Red CPC type because all of the stages chosen for review via XPS were found on a single coupon.
Figure 20. Photographs of the points where XPS measurements were taken on each coupon, designated by CPC type. The points are circled in black on each of the coupons.
Chapter 4

4.0 Results

4.1 As-Applied CPC Films on 1018 Steel

To understand the degradation of a CPC film on the 1018 steel substrate surface, it was necessary to establish the condition and composition of the initial as-applied film. Surface chemistry techniques, FT-IR and XPS, were used to identify the chemical composition of the surface film. Film thickness, hydrophobicity, and homogeneity were measured to understand some physical characteristics of the initial film.

4.1.1 Fourier Transform-Infrared Spectroscopy

In general, only hydrocarbon-based characteristics could be identified via FT-IR because the CPCs primarily consisted of organic compounds (namely petroleum-based oils), and the IR method only provided information regarding functional groups. C-H groups, noted as the primary or stretching (3000-2840cm⁻¹), secondary or bending (1470-1375cm⁻¹), and rocking (730-720m⁻¹) C-H groups, were identified in the IR spectra shown in Figure 21 for all of the CPC types. The spectra in Figure 21 also included peaks relating to carbonyl groups, C=O stretching (1750-1735cm⁻¹), that are indicative of saturated ester components comprising the CPC films. All of the components identified via IR, (C-H and C/O based) correlated well with the bulk chemical composition analysis previously obtained for these CPC types; Table 1 identifies the CPCs primarily as CPCs aliphatic C-based compounds with O-based groups. The spectrum for the Brown CPC type, shown in Figure 22, included an additional peak at 1058cm⁻¹ that was characteristic of either C-O stretching from a noncyclic acid anhydride (1060-1035cm⁻¹) or O-C-C stretching from aromatic esters (1100-1030cm⁻¹). Along with the spectra for
the Brown CPC type, Figure 22 shows two spectra, n-decane (top spectrum) and Vaseline 8401\textsuperscript{[103]} (middle spectrum), that most closely matched the spectra for cured CPC types.

Figure 21. Surface reflectance IR spectra (with background subtraction of untreated 1018 steel) for the Brown (bottom), Blue (middle), and Red (top) CPC types applied via the spraying method.

Figure 22. Surface reflectance IR spectra (with background subtraction of untreated 1018 steel) for the Brown CPC applied via the spraying method, compared to two peak-fitted matches, Vaseline 8401 (middle spectrum) and n-decane (top spectrum).
N-decane is a standard alkane hydrocarbon and Vaseline 8401 is characterized as a general chassis lubricant\textsuperscript{[104-106]}. These results were relatively predictable, as the CPCs are known to be primarily hydrocarbon oil-based and the other CPC components, such as barium, silicon, and sulfur, were likely located near the metal/film interface and would be difficult to detect via FT-IR anyhow.

IR spectra were also measured after the coupons were treated via spin-coating to confirm consistency between the as-applied CPC compositions, especially the thinner layer necessary for XPS analysis. The resulting spectra for the Red and Blue were similar to results from the spray-application (same as Figure 21), except the C-H peak intensities were decreased. The spectra for the spin-coated Brown CPC also included peaks indicating the presence of additional oxygen groups, shown in Figure 23 along with two spectral matches for the Brown CPC type. The only difference between the spectral matches for the Brown type, n-decane (C\textsubscript{10}H\textsubscript{22}) and 1-decanol (a straight-chain fatty alcohol C\textsubscript{10}H\textsubscript{22}O), was the addition of oxygen. The same could be said for the two spectrum types identified for the Brown CPC, where one spectrum (Brown’s spectrum in Figure 23) contains a more considerable amount of oxygen than the other (Brown’s spectrum in Figure 22). A common indicator of oxygenated species is a broad hump from 3500-3000cm\textsuperscript{-1} due to O-H stretching. The broad hump in Figure 23 for the Brown CPC type was identified as a carboxylic acid functionality, namely carbonyl groups (C=O stretching at 1739cm\textsuperscript{-1}). Either spectrum type for the Brown CPC type was considered characteristic of this CPC type, since bulk chemical analysis\textsuperscript{[2]} found that the Brown was comprised of a large percent of oxygen-related aromatic and alcohol groups, as well as oxygen attached to the parent C-C backbone. Oxygen is known to be a method of attachment for a film layer of this type (hydrocarbon) via physisorption and/or chemisorption\textsuperscript{[68, 107]} to a steel substrate. The thinner spin-coated film likely revealed oxygen functionalities that are located closer to the interface\textsuperscript{[108]}. The oxygen is less likely to have originated from the iron oxide layer (since the spin-coated versions of Red and Blue did not also contain the broad O-H peaks).
4.1.2 X-ray Photoelectron Spectroscopy

The constituents of the CPC types were identified via XPS, using both broad survey and element-specific high resolution measurements. The CPCs were all comprised of similar components, C, O, S, and Si, found commonly in petroleum-based lubricating materials. Several components, Na, Ca, Zn, and Ba, were detected in varying concentrations for the different CPC types and could be used to better distinguish the CPCs from each other. Figure 24 represents a typical survey spectrum for the CPC film, showing that the film was overwhelmingly comprised of C and O-based components, with a smaller percentage of S and Si-related components. In an ideal setting to obtain CPC components at the 1018 steel/CPC interface, the spectra background would include a broad hump originating from the Fe-based substrate (shown as a broad hump in the 1200 – 700eV range). When the deposited CPC film was thin enough, as was the case for the Blue and Red CPC types only, these broad background humps appeared. Figures
24, 25, and 26 display the survey spectra for CPC types Brown, Red, and Blue, in which the components are labeled by general peak location. Although an ideal thickness (thinner or equal to the sampling depth of ~5-10nm) could not be obtained for the Brown CPC film, shown in by the absence of Fe-based broad hump in Figure 24, elemental components other than C, O, Si, and S could still be detected using high resolution scans over the known constituent binding energies. Table 2 lists the percent composition results for two representative survey scans performed on each CPC type. Results varied somewhat between the different survey scans that were taken on different days. Overall, the atomic percent values for the different elemental components were similar enough between scan numbers to be considered satisfactory.

![Graph of XPS survey scan spectrum of the Brown CPC type applied to the polished 1018 steel surface via spin coating. Results typical of C, O, S, and Si components representing any of the CPC types.](graph)

Figure 24. XPS survey scan spectrum of the Brown CPC type applied to the polished 1018 steel surface via spin coating. Results typical of C, O, S, and Si components representing any of the CPC types.
Figure 25. XPS survey scan spectrum of the Red CPC type applied to the polished 1018 steel surface via spin coating, with elemental peak identification. The broad peak between 1200 and 700eV was from signals representing the Fe components of the steel substrate.

Figure 26. XPS survey scan spectrum of the Blue CPC type applied to the polished 1018 steel surface via spin coating, with elemental peak identification. The broad peak between 1200 and 700eV is from signals representing the Fe components of the steel substrate.
Table 2. XPS survey scan composition of the CPC films applied to the polished 1018 steel substrate. Survey numbers refer to two different applications of the CPC and the corresponding XPS results. The spectra from Figures 24, 25, and 26 were from survey 1.

<table>
<thead>
<tr>
<th>CPC Type and Survey Number</th>
<th>Peak and Composition (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C 1s</td>
</tr>
<tr>
<td>Brown 1</td>
<td>85.74</td>
</tr>
<tr>
<td>Brown 2</td>
<td>84.34</td>
</tr>
<tr>
<td>Red 1</td>
<td>84.40</td>
</tr>
<tr>
<td>Red 2</td>
<td>87.21</td>
</tr>
<tr>
<td>Blue 1</td>
<td>77.39</td>
</tr>
<tr>
<td>Blue 2</td>
<td>67.74</td>
</tr>
</tbody>
</table>

The three different CPC types were comprised of elemental components with similar, and in some cases the same, chemical states. Peak fitting was performed on high resolution scans of the various elements, many of which were also identified in the survey scans. Figures 27, 28, and 29 display the various peaks after fitting was performed for each CPC type. Tables 3, 4, and 5 list the binding energies and most likely chemical states of each elemental component for the CPC types.

Deconvolution of the XPS spectra was used to identify the chemical states of each elemental component with relative certainty. The carbon deconvolution for each CPC type was simple, as the CPCs are known to be aliphatic-based materials. The state of the oxygen, as measured by XPS, was more ambiguous for the CPC types because previous work using NMR and GC-MS showed that oxygen existed within the CPCs connected to various C groups in each of the CPCs (O within aromatic compounds, O as OH, and O as carboxyl groups). In some cases, such as for Si, the states were not listed as organic versions of the components in the reference literature; however, knowing from previous work that the CPCs were hydrocarbon-based, the organic silane (silicon oil) identification was the most probable possibility. The Ca component, found
only in the Brown and Blue CPC types, and Ba component, found only in the Red CPC type, were the distinguishing components for each of these CPC types. These components could be identified as additives to the oil mixture, which actually consisted of 100’s to 1000’s of different oil-based compounds\cite{2}. Because both the S2p and Ca2p or Ba3d components were identified as sulfate-based, a very likely possibility was that the compounds BaSO₄ (for the Red CPC) and CaSO₄ (for the Blue and Brown CPCs) were additives to the oil mixtures and may have served as corrosion inhibitors. The Na1s component was identified as belonging to sodium sulfate, a typical ionic sulfate that is used often as a surfactant.

The chemical states identified in Tables 3, 4, and 5 for each component within the CPC types were considered to be the most likely candidate based on reference manuals\cite{109,110} and previously known state information from bulk chemical analysis\cite{2}. Based on XPS results, the Brown and Red CPC types were most similar to each other, a point not surprising since they originate from the same manufacturer. Due to the large percentage of oil-based components comprising the CPC, it was less likely that only an additive served as the corrosion inhibitor component. The function of the oil components could not be discounted in terms of their corrosion inhibiting properties.
Table 3  XPS high-resolution peak assignments for the Brown CPC type applied to polished 1018 steel substrates.

<table>
<thead>
<tr>
<th>Elemental Component</th>
<th>Brown CPC Binding Energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>285.0</td>
<td>C-C*</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.30</td>
<td>O=C** or OH*</td>
</tr>
<tr>
<td>S 2p</td>
<td>168.36</td>
<td>SO$_4^{2-}$*</td>
</tr>
<tr>
<td>Si 2p</td>
<td>102.37</td>
<td>Silicones (silane) organic*</td>
</tr>
<tr>
<td>Ca 2p</td>
<td>347.50</td>
<td>CaSO$_4$*</td>
</tr>
<tr>
<td>Na 1s</td>
<td>1071.30</td>
<td>Na$_2$SO$_4$*</td>
</tr>
</tbody>
</table>

*107, **108

Figure 27. High resolution XPS peaks (solid line) with corresponding peak fitting (dashed lines) for elemental components comprising the Brown CPC type, including C, O, Si, S, Ca, and Na. The peaks are assigned to chemical states, listed in Table 4.
Table 4 XPS high-resolution peak assignments for the Blue CPC types applied to polished 1018 steel substrates.

<table>
<thead>
<tr>
<th>Elemental Component</th>
<th>Blue CPC</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>285.0 (93 at.%) 287.6 (7 at.%)</td>
<td>C-C*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C w/ S or C w/ O (ether)*</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.30</td>
<td>O=C** or OH*</td>
</tr>
<tr>
<td>S 2p</td>
<td>169.39</td>
<td>SO₄²⁻*</td>
</tr>
<tr>
<td>Si 2p</td>
<td>102.55</td>
<td>Silicones (silane) organic*</td>
</tr>
<tr>
<td>Ca 2p</td>
<td>347.95</td>
<td>CaSO₄*</td>
</tr>
<tr>
<td>Zn 2p</td>
<td>1022.70</td>
<td>ZnO or halides</td>
</tr>
</tbody>
</table>

*107, **108
Table 5. XPS high-resolution peak assignments for the Red CPC types applied to polished 1018 steel substrates.

<table>
<thead>
<tr>
<th>Elemental Component</th>
<th>Red CPC</th>
<th>Binding Energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td></td>
<td>285.0</td>
<td>C-C*</td>
</tr>
<tr>
<td>O 1s</td>
<td></td>
<td>532.35</td>
<td>O=C** or OH*</td>
</tr>
<tr>
<td>S 2p</td>
<td></td>
<td>169.33</td>
<td>SO\textsubscript{4}\textsuperscript{2-}*</td>
</tr>
<tr>
<td>Si 2p</td>
<td></td>
<td>102.56</td>
<td>Silicones (silane) organic*</td>
</tr>
<tr>
<td>Ba 2p</td>
<td></td>
<td>780.32</td>
<td>BaSO\textsubscript{4}, BaCO\textsubscript{3}, or BaS*</td>
</tr>
<tr>
<td>Na 1s</td>
<td></td>
<td>1071.2</td>
<td>Na\textsubscript{2}SO\textsubscript{4}*</td>
</tr>
</tbody>
</table>

*107, **108

Figure 29. High resolution XPS peaks (solid line) with corresponding peak fitting (dashed lines) for elemental components comprising the Red CPC type, including C, O, Si, S, Ba, and Na. The peaks are assigned to chemical states, listed in Table 6.
4.1.3 CPC Film Thickness

Obtaining the thickness of the CPC films was not as simple as originally thought, mostly due to the fact that the films remained in a less viscous liquid state than anticipated, even after longer than usual periods of curing. CPC film thickness results, although preliminary, were obtained for the Brown CPC type on the grit-blasted surface finish using the dipping and spraying CPC application methods. Results collected by light-based optical profilometry and obtained for the Brown CPC type applied on the grit-blasted 1018 surface by the dipping application are shown in Figure 30. The thickness close to the metal/film interface was measured at 21μm using the step height difference between the bare metal surface and the CPC film-coated surface (ignoring the interfacial area near the resist tape). Unfortunately, the apparatus suffered mechanical failures after the initial proof-of-concept study was complete, rendering the specific technique unavailable for this research at The Pennsylvania State University. The biggest advantage to the optical profilometer, although the equipment was relatively dated, was that it scanned areas over a long length (8cm). The thickness of the surface film could be measured along the entire length of the 1018 steel coupons using topography of step-heights between the bare metal and the CPC film, and the film thickness gradient due to the vertical hanging cure could also be determined.

Figure 30. Height profile of the Brown CPC type applied to a grit-blasted 1018 steel surface using the dipping application.
AFM was used in an effort to obtain thickness measurements on the grit-blasted 1018 steel surfaces that were treated with the sprayed Brown CPC. When using step height to measure film thickness, results at or closest to the interface of the metal and the film are less accurate; the interface is unpredictable due to the liquid nature of the film (the film height at the interface is not related to the film height across the bulk of the coupon because the film is physically moving at the interface). Topography results at the interface should be discounted due to their inaccuracies, and measurements should be made away from the interface. The scan area of the AFM, 3mm x 3mm, was too small to provide accurate step-height information for film thickness. Figure 31 shows that the film thickness was measured at 2.0 – 3.0μm for the grit-blasted surface finished.

Intermittent contact AFM proved to be initially successful; however, once the liquid surface came in contact with the cantilever tip, the measurements were no longer possible. A true non-contact AFM method was not available. Au-coating the CPC film (in order to produce an obvious surface for the AFM to detect) was not successful, as the film was still too wet to be successfully coated without causing an inhomogeneous surface film. After the surface was Au-coated, the CPC physically moved under the coating and overtook the interfacial area at which the initial step height between the metal/film interface was to be measured.

![Figure 31](image-url)

**Figure 31.** Step height results from AFM measurements taken at two locations on 1018 steel for the Brown CPC type, applied via the spray method. The interface was too close to the measurements for the metal and CPC film to provide accurate thickness results.
Based on the results for CPC film thickness and problems with the AFM method, the thicknesses between application methods could not be compared. The dipping method allows a larger amount of CPC to be initially deposited on the substrate surface; therefore it is likely that the resulting cured thickness is also greater. Thickness results for the polished surface finish were discarded because the CPC films did not remain static in the vacuum during Au-coating on the smooth surface. When the polished surfaces were configured horizontally, islands of the CPC film formed on the surface (caused by the surface tension between the oil liquid and the smooth polished surface). In the vacuum conditions, this film inconsistency was exaggerated and caused the film to become very inhomogeneous across the surface.

4.1.4 CPC Film Homogeneity and Hydrophobicity

Initial hydrophobicity and homogeneity information for the CPC surface films determines if the as-applied films are initially continuous across the metal surface. Contact angle and hysteresis values for the CPC types with the polished and grit-blasted 1018 steel surfaces are shown in Figure 32a and 32b. The advancing contact angle relates to the degree of hydrophobicity, where 90° equals a hydrophobic surface and 0° equals complete surface wetting. Values of ~70°-~105° are more common for hydrophobic SAMs \[^{[42, 44, 90, 111, 112]}\], and will be used as a guideline for this research as well. The hydrophobicity for all of the CPC-treated coupons was relatively high, between 60° and 70° for most of the replicates. These contact angle values, although not as high as for typical SAM values, still indicated a hydrophobic, rather than hydrophilic, surface. The control coupons (untreated) of either surface finish were hydrophobic; however, they easily wetted, as shown by the high hysteresis values in Figure 32b. Typically a hysteresis value of 1.0 equates to non-continuity in a surface film and/or high water adsorption. The high hysteresis results for the control coupon are due to the discontinuous surface rather than water adsorption. Water adsorption would have been also indicated by a hydrophilic surface (low contact angle values), which the control
The hysteresis values for the rougher grit-blasted surface finish were about twice as high as for the polished surfaces. This difference in hysteresis values is likely related to the difference in surface roughness rather than a difference in surface film homogeneity; therefore the grit and polished results should not be directly compared.

Overall, the surface films for all of the CPC types were quite homogeneous, at least when comparing results after an initial immersion in deionized water for a total of about 60 seconds. This method of evaluation did not take into account the film homogeneity after immersion in electrolyte or the initiation of corrosion, and thereby only related to the condition of the initial as-applied surface film. The hydrophobicity of the wetted films indicates that the CPCs did initially provide a successful water-displacing protective barrier against aqueous environments. All of the CPCs were applied as a continuous film; therefore the degradation of the films in the corrosion study (discussed in a later section) most likely did not originate at areas of exposed metal amidst the initially-applied film.
4.2 Corrosion Behavior of the CPC Films Immersed in ¼-strength Artificial Seawater

The type of protection that the CPC films provided and the manner in which they degraded after immersion were evaluated using electrochemical and surface chemistry methods. Analysis of both approaches produced the same general observations: the CPC film protected the 1018 steel substrate in the dilute artificial seawater environment, at least temporarily, and degraded in distinct stages as a function of immersion time.

4.2.1 Electrochemical Behavior of the Surface Film as a Function of Immersion Time

Regardless of CPC type, observations could be made regarding the manner in which the CPC films altered the corrosion behavior of the 1018 steel substrate in ¼-strength artificial seawater. CPC films protected the 1018 steel substrate, at least initially, by slowing the anodic corrosion reactions. In the electrochemical study, most of the results were reported by day, where day 0 referred to measurements made after the potential value reached an initial steady-state value (between 1500 seconds and 6000 seconds depending on CPC type). Each successive day referred to 20-24 hours after the initial measurements were made.

4.2.1.1 Corrosion Potential

The corrosion potential, $E_{\text{CORR}}$, values were initially more noble after immersion into the electrolyte solution for the substrates treated with CPCs. The increase to more noble (higher value) potentials for the CPC-treated coupons was due to the initially hydrophobic and homogeneous CPC film that acted as a barrier between the electrolyte and metal electrode. Figures 33a, 34a, and 35a, show $E_{\text{CORR}}$ vs. SCE results as a function
of immersion time for continuous measurements of multiple replicates of the Brown, Blue, and Red CPC types. As the immersion time progressed, shown in Figures 33b, 34b, and 35b for up to 23 days of continuous immersion, the $E_{\text{CORR}}$ values of the CPC-treated electrodes became less noble. The decrease in nobility of the potential values was due to the degradation of the protective CPC layer and eventual formation of corrosion product on the substrate surface. The corroded control coupon reached a steady-state potential value of $\sim -730\text{mV vs SCE}$ by day 1 that did not change significantly even after 14 days of continuous immersion. Eventually, the corrosion potentials for the CPC-treated coupons reached potential values closer to those of the control coupon. For the Brown CPC type, the potential values were consistently $\sim 100\text{mV}$ more noble than values for the control. This consistently higher potential value is surmised to be due to the fact that the Brown CPC film remained at least partially intact across the coupon surface despite the presence of corrosion product on the substrate surface.

![Graph](image)

**Figure 33.** Plots of the corrosion potential as a function of continuous immersion a) initial time period (up to 5500 sec.) and b) extended immersion periods of up to 23 days in ¼-strength artificial seawater for six 1018 steel replicates treated with the Brown CPC type as compared to the untreated control (dashed line).
4.2.1.2 Corrosion Rate from Polarization Resistance

In all cases, the initial CPC barrier increased the $R_p$ value in comparison to those obtained for the untreated 1018 steel coupons. Because polarization resistance is the slope of potential versus current at the corrosion potential, it can be related to the corrosion current by the Stern-Geary equation\cite{61, 62}: $R_p = B/i_{CORR} = (\Delta E)/(\Delta i)_{E \rightarrow E_{CORR}}$, where $B = (b_ab_c)/2.3(b_a+b_c)$. The corrosion currents were converted to penetration rates...
(corrosion rates), commonly in mm/yr, using Faraday’s law and the following equation: \[7, 113\]

\[
\text{mm/yr} = K_1 \text{ EW} \left( \frac{i_{\text{CORR}}}{\rho} \right) \tag{Eq. 1}
\]

where \( K_1 = 3.27 \times 10^{-3}(\text{mm})(\text{g})/(\mu\text{A})(\text{cm})(\text{yr}) \), \( \rho = 7.87\text{g/cm}^3 \) for the steel substrate, and \( \text{EW} \) = equivalent weight(W/n = molecular weight/# of electrons) at 27.92 for iron. The equivalent weight for iron was used instead of for 1018 steel because the percent of iron in 1018 steel is, at the least, 98.81 percent. The equivalent weight value for iron is often used when for electrochemical testing of low carbon steels because the error is very small (less than 1% error).

For determining general corrosion rates, the Tafel slope values, \( b_a \) and \( b_c \), were estimated to be 0.10 (a common estimation when actual values are unknown)\(^{[7]}\) because the actual Tafel slope values changed and could not be legitimately determined as the film degraded over time. For more accurate values of \( R_P \), anodic and cathodic polarization measurements would need to be made at each proposed immersion time period to obtain more realistic Tafel slopes. The polarization resistance method does not measure the behavior of the coupon surface continuously, but rather provides instantaneous information about the corrosion reaction occurring at the surface in the electrolyte. The daily behavior of any CPC in this study was partially unknown due to inconsistencies within the film surface during degradation that caused the corrosion reactions to occur inhomogeneously within each individual corrosion cell. The replicates for the CPC-treated coupons did not have identical, only similar, potential and corresponding current values. Defining Tafel slope values for a particular period of immersion would therefore not be legitimate for this limited and more comparative-based study.

The Brown CPC film did not degrade quickly or become replaced as corrosion initiated, but rather the corrosion product appeared to become incorporated into the CPC film and caused the film to degrade slowly as a function of immersion time. Figure 36 shows that the protective Brown CPC film type initially (on day 0) decreased the
corrosion rate as compared to the corrosion rates of the control. The corrosion rates then increased slowly over time, much at the same rate as $E_{\text{CORR}}$ decreased. The Blue CPC film degraded quickly (a high corrosion rate of 0.12mm/yr) and corrosion product formed by day 1 of immersion (shown in Figure 37). The corrosion rate results for Red CPC-treated coupons were similar to the results for Blue CPC. As shown in Figure 38, the majority of the coupons remained protected for a slightly longer than 2 days of immersion. In the case for the Red and Blue CPCs, the fluctuations in corrosion rates that occurred after the failure criteria were met was likely due to the formation of a porous corrosion product that intermittently provided protection from further active corrosion.

![Figure 36. Plots of corrosion rate results for six replicates of Brown CPC-treated 1018 steel coupons after immersion in ¼-strength artificial seawater, as compared to the control coupon results (dashed line). The straight solid line is the CPC failure criteria. The points represent each day.](image-url)
Important to note is the fact that the CPC films on the 1018 steel surfaces did not degrade homogeneously across the electrolyte-exposed surface as a function of immersion time, nor did corrosion product form evenly across the coupon surfaces. This disproportion in surface reactions weighed heavily on both the corrosion potential and corrosion rate values. The values representing the corroded areas (at more negative potential and higher corrosion current values) impacted more heavily the final values than

Figure 37. Plots of corrosion rate results for six replicates of Blue CPC-treated 1018 steel coupons after immersion in ¼-strength artificial seawater, as compared to the control coupon results (dashed line). The straight solid line is the CPC failure criteria. The points represent each day.

Figure 38. Plots of corrosion rate results for five replicates of Red CPC-treated 1018 steel coupons after immersion in ¼-strength artificial seawater, as compared to the control coupon results (dashed line). The straight solid line is the CPC failure criteria. The points represent each day.
did the values resulting from areas of more protective CPC film (at more positive potential and lower corrosion current values). In any electrochemical cell in this research, the corrosion potential and corrosion rate results were representative of the average of all the reactions occurring at the electrode surface. For instance, $i_{\text{CORR}}$ values for a protective CPC film were in the nA/cm$^2$ range and in the μA/cm$^2$ range for a corroding surface. When the two values were averaged, the final value for $i_{\text{CORR}}$ would obviously be in the μA/cm$^2$ range, only slightly impacted by the values for protected regions even though the total area of the protected regions may have been much larger than the corroding region (as was more commonly the case for the Brown CPC-treated surfaces than for the Red and Blue CPC types).

Photographs of the actual CPC-treated coupons after 23 days of immersion (with the corrosion product intact) and then after rinsing of the corrosion product are shown along with the control coupons (after 20 days of immersion) in Figure 39. For the Brown CPC-treated coupons, shown in Figure 39b, much of the CPC film is intact, even without the removal of the corrosion product. Photographic representations for the Red and Blue coupons show that some areas across the surface of the coupons (immersed for a total of 23 days) did remain protected although the corrosion product covered the majority of the coupon surfaces. These areas are indicated in Figures 39c and 39d for the Blue and Red CPC-treated coupons.
The rinsed coupon surfaces were further evaluated by their visual appearance to account for the inhomogeneity of the corrosion product across the immersed coupon surfaces. The coupons were visually evaluated in terms of the percent of the surface that remained protected after immersion versus the total area initially protected. Table 6 displays the percent of protected areas that the Brown, Blue, and Red CPC types had after immersion. Using Table 6 to rank the CPCs, the Brown CPC type provided protection most consistently and over the largest percent area (an average of 37%) than the other CPC types. The Blue CPC type had a range of results that showed high protection (35%) and also low (10%). The Red CPC type had one less replicate (two instead of three),
therefore the average percent protection value is not as reliable as for the Brown and Blue CPC types. The Red CPC type, described in Table 6, had one replicate that had no protected areas after 23 days of immersion, and the other replicate showed 17 percent of its area protected after the immersion and subsequent rinsing.

Table 6. Estimated percent protection that the CPC treatments provided to the 1018 steel substrate provided after immersion in ¼-strength artificial seawater for twenty-three days. Results for the control are from twenty days of immersion.

<table>
<thead>
<tr>
<th>Surface Treatment</th>
<th>Percent Protection (area intact after immersion/total area immersed) listed by replicate</th>
<th>Average Percent Protection</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Untreated/Control</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Brown CPC</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>Blue CPC</td>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td>Red CPC</td>
<td>0</td>
<td>17</td>
</tr>
</tbody>
</table>

n/a refers to no specimen

While determining percent protection is a useful tool in quantifying the ability of each CPC to provide protection to the 1018 steel surface after immersion, it does not describe the degradation of the CPC films. The manner in which the corrosion product is distributed across the surface of the coupons is also an important consideration for determining the corrosion inhibiting performance of the CPCs. As shown in Figure 39b, the interface between the corrosion product and the Brown CPC film for all replicates is not distinct, but instead consisted of areas where the film and corrosion product overlapped and co-mingled. Visually, this co-mingling of CPC and corrosion product appears as a lightly shaded rust-colored film, displayed as the area adjacent to the corrosion product in the before rinsing category in Figure 39b and the enlarged photograph in Figure 40. Further from the corrosion product, the rust-coloring in the film seemed to visually fade until the film was the same color as the as-applied film.
The Brown CPC film seemed to be incorporated or intermixed with the corrosion product, rather than replaced by it. This intermixing is likely the reason that the degradation of the Brown CPC film occurred more slowly over time than the Red and Blue CPCs.

In the case of both the Blue and Red CPC-treated replicates, the corrosion product/metal interfaces were well defined and visually obvious in Figures 39c and 39d. The corrosion products seemed to replace the CPC film when it formed on the substrate surface. As shown in Figures 39c and 39d, areas of rust-colored CPC film did exist, before rinsing, on top of the areas that were deemed “protected” after rinsing. The degradation of the Blue and Red CPC films seemed to occur in less numbers of stages than the Brown CPC type did. Visually, the Red and Blue films appeared to consist of areas of protective and intact CPC film, areas of un-protective and degrading film, or areas that were replaced by corrosion product. The existence of these simpler degradation stages is supported by the corrosion potential and rate results in Figures 34 and 37 for the Blue CPC and Figures 35 and 38 for the Red CPC type. Shown in Figures 37 and 38, when the corrosion rate begins to increase in value, it quickly reaches the failure criteria. The same pattern is true for the corrosion potential results, Figures 34 and 35, where the corrosion potential quickly decreases (within 1-2 days) and reached the same value as the control.
4.2.1.3 Suppression of Corrosion Reactions

Electrochemical Impedance Spectroscopy measurements were used in this study to monitor the ability of the CPC films protect to the 1018 steel substrate. Bode impedance magnitude plots most clearly displayed the film degradation pattern that existed for all of the CPC types. A series of Bode plots in Figures 41-43 are shown for one representative coupon for each CPC type, and the chosen results were considered typical for over 75% of the replicates for each set of CPC-treated coupons.

Initial measurements for the Brown CPC type indicated protection of the 1018 steel substrate via the film, shown having the highest impedance value (at low frequencies) in Figure 41 for stage a. High impedance values at low frequencies generally relate to a protective film, since a film with high impedance values should have the ability to resist the flow of electric current. The impedance values (Mega-ohms) for the initially-immersed Brown CPC type are not as high as a for a highly capacitive protective film such as a paint (Giga-ohms)\(^{[114]}\). The impedance values are indicative of a coating that has a low pore resistance, meaning that the electrolyte can penetrate through the coating\(^{[114]}\). The impedance values for the Brown CPC film (at Mega-ohms) are considered successful for a CPC, since it is an oil-based film that provides only temporary protection and exists in a liquid phase after curing. Shown in Figure 41 as stages b-d, as immersion time continued, the impedance values decreased to indicate a breakdown in the protective nature of the film. Eventually after 23 days of continuous immersion, the CPC film was degraded and the Bode plot for stage e in Figure 41 resembled that of the control.

Bode plots, shown in Figure 42 for the Blue CPC type, indicated a relatively quick breakdown in the protective film by the notably lower impedance values (as compared to the more fully-protecting Brown CPC film) for measurements made after the initial immersion. These impedance values as a function of frequency quickly resembled the corroded control results by day 1. The Red CPC film also degraded quickly and without an obvious intermediate stage being formed. Figure 43 displays Bode plots for the Red CPC type that show the film’s degradation over a period of 2 days of immersion.
The results indicated a quick change from a protective film to corroding surface as the impedance values decreased, shown in Figure 43 for stages a-c. No impedance results from the Red or Blue CPCs indicated an obvious incorporation of CPC film into the corrosion product.

Figure 41. Bode plots of the Brown CPC type (top 5 curves) and the control (bottom curve) immersed in 1/4-strength artificial seawater for over 23 days. The curves relate to different stages of degradation: a) intact film on day 0, and b-d) decreasing protection as impedance values decrease over days 6, 10, and 20, and e) eventually an unprotected surface by day 23 as the curve is similar to the corroded control curve.

Figure 42. Bode plots of the Blue CPC type (top 2 curves) and the control (bottom curve) immersed in 1/4-strength artificial seawater for 1 day. The curves relate to different stages of degradation: a) degrading film and corrosion on day 0, and b) failed film and corrosion product on day 1.
4.2.2 Electrochemical Behavior of the Surface Film as a Function of Applied Potential

For an oil-based CPC on a metal surface submerged in neutral electrolyte environments, often qualitative information, rather than quantitative, can be obtained for system analysis. Tafel slope information can, in some cases, be extrapolated from the anodic and cathodic curves to determine the corrosion rate of the metal system. In other cases, especially with corrosion inhibitors in neutral solutions containing oxygen, the criteria for obtaining useful Tafel slopes cannot be met and only qualitative comparisons can be made from the analysis. Anodic polarization of the system provided information regarding oxidation of the 1018 steel, and whether active and passive states were occurring at the metal surface. Cathodic scanning would have ideally provided separate hydrogen evolution and oxygen reduction reaction information; however, these two reactions are rarely able to be separated for neutral aerated solutions. The potential for 1018 steel in ¼-strength artificial seawater (on average -730mV vs. SCE) was within...
the potential for oxygen reduction (+160mV vs. SCE – general estimation for pH of 7) and hydrogen evolution (-241mV vs. SCE – general estimation for pH of 7); therefore, the effects of oxygen reduction overshadowed the effects of hydrogen evolution\textsuperscript{[74]}. Because the hydrogen evolution reaction could not be deconvoluted, legitimate Tafel slope values for the cathodic reaction could not be obtained and the reported results were qualitative.

The anodic and cathodic polarization measurements were made in ambient laboratory conditions after the initial immersion of the CPC-treated coupons into the corrosive solution. The coupons were immersed until steady-state potential values were reached prior to the anodic or cathodic polarization measurements. Figures 44, 45, and 46 display the anodic and cathodic polarization curves, overlaid on the same plot, for the 1018 steel coupons treated with the Brown, Blue, and Red CPC types. The figures show that the anodic curves all shifted to more noble $E_{\text{CORR}}$ and lower $i_{\text{CORR}}$ values as compared to the control; the Brown CPC-treated coupons had an average corrosion potential value of -276mV vs. SCE, the Blue an average of -366mV vs. SCE, and the Red an average of -370mV vs. SCE. The average $E_{\text{CORR}}$ and $i_{\text{CORR}}$ values, extrapolated from the polarization plots, for the treated and control coupons are shown in Table 7. The shift to more noble $E_{\text{CORR}}$ values decrease in $i_{\text{CORR}}$ correlates to a protective film that controls the anodic reaction more dominantly than the cathodic reaction\textsuperscript{[5]}. The $E_{\text{CORR}}$ and $i_{\text{CORR}}$ results show that the anodic reactions were slowed for the treated results when compared to the control. The cathodic polarization plots, shown in Figures 44-46, all appeared similar to the control. The plots show that the dominant cathodic reaction, oxygen reduction, was not suppressed by any of the CPC types. The CPC films were thereby categorized as anodic inhibitor types.
Figure 44. Anodic and cathodic polarization plots for 1018 steel coupons a) untreated and b) treated with the Brown CPC type and immersed in ¼-strength artificial seawater. Plots were recorded after initial steady-state potentials were reached (less than 90 minutes). Representative plots were chosen for this comparison. Inset is an enlargement of the possible semi-passive region on the anodic curve.

Figure 45. Anodic and cathodic polarization plots for 1018 steel coupons a) untreated and b) treated with the Blue CPC type and immersed in ¼-strength artificial seawater. Plots were recorded after initial steady-state potentials were reached (less than 90 minutes). Representative plots were chosen for this comparison.
Although the polarization plots showed that the anodic reactions were slowed (shift to more noble $E_{\text{CORR}}$ values), they degraded as higher potentials were applied. The degradation was shown by the fact that the current density increased into the $\mu\text{A/cm}^2$ and

Table 7. Corrosion current density, potential, and (average results) determined by anodic and cathodic polarization measurements for 1018 steel coupons untreated and treated with CPC types Brown, Red, and Blue after immersion in $\frac{1}{4}$-strength artificial seawater. The results are provided for the initial aerated polarization measurements in the barnacle cell, the second open-to-air measurements in the deaeration cell, and deaerated polarization measurements.

<table>
<thead>
<tr>
<th>Surface Treatment</th>
<th>open to air – barnacle cell</th>
<th>open to air – deaeration cell</th>
<th>deaerated – deaeration cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$i_{\text{CORR}}$ (A/cm$^2$)</td>
<td>$E_{\text{CORR}}$ (mV vs SCE)</td>
<td>$i_{\text{CORR}}$ (A/cm$^2$)</td>
</tr>
<tr>
<td>Control (untreated)</td>
<td>$1.6 \times 10^{-5}$</td>
<td>-725</td>
<td>$2.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>Brown CPC</td>
<td>$3.6 \times 10^{-7}$</td>
<td>-276</td>
<td>$2.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>Blue CPC</td>
<td>$4.5 \times 10^{-7}$</td>
<td>-366</td>
<td>$3.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>Red CPC</td>
<td>$6.3 \times 10^{-7}$</td>
<td>-370</td>
<td>$5.0 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Figure 46. Anodic and cathodic polarization plots for 1018 steel coupons a) untreated and b) treated with the Red CPC type and immersed in $\frac{1}{4}$-strength artificial seawater. Plots were recorded after initial steady-state potentials were reached (less than 90 minutes). Representative plots were chosen for this comparison. Inset is an enlargement of the possible semi-passive region on the anodic curve.
higher range as more noble potentials were applied in the anodic plots. In plots 44 and 46, an expanded view of the anodic curves for the Brown and Red CPC types indicated the possibility of “semi-passive” regions. In order to determine if the CPC films could be described as “passivating” films (albeit temporary), new treated coupons were exposed to deaerated ¼-strength artificial seawater and anodically polarized. The deaerated solution greatly reduced the presence of the oxygen reduction reaction, and the passive region on the anodic curve would have been obvious by a low and independent of applied voltage i_PASS region. Due to the larger size of the N₂ bubbler used to deaerate the solution compared to the smaller area of the barnacle cells, a new and larger cell was used for the deaerated experiments (the details are described in the Experimental section in this body of work). Anodic polarization plots for the Brown, Blue, and Red CPC types immersed in both open-to-air and deaerated ¼-strength artificial seawater solutions are shown in Figures 47 and 48, respectively. The E_CORR and i_CORR results are shown in Table 7, and are listed as “open to air – deaeration cell” and “deaerated – deaeration cell”. No regions of “semi-passive” behavior appeared in the aerated plots in Figure 47a, for any of the CPC types, and the plots in Figure 47b using the deaerated solution showed no signs of i_PASS.
Figure 47. Anodic polarization plots for 1018 steel coupons treated with the Brown, Blue, and Red CPC types and measured a) in open-to-air conditions and b) in deaerated conditions after immersion in ¼-strength artificial seawater. Plots were recorded after initial steady-state potentials were reached (less than 90 minutes). The CPC types are designed by color and line style as Brown (---), Blue (......), Red (- - - -), and control (—).
4.2.3 Compositional Chemistry of the CPC Surface Film as a Function of Immersion Time

The transformation of the CPC film from an as-applied protective film to a fully degraded film occurred on the surface of the 1018 steel upon immersion in ¼-strength artificial seawater solution in several stages. Most generally, the protective film either washed away to expose the steel to the corrosive environment or remained on the surface and became incorporated into the corrosion product to form an intermediate type of film that provided some partial protection. These two general scenarios also occurred simultaneously on the same substrate in some cases.

4.2.3.1 Electrochemical Behavior Coupons Used in Surface Film Study

The immersion environment for the coupons used in the surface film study were more like alternate immersion conditions than continuous immersion; they were repeatedly dried in preparation for surface chemistry measurements and subsequently re-immersed for continuation of the corrosion study. Alternate immersion of steel coupons is known to be more aggressive in causing corrosion because of a higher concentration of dissolved oxygen is replenished at the metal surface when the cyclic conditions of drying and re-immersion of the coupons occur[6, 117]. Electrochemical results were used, in this surface chemistry study, as a means to monitor the general behaviors of the CPC films during the repeated cycling of immersion and re-immersion.

The same general electrochemical behavior was observed for all CPC types in the surface film study as in the continuous immersion study previously reported above. Figure 48a displays the corrosion potential results for all of the CPC films, where the potential values for all the CPC-treated coupons decreased in nobility by day 1 of immersion. The decrease in corrosion potential was directly related to the film degradation. The corrosion potential values for the Brown CPC type remained between
40mV and 80mV more positive than values for the control for a majority of the test period, indicating that the film was providing some degree of protection to the steel surface. The corrosion potential values for the Red and Blue CPC types reached the same value, ~730mV, as for the control by days 3 and 4 correspondingly. Shown in Figure 48b, the corrosion rate results indicated that the Blue and Red CPC type films degraded quickly after immersion, while the Brown CPC type film was slower to degrade over time. The electrochemical results for all of the CPC types were recorded as averages of the surface area exposed to electrolyte for each coupon; the exposed areas on any given coupon exhibited different stages of protection across the surface. The forthcoming surface chemistry results using FT-IR and XPS highlight the different stages of protection that existed on a single coupon surface for each CPC type.

Figure 48. Representative a) corrosion potential (Brown, Blue, Red, and control) and b) corrosion rate results (ordered in the bar chart as Brown, Blue, Red, and control) for the CPC types immersed non-continuously in ¼-strength artificial seawater solution. The straight dashed line is the corrosion rate failure criteria of 0.04mm/yr.
4.2.3.2 Determination of CPC Film Degradation Stages via Fourier Transform-Infrared Spectroscopy and X-ray Phototelectron Spectroscopy

Distinct phases or degradation stages of the CPC film were identified via FT-IR and correlated to visual results. In general, the CPC film stages found on the immersed substrates could be described by 6 distinct types: a) intact CPC film, b) one or several exposed area(s) with no CPC or nearly nonexistent thin film, c) initial film degradation with light corrosion, d) medium corrosion with CPC film incorporated, e) heavy corrosion with CPC film incorporated, and f) corrosion with no CPC component. To ease data interpretation, a key, shown in Table 8, identifying the various film stages and corresponding visual and IR spectra is presented. The key only relates to the CPCs within this study under the specified conditions (immersion in ¼-strength artificial seawater at ambient laboratory conditions). Table 8 includes descriptions of the different CPC film stages, digital images from the CCD camera attached to the FT-IR that represent the film stages, and spectral representations with peak identifications corresponding to the images. The images shown in Table 8 have an area of 80μm x 80μm within each boxed region in the images. When two different images and peaks are shown in one stage, they represent the ranges occurring within that stage.

The CPC film was measured at the same spot, chosen as the center spot in the immersed area, over a period of days to monitor the degradation of the film over time. The center spot typically degraded the slowest, with corrosion product often initiating along the edges of the o-ring in the barnacle cell. Because all the distinct degradation stages for each CPC type were not necessarily represented at the center spot, various areas across each coupon surface were also measured. A general sampling of the degradation stages occurring across coupon surfaces on each immersion day was measured. One representative coupon was chosen for analysis of each CPC type, as the replicates within each CPC set had the same general behavior.

XPS was used to provide elemental composition information of each stage, when possible, to correlate with the IR results. XPS was intended to determine which
components of the as-applied film remained on the surface after the coated coupons were immersed in electrolyte. As noted previously, the coupons used for IR could not be used for the XPS measurements due to magnetization issues, so different coupons needed to be used to the XPS measurements. Obtaining all of the different corrosion stages on the smaller coupons was not possible due to edge effects. The primary stages were, in most cases, able to be duplicated. The coupons used for the XPS measurements were not immersed for the same amount of time because the different stages formed on the surfaces at different time lengths depending on the protective nature of the film. The coupons were taken out of immersion according to when the desired stages were present on the surface for each CPC type.
Table 8. Representative Surface Stages Existing on the 1018 Steel Surfaces with Corresponding Visual and IR-Spectral Illustrations.

<table>
<thead>
<tr>
<th>Description of CPC Film Stages</th>
<th>Visual Representation of CPC Film Stages</th>
<th>IR Spectral Representation with Peak Identification of CPC Film Stages</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Intact CPC film</td>
<td><img src="image1" alt="Visual Representation" /></td>
<td><img src="image2" alt="IR Spectral Representation" /></td>
</tr>
<tr>
<td>b) Exposed area with no CPC or sparse CPC film (bare metal)</td>
<td><img src="image3" alt="Visual Representation" /></td>
<td><img src="image4" alt="IR Spectral Representation" /></td>
</tr>
<tr>
<td>c) Initial CPC film degradation (initial or light corrosion)</td>
<td><img src="image5" alt="Visual Representation" /></td>
<td><img src="image6" alt="IR Spectral Representation" /></td>
</tr>
<tr>
<td>d) Medium corrosion with CPC film incorporated</td>
<td><img src="image7" alt="Visual Representation" /></td>
<td><img src="image8" alt="IR Spectral Representation" /></td>
</tr>
<tr>
<td>e) Heavy or dense corrosion with CPC film incorporated</td>
<td><img src="image9" alt="Visual Representation" /></td>
<td><img src="image10" alt="IR Spectral Representation" /></td>
</tr>
<tr>
<td>f) Corrosion with no CPC incorporated</td>
<td><img src="image11" alt="Visual Representation" /></td>
<td><img src="image12" alt="IR Spectral Representation" /></td>
</tr>
</tbody>
</table>
4.3.2.2.1 Control – Untreated 1018 Steel

Corrosion products initiated on the control coupon over a period of 6 immersion days. Figure 49 displays photographs of the coupon as a function of time, where the location and pictures of the points selected to represent spectra of the various stages shown in Figure 50 are also highlighted. The spectra, shown in Figure 50, could be classified into two general groups: spectra for points 1-3 correspond to a mix of uncorroded steel and initial corrosion product (from immersion days 1 and 2), and spectra for points 5-7 correspond to a thick corrosion product layer (formed on days 5 and 6). The spectrum for point 4 corresponds to an intermediate stage that consisted of both uncorroded metal and corrosion product phases across the substrate surface. Spectra similar to or the same as shown in Figure 50 can be found on any of the control coupons for immersion days 1-6. The spectra are shown in absorbance units, where the spectrum for the untreated and uncorroded 1018 steel has been subtracted from each spectrum in order to identify only the changes that occurred at the surface. The corrosion products for spectra for points 1-3 show an addition of an O-H stretch located between 2500 and 3500 cm\(^{-1}\); this broadening indicated the formation of the iron complex containing water.

Figure 49. Photographs of the control coupon surface by immersion day after drying and prior to IR measurements. The points in the top photos correspond to locations where selected spectra were taken. The corresponding CCD camera photos (from the FT-IR technique) of the selected points are shown in the lower set of photos (the boxed area between the gridlines are 80 μm x 80 μm. The 1018 steel coupons were immersed in ¼-strength artificial seawater.
As the corrosion product became denser on the steel surface and no uncorroded metal was present on the surface (spectra 4-7), peaks relating to the O-H stretching became more intense. These peaks and the remaining peaks found at 1646, 1500, 1355, 1018, 911, 733, and 537 cm\(^{-1}\) all correlate well to known IR signatures for phases of the primary corrosion product for the metal electrolyte system in this study, FeOOH(s)\(^{[118-120]}\). All of the measured points, 1-7, in Figure 50 correlate to degradation stages for stage \(f\) in Table 8.

![Figure 50](image-url)  
Figure 50. Surface reflectance IR spectra (shown as absorbance spectra with background subtraction of non-immersed 1018 steel) for the control coupon after immersion in \(\frac{1}{4}\)-strength artificial seawater. Spectra are numbered corresponding to the location and immersion day labeled in Figure 49.
4.3.2.2 Brown CPC Type

FT-IR

The Brown CPC-treated coupons withstood degradation of the CPC film over an immersion time of 10 days, the longest of any CPC type included in this study. The length of immersion time is not as relevant to this study as are the types of degradation stages that resulted and corresponding protection that the CPC films provided; therefore immersion time will not be highlighted. Corrosion product was slow to form on the 1018 steel surface and signature spectral peaks (C-H) that related to the Brown CPC type did not completely disappear from the IR-spectra as the corrosion product formed and progressed. Only IR spectra from days 0-3 will be considered in this body of work, as the stages did not change in terms of type, but rather only amount of each type of degradation stage on the surface, after day 3. Figure 51 displays photographs of the degradation of the representative replicate as a function of immersion time, while Figure 52 displays the corresponding IR-spectra taken at the coupon’s center spot within the immersed area over the same time period (10 days). Although the CCD camera photographs in Figure 52 indicated that corrosion product was present on the substrate surface, the corresponding spectra for days 1 and 2 were nearly identical to the spectra for both the day 0 and the as-applied Brown CPC film type. This apparent lack of change indicated that the CPC was likely integrated into the newly forming corrosion product, rather than being replaced by it. Once corrosion product appeared on the substrate surface and the film seemed to degrade (day 4), its progression was slow (nearly

![Figure 51. Photographs of the Brown CPC-treated coupon surface by immersion day after drying and prior to IR measurements. The 1018 steel coupons were immersed in ¼-strength artificial seawater.](image-url)
unchanging from *days 4-9*), and the CPC film remained as part of the surface film throughout. Over *days 4-9*, presence of the CPC film decreased (C-H peaks) and the presence of corrosion products (OH) increased. During this period, the corrosion product was still incorporated into the CPC film-coated substrate surface as an intermediate protective film across the entire substrate surface. The stages and spectra represented at the center spot on the substrate treated with the Brown CPC type did not represent all of the stage types present on the 1018 steel surface after immersion. The other stages present on the coupon surface will be highlighted next.

Spectra and corresponding CCD camera photographs for *days 1* and 3 of immersion were chosen to more completely represent all the stages relevant to the degradation of the Brown CPC film type on the steel substrate. After *day 1* of immersion, the majority of the CPC film was intact and can be shown as points 1 – 3 in Figure 53. During stages of initial and more progressive corrosion product formation, shown as points 4 and 5 in Figure 53, the substrate surface appeared to have a visually spotty pattern where areas of both corrosion product-containing film and corrosion-less CPC film existed simultaneously. The CPC remained as part of the surface film despite  

*Figure 52. Surface reflectance IR spectra (shown as absorbance spectra with background subtraction of non-immersed 1018 steel) for the central spot on the Brown CPC-treated coupon after immersion in ¼-strength artificial seawater. Spectra and corresponding photos are labeled by immersion day and degradation stage. The total area measured is 80 x 80μm (within boxed area). Bottom spectrum is as-applied CPC film.*
the corrosion product formation. Even after more obvious and heavy corrosion product had formed, shown specifically for the case of point 5 in Figure 53, the CPC film-related spectrum peaks (C-H peaks) did not decrease in intensity. Instead, the two types of phases, corrosion product and CPC film, both existed simultaneously on the 1018 steel coupon surface.

Figure 53. Surface reflectance IR spectra (shown as absorbance spectra with background subtraction of non-immersed 1018 steel) for the labeled points on the Brown CPC-treated coupon after immersion in \( \frac{1}{4} \)-strength artificial seawater for 1 day. Spectra and corresponding photos are labeled by measurement point and degradation stage (Table 8). The total area measured is 80 x 80 μm (within boxed region). As-applied CPC film is included (bottom spectra) for comparison.

After day 3, the amount of corrosion product increased across the coupon surface and the CPC film visually appeared to have some degree of corrosion product incorporated into it; Figure 54 shows photograph of the entire immersed surface, photographs of where the IR measurements were made, and the corresponding IR spectra. As the presence and volume of corrosion product increased across the surface, shown as the gradient-like progression in intensity of corrosion product from point 4 to point 8 in Figure 54, the intensity of broad O-H peaks between 2500 and 3500 cm\(^{-1}\) increased. As the corrosion product increased (visually and according to the additional OH peaks in the IR spectra), the intensity of the CPC components (primarily the various C-H peaks) did not necessarily decrease as a result. The simultaneous presence of peaks representing corrosion products and the CPC film indicated that the Brown CPC type film was not
degraded and then replaced by corrosion product as it formed. Even in the midst of an apparently thick corrosion product, as is the case for point 8 in Figure 54, the CPC was detected in significant amounts. The film remained at least partially intact and provided protection to the steel surface in the form of an intermediate protective film. Spectra were originally supposed to be taken until the CPC film could no longer be detected by IR-measurements. Even though by day 10 of immersion the corrosion product covered the entire immersed surface, peaks indicating the presence of the CPC remained present (although less intense) at many measured points. An example of day 10 IR results is shown in Figure 52.

![Figure 54. Surface reflectance IR spectra (shown as absorbance spectra with background subtraction of non-immersed 1018 steel) for the labeled points on the Brown CPC-treated coupon after immersion in ¼-strength artificial seawater for 3 days. Spectra and corresponding photos are numbered by measurement point. The total area measured is 80 x 80μm (within boxed area). Bottom spectrum is as-applied CPC film.](image)

XPS: Survey scans and corresponding IR

For the Brown CPC-treated coupons used for XPS measurements, three different stages of CPC film degradation (referenced from Table 8), stage a) intact CPC film, stage d) medium corrosion with CPC film incorporated, and stage e) dense corrosion with CPC incorporation, formed most readily on the immersed coupons. The stages of degradation that formed on the smaller coupons used for XPS (10 x 20mm surface area) were more
limited than those that formed on the larger coupons simply due to edge effects when the CPC was applied to the substrate. Figure 55 displays the IR spectra for these stages, as well as photographs of the measured points and the original coupon surfaces from which the points were selected. Shown in Figure 56, the resulting XPS data from these selected points showed a clear degradation of the film as the C1s peaks decreased in intensity. The O1s peaks increased and the Fe2p background immersed into more distinguishable peaks as the corrosion product (FeOOH) formed on the surface. The XPS spectra corresponding to stage a in Table 8 was similar to the as-applied film, but appeared with the addition of the Fe-related background. The remaining stages, stages d and e, corresponded more so to corrosion product only; newly-measurable Fe2p peaks and only nominal amounts of the CPC film were detected.

Table 9 lists the compositions and atomic percents of each element comprising the film stages detected in Figures 55 and 56, where the concentrations of S, Na, and Ca seemed to increase. This increase was not likely due to the components that originally comprised the film, but rather the increase in salt components on the substrate surface left behind after the gentle rinse and subsequent drying. This notion was considered after the identification of Mg components in the spectra at locations of heavier corrosion products. The Mg components were not detected on the surface using XPS prior to exposure to the
sea-salt electrolyte. The artificial sea-salt is known to contain high concentrations of NaCl (58.5%), MgCl₂6H₂O (26.5%), Na₂SO₄ (9.8%), and CaCl₂ (2.8%)\cite{121}. The Na, Mg, and Ca sea-salt components were most likely detected on the surface at regions of heavier corrosion product, as these ions became intermixed with the thick corrosion product.

Figure 56. XPS survey scans of the degradation stages a, d, and e (corresponding to IR-spectra in Figure 55) for a 1018 steel surface treated with the Brown CPC type and immersed in ¼-strength artificial seawater. The peaks are labeled according to elemental components.
Table 9. XPS survey scan composition and peak assignments of the Brown CPC film applied to the polished 1018 steel substrate and immersed in ¼-strength artificial seawater until the desired degradation stages were obtained. The stage labels correspond to the degradation stages in Figures 55 and 56. The compositional values were measured from survey spectra, while the peak assignments correspond to high resolution spectra, shown in Figures 58-61.

<table>
<thead>
<tr>
<th>CPC Film Stage #</th>
<th>C1s Atomic %</th>
<th>O1s Atomic %</th>
<th>Si2p %</th>
<th>S2p %</th>
<th>Ca2p %</th>
<th>Na1s %</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>82.09</td>
<td>6.75</td>
<td>10.32</td>
<td>0.48</td>
<td>0.22</td>
<td>0.14</td>
<td>0</td>
</tr>
<tr>
<td>Assignment</td>
<td>C-C &amp; Cw/S, Cw/OH, or Cw/Cl</td>
<td>OH or sulfate</td>
<td>organic silicone</td>
<td>sulfone or sulfate</td>
<td>CaCO₃ or CaSO₄</td>
<td>Na₂SO₄</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>57.45</td>
<td>34.35</td>
<td>3.6</td>
<td>2.0</td>
<td>0.41</td>
<td>1.51</td>
<td>0</td>
</tr>
<tr>
<td>Assignment</td>
<td>C-C &amp; Cw/S, Cw/OH, or Cw/Cl</td>
<td>OH or CO₂ &amp; Fe₂O₃</td>
<td>organic silicone</td>
<td>sulfone or sulfate</td>
<td>CaCO₃ or CaSO₄</td>
<td>Na₂SO₄</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>28.10</td>
<td>58.96</td>
<td>11.00</td>
<td>0.50</td>
<td>0.37</td>
<td>0.73</td>
<td>0.35</td>
</tr>
<tr>
<td>Assignment</td>
<td>C-C &amp; Cw/S, Cw/OH, or Cw/Cl</td>
<td>OH or CO₂ &amp; Fe₂O₃</td>
<td>organic silicone</td>
<td>sulfone or sulfate</td>
<td>CaCO₃ or CaSO₄</td>
<td>Na₂SO₄</td>
<td></td>
</tr>
</tbody>
</table>

XPS: High resolution scans

High resolution XPS scans were performed on the three different degradation stages, a, d, and e, that were identified on the Brown CPC-treated coupons. The resulting spectra were used to detect changes in the surface composition relating to the different stages. The stage a surface film was determined to be the same as the as-applied surface film, indicating that the initially-immersed CPC film was fully protective of the metal surface. For scans of stages d and e, additional peaks appeared within the C1s and O1s regions that indicated a definite change in the composition of the surface film. Figure 57 includes the deconvolution of C1s and O1s peaks as they changed during stages a, d, and e. The peak assignment for the new peaks for C1s and O1s are listed as possibilities in Table 9, although the origin of these peaks could not be definitively determined. Peaks representing S2p, Na1s, Ca2p, and Si2p are displayed in Figures 58 and 59; they did not change in composition, but rather in intensity, for the different degradation stages. New
peaks representing Cl2p and Fe2p appeared in the spectra during stages d and e, and are shown in Figure 60. The Cl and Fe-based peaks relate directly to the increased formation of corrosion product on the coupon surface. The addition of new peaks, originating from corrosion product formation and the electrolyte salts, made peak assignments in Table 9 more ambiguous. For instance, the origin of the Ca2p peaks, shown in Figure 59, became indecipherable with the addition of the salts, of which CaCl2 was included. Because XPS is a very surface sensitive technique, the additional corrosion product on the substrate surface likely became the primary source of peaks for spectra for stages d and e. The CPC film could have been more intact at the metal/film interface; however, the surface scans would not have been able to resolve this unknown without obtaining a cross-section of the film. Also, assigning peaks, such as the additional C1s peaks in Figure 57, definitively to chloride, hydroxyl, or sulfur-related compounds was impossible due to the fact that assignment to one component would then discount the remaining two possibilities (which were also likely to have existed). The additional peaks in Figure 57 that emerged for the O1s component were most likely from Fe2O3 or other forms of iron-based corrosion product that formed on the surface$^{110}$, especially since the intensity of the O1s peaks increased substantially relative to the C1s peaks as corrosion product formed on the surface. Doublet peaks from Fe2p indicated the presence of both Fe$^{3+}$ and Fe$^{2+}$ components that obviously related to corrosion product$^{115, 110, 122, 123}$. Figure 60 displays the peaks for Fe2p, where products of corrosion reactions do seem to be the origin of the Fe peaks, in this case either FeCl2 or FeOOH.
Figure 57. High resolution XPS spectra of the degradation stages \(a, d,\) and \(e\) (corresponding to IR-spectra in Figure 55) for a) C1s and b) O1s components for a 1018 steel surface treated with the Brown CPC type and immersed in \(\frac{1}{4}\)-strength artificial seawater. The intensity of stages \(d\) and \(e\) were exaggerated for the C1s plot to display the new peaks that emerged as the film degraded.

Figure 58. High resolution XPS spectra of the degradation stages \(a, d,\) and \(e\) (corresponding to IR-spectra in Figure 55) for a) Si 2p and b) S 2p components for a 1018 steel surface treated with the Brown CPC type and immersed in \(\frac{1}{4}\)-strength artificial seawater.
Figure. 59. High resolution XPS spectra of the degradation stages \(a, d,\) and \(e\) (corresponding to IR-spectra in Figure 55) for a) Ca 2p and b) Na 1s components for a 1018 steel surface treated with the Brown CPC type and immersed in \(\frac{1}{4}\)-strength artificial seawater.

Figure. 60. High resolution XPS spectra of the degradation stages \(a, d,\) and \(e\) (corresponding to IR-spectra in Figure 55) for a) Cl 1s and b) Fe 2p components for a 1018 steel surface treated with the Brown CPC type and immersed in \(\frac{1}{4}\)-strength artificial seawater.
4.3.2.2.3 Blue CPC Type

FTIR

The Blue CPC-treated coupons were immersed in artificial seawater solution for 6 days; however, only the first 4 days will be considered for IR analysis because the types of phases did not change on the coupons after day 4. The distribution of the film stages, namely an increase in amount of corrosion product across the 1018 steel surface, did change as immersion time progressed. Photographs of the progression of film degradation for the replicate selected for IR analysis is shown in Figure 61.

Due to the inhomogeneous nature of the CPC films, the initial analysis focused on comparing the CPC films at one spot, the center spot, as it degraded progressively as a function of immersion time. At the center point on all of the Blue CPC type coupons, the CPC film degraded the slowest and corrosion product formed most gradually as compared to the other areas on the same surface. The spectra for IR measurements taken at the center spot over time is shown in Figure 62, with the corresponding CCD camera photographs of the measured spot included for each day. The heavier corrosion product tended to appear more washed out in the photos, due to the lower reflection of the surface. In actuality, after day 5 and 6 of immersion the surfaces were covered by a thick
corrosion product. As the Blue CPC film degraded, beginning on day 2 and most apparent by day 4, the intensity of the CPC film spectrum peaks (C-H) decreased and the peaks indicating corrosion product (broadened O-H stretching) increase in intensity between 2500 – 3500cm⁻¹. The spectrum for the corroded Blue CPC-treated coupon during on day 6 was similar to the characteristic spectral peaks measured for the corroded control coupon spectra in Figure 50. The central spot did not represent all of the degradation stages that existed across the coupon surface for the Blue CPC; therefore, other areas across the coupon surface were measured via IR.

A second approach to IR analysis focused on comparing the different stages typically present on the same coupon surface on one day. For the Blue CPC type, IR and visual results from day 1 were chosen and are shown in Figure 63. The results on this day were selected because they represented the array of different stages present on most of the representative coupons at any given time. Stage b was identified by points 2 and 3 in Figure 63; areas were found on the coupon surface where no CPC existed amidst the intact film or corrosion product. These open spots were common across the Blue CPC-
treated surface after immersion. *Stage a*, the intact CPC film, was correlated to point #1 on the *day 1* coupon, where strong IR signals were present although corrosion product had begun to lightly form on the surface. According to the IR results for points 5 and 6 in Figure 63, the CPC film was sparse and intermixed with light corrosion on the steel surface (identified as *stage c*); the light corrosion product formation could have caused the CPC film to thin out or detach from the metal surface, and the IR signals for these points to be low. *Stage e*, identified at point 4 in Figure 63, is an ideal example of the CPC film co-mingling with the corrosion product. At point 4, the peaks for the corrosion product (O-H) and the CPC (C-H) were both intense, indicating some regions where the CPC film and corrosion product co-mingled. After day 1, corrosion product became thicker on some regions on the surface and the CPC film was not detected at those sites. Eventually, after corrosion product formed over the entire coupon surface by *day 6* (shown pictorially in Figure 62), the CPC film (C-H peaks) was not detected by IR measurements at any region on the surface (not represented in any figure). The absence of CPC film-related peaks implied that the CPC film had been replaced by corrosion product.
XPS: Survey scans and corresponding IR

Five CPC film degradation stages, stages b-f described in Table 8, were identified on the immersed coupons treated with the Blue CPC type and measured using XPS. Because the Blue CPC was applied thin enough to obtain interfacial data, the intensity of the IR peaks, shown in Figure 64, were much lower than those obtained in the above figures (Figures 62 and 63). Figure 64 displays photographs of the coupon surfaces and exact locations where IR and XPS spectra were measured. The stages identified and measured on the Blue CPC-treated coupons were representative of all of the stages present during the film degradation and initiation of corrosion product. The XPS spectra that correspond to the stages identified in the IR spectra and photographs in Figure 64 are shown in Figure 65. XPS spectra of the stages chosen for the Blue CPC type indicated a shift from protective film, stages b and c, to heavily corroded surface at stage f. Although the IR-spectrum for stage b indicated that the CPC was not present or was in very small amounts, the XPS spectra in Figure 65 showed that the peak assignments were
the same as for the as-applied film, although much lower in intensity. It is likely that the CPC film was on the surface, but in such small amounts that it was detectable during the XPS scans, but hidden in the background during IR scanning. Compositional values and peak assumptions for the Blue CPC-treated substrate are identified in Table 10. As the CPC film degraded (stages d and e), peaks indicating the addition of corrosion product (O1s peaks assigned to OH and Fe2O3 components) became apparent visually as well as via the spectra in Figures 64 and 65. The spectra for stage f, displayed in Figures 66 and 65, show that the corrosion product overtook the CPC film and likely replaced it; the IR spectra contains no CPC-related components (C-H), and the XPS spectra showed little amounts of C1s and an increased presence of Fe2p and O1s peaks relating to corrosion product and the metal substrate. Mg1s peaks appeared during stages d-f, originating from the sea-salt remaining on the scanned surface. A more detailed discussion of the Mg1s component was included in the results for the Brown CPC type and will not be repeated.

Figure 64. Surface reflectance IR spectra of the degradation stages b-f (pictured on the left and labeled by stage type) for a 1018 steel surface treated with the Blue CPC type and immersed in ¼-strength artificial seawater until the appropriate stages were present. The total area measured is 80 x 80 μm (within boxed area). The bottom spectrum is the as-applied film.
Figure 65. XPS survey spectra of the degradation stages (corresponding to IR-spectra in Figure 64) for a 1018 steel surface treated with the Blue CPC type and immersed in ¼-strength artificial seawater.
Table 10. XPS survey scan composition and peak assignments of the Blue CPC film applied to the polished 1018 steel substrate and immersed in ¼-strength artificial seawater. The stages correspond to the degradation stages in Figures 64 and 65. The compositional values were measured from survey spectra, while the peak assignments correspond to high resolution spectra.

<table>
<thead>
<tr>
<th>CPC Film Stage</th>
<th>C1s</th>
<th>O1s</th>
<th>Si2p</th>
<th>S2p</th>
<th>Ca2p</th>
<th>Na1s</th>
<th>Mg</th>
<th>Cl2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>84.43</td>
<td>11.48</td>
<td>2.06</td>
<td>1.36</td>
<td>0.36</td>
<td>0.21</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Assignment</td>
<td>C-C &amp; Cw/S or Cw/ether</td>
<td>OH or SO$_4$</td>
<td>organic silicone</td>
<td>sulfone or sulfate</td>
<td>CaCO$_3$ or CaSO$_4$</td>
<td>Na$_2$SO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>80.78</td>
<td>11.20</td>
<td>7.11</td>
<td>0.53</td>
<td>0.17</td>
<td>0.21</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Assignment</td>
<td>C-C &amp; Cw/S or Cw/ether</td>
<td>OH or SO$_4$</td>
<td>organic silicone</td>
<td>sulfone or sulfate</td>
<td>CaCO$_3$ or CaSO$_4$</td>
<td>Na$_2$SO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>52.47</td>
<td>41.90</td>
<td>2.52</td>
<td>0.59</td>
<td>0.94</td>
<td>0.47</td>
<td>1.27</td>
<td>0.35</td>
</tr>
<tr>
<td>Assignment</td>
<td>C-C &amp; Cw/S or Cw/OH, Cw/Cl &amp; carbonate</td>
<td>OH or CO$_3$ &amp; Fe$_2$O$_3$ &amp; SO$_4$</td>
<td>organic silicone</td>
<td>sulfone or sulfate</td>
<td>CaCO$_3$ or CaSO$_4$</td>
<td>Na$_2$SO$_4$</td>
<td>alkali Cl</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>37.41</td>
<td>54.60</td>
<td>4.83</td>
<td>0.49</td>
<td>0.74</td>
<td>0.80</td>
<td>0.78</td>
<td>0.36</td>
</tr>
<tr>
<td>Assignment</td>
<td>C-C &amp; Cw/S or Cw/OH, Cw/Cl &amp; carbonate</td>
<td>OH or CO$_3$ &amp; Fe$_2$O$_3$ &amp; SO$_4$</td>
<td>organic silicone</td>
<td>sulfone or sulfate</td>
<td>CaCO$_3$ or CaSO$_4$</td>
<td>Na$_2$SO$_4$</td>
<td>alkali Cl</td>
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<tr>
<td>f</td>
<td>24.91</td>
<td>66.90</td>
<td>6.50</td>
<td>0.50</td>
<td>0</td>
<td>0.70</td>
<td>0.49</td>
<td>0</td>
</tr>
<tr>
<td>Assignment</td>
<td>C-C &amp; Cw/OH, Cw/Cl Cw/ether</td>
<td>Fe$_2$O$_3$</td>
<td>organic silicone</td>
<td>sulfone or sulfate</td>
<td></td>
<td>Na$_2$SO$_4$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

XPS: High resolution scans

High resolution spectra further describe the degradation stages identified using IR and XPS. Shown in Figures 66, 67, 68, and 69, high resolution scans were measured for the C1s and O1s, the Si2p and S2p, the Na1s and Ca2p, and the Cl1s and Fe2p components respectively. In Figure 66, the C1s peaks for stages b and c consisted primarily of aliphatic carbons and sulfur or ether-containing components, while the corroded stages, d-f, also included peaks originating from carbonate or chloride.
Identification of the specific state was impossible because the elements S, OH, and Cl, are known components of the surface film and the binding energies for all three of the options are within similar range; the peaks could therefore not be further deconvoluted with the XPS data provided. Figure 66 displays O1s high resolution spectra, where the distinct shift occurred when comparing *stages b* and *c* to *stages d-f*. The O1s states related to the intact CPC film comprised of OH or SO₄ components for *stages b* and *c*, and related to the corroded surface comprised of Fe₂O₃ and other generally-identified Fe oxide states for *stages d-f*. The Si2p peaks, shown in Figure 67, did not change in terms of composition (no shift in binding energy), but did decrease in intensity to only trace amounts when comparing *stages b-f*. The S2p peaks, shown in Figure 67, were identified as sulfates or sulfones until *stage f*, where the peaks shifted and were identified as sulfites. The origin of Ca2p peaks, shown in Figure 68, was ambiguous because CaCl₂ was a component of the sea-salt and is likely to be at least one source of the Ca2p peaks. The Na1s peaks, shown in Figure 68, did not change in terms of assignment of compound, Na₂SO₄, but the origin of the component was not necessarily the same since Na₂SO₄ is also a component in artificial seawater. Peak assignments for NaCl did not appear in any of the spectra, although known to be a large constituent of sea-salt. The peaks specific to NaCl identification, binding energy of 1071.5 – 1072.5eV for Na1s peaks, did not appear in the high resolution spectra, Figure 68. Cl 2p peaks, shown in Figure 69, appeared in spectra for *stages d-f* and were identified as alkali chlorides (salts). Figure 69 also displays Fe2p peaks that appeared during the scan of *stages d-f*, identified as FeCl₂ or FeOOH components. Overall the high resolution spectra showed that, after corrosion product formed, the CPC film was degraded and nearly non-existent on the substrate surface. The film’s behavior was most apparent with the drastic lowering in intensity of the C1s peaks (the primary marker for the CPC film) from *stage c* to *stage d* and beyond.
Figure 66. High resolution XPS spectra of the degradation stages b-f (corresponding to IR-spectra in Figure 64) for C1s and O1s on a 1018 steel surface treated with the Blue CPC type and immersed in 1/4-strength artificial seawater. The peak intensities are the same for stages b-c, and d-f for the C1s spectra.
Figure 67. High resolution XPS spectra of the degradation stages b-f (corresponding to IR-spectra in Figure 64) for Si2p and S2p on a 1018 steel surface treated with the Blue CPC type and immersed in ¼-strength artificial seawater.
Figure 68. High resolution XPS spectra of the degradation stages b-f (corresponding to IR-spectra in Figure 64) for Ca2p and Na1s on a 1018 steel surface treated with the Blue CPC type and immersed in ⅛-strength artificial seawater.
Figure 69. High resolution XPS spectra of the degradation stages b-f (corresponding to IR-spectra in Figure 64) for Cl2p and Fe2p on a 1018 steel surface treated with the Blue CPC type and immersed in ¼-strength artificial seawater.
4.3.2.2.4 Red CPC Type

FT-IR

The 1018 steel coupons treated with the Red CPC type were immersed in artificial seawater solution for 8 days, until all of the replicates exhibited no signs of the CPC being incorporated into the surface film via IR-measurements. The different phases that existed on the representative coupon surface did not significantly alter in terms of types of degradation stages after 3 days of immersion, but the distribution of the stages did change (corrosion product stages increased in volume). One coupon was chosen to represent all of the replicates, and the visual degradation of the CPC film on that coupon surface is shown in Figure 70 for the entire 8-day immersion period. IR spectra were monitored to determine the condition of the CPC film at the center of the coupon, shown in Figure 71, as a function of immersion time. The center point (visually shown in Figure 70) remained intact for the longest time compared to other areas on the immersed coupon surface. During immersion (days 0-2), the CPC film gradually decreased in intensity according to the spectra in Figure 71. By day 3, the majority of the CPC film had degraded and corrosion product had formed in its place. The condition of the CPC film did not noticeably change (via either IR spectra or visually) between immersion day 3 through day 6. After day 6, corrosion product began to form more prevalently (increased presence of peaks representing O-H groups between 2500-3500cm⁻¹) as the CPC film degraded (intensity of primary and secondary C-H groups between 2840-3000cm⁻¹ and 1375-1470cm⁻¹ correspondingly). By day 8 the IR spectra contained very little traces of the CPC film (C-H peaks) and O-H groups and other peaks relating to corrosion product primarily remained (spectra was very similar to IR spectra shown in Figure 50 for the
corroded control coupon). The variety of spectra for the Red CPC type, shown in Figure 71, are representative of nearly all of the stages that existed across the coupon surface over the immersion period. Although not shown in any figures, regions also existed within the intact Red CPC film where no CPC was present and only the 1018 steel substrate was measured using FT-IR.

![Figure 71. Surface reflectance IR spectra (shown as absorbance spectra with background subtraction of non-immersed 1018 steel) for the central spot on the Red CPC-treated coupon after immersion in ¼-strength artificial seawater. Spectra and corresponding photos are numbered by immersion day. The total area measured is 80 x 80μm (within boxed area). Bottom spectrum is as-applied CPC film.](image)

XPS: Survey scans and corresponding IR

Degradation stages c, e, and f (represented in Table 8) were identified across the coupons that were treated with the Red CPC after immersion and measured using XPS. These stages consist of either initial or heavy corrosion product with or without the presence of the CPC film. The stages of degradation were identified using IR, and are represented by their spectra and in photographs in Figure 72. The points, identified using IR, were then measured using XPS; Figure 73 displays the corresponding XPS survey spectra for the measured points. The IR spectra for the Red CPC film applied for XPS was thin enough to obtain interfacial measurements; however, this also caused the IR-related peaks to be significantly less intense. Figure 72 shows the presence of the CPC
film combined with the corrosion product for stages c and e, and the absence of the film in stage f. Table 11 displays the components comprising the steel surface during stages c, e, and f and their atomic percents from the survey scan. Based on the XPS spectra in Figure 73, the CPC film seems to have been highly degraded and even likely replaced by the corrosion that formed on the substrate surface. Even in stage c, the intensity of the C1s peaks, the primary peaks for identifying the CPC film, was low compared to the intensity of the as-applied film. Peaks representing corrosion product, O1s and Fe2p, increased in intensity from stages c to f, such that the only surface component measured was the corrosion product. Peaks for Mg1s and Cl 2p were present in all of the stages measured by XPS, indicating that remnants of the sea-salt were not fully rinsed away prior to measurements.

Figure 72. Surface reflectance IR spectra of the degradation stages b-f (pictured on the left and labeled by stage type) for a 1018 steel surface treated with the Red CPC type and immersed in ¼-strength artificial seawater until the appropriate stages were present. The total area measured is 80 x 80μm (within boxed area). The bottom spectrum is the as-applied film.
Figure 73. XPS survey spectra of the degradation stages c, e, and f (corresponding to IR-spectra in Figure 72) for a 1018 steel surface treated with the Red CPC type and immersed in 1/4-strength artificial seawater.
Table 11. XPS survey scan composition and peak assignments of the Red CPC film applied to the polished 1018 steel substrate and immersed in ¼-strength artificial seawater. The stage numbers correspond to the degradation stages in Figures 72 and 73. The compositional values were measured from survey spectra, while the peak assignments correspond to high resolution spectra.

<table>
<thead>
<tr>
<th>CPC Film Stage #</th>
<th>C1s</th>
<th>O1s</th>
<th>Si2p</th>
<th>S2p</th>
<th>Ba3d</th>
<th>Ca2p</th>
<th>Na1s</th>
<th>Mg1s</th>
</tr>
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<tr>
<td>e</td>
<td>34.87 Atomic %</td>
<td>C-C &amp; Cw/S, Cw/OH or Cw/Cl</td>
<td>43.38</td>
<td>4.69</td>
<td>Organic silicone</td>
<td>*</td>
<td>2.44 CaSO4</td>
<td>4.12 Na2SO4</td>
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<tr>
<td>Assignment</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>e</td>
<td>30.90 Atomic %</td>
<td>C-C &amp; Cw/S, Cw/OH or Cw/Cl</td>
<td>65.95</td>
<td>0.55</td>
<td>Organic silicone</td>
<td>0</td>
<td>*</td>
<td>0.61 CaCO3</td>
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<td>Assignment</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>f</td>
<td>30.52 Atomic %</td>
<td>C-C &amp; Cw/S, Cw/OH or Cw/Cl</td>
<td>67.38</td>
<td>**</td>
<td>0</td>
<td>*</td>
<td>0.44 CaCO3</td>
<td>0.85 Na2SO4</td>
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<tr>
<td>Assignment</td>
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<td></td>
</tr>
</tbody>
</table>

*Peaks were indistinguishable from Fe LMM peaks in the survey scan
**Peaks were indistinguishable from Fe 3s peaks in the survey scan

XPS: High resolution scans

High resolution scans of the surface degradation stages, c, e, and f, for the Red CPC type measured the chemical states comprising the corrosion product and the CPC film as it degraded. Table 11 displays the peak assignments for the elemental components comprising the Red CPC type for stages c, e, and f. Because stage a was not located on the XPS coupons treated with the Red CPC film, high resolution spectra from the as-applied film was included in all of the related figures for comparison purposes. C1s peaks, shown as deconvoluted peaks in Figure 74 for degradation stages c, e, and f, indicated a breakdown of the CPC film; the breakdown was designated by the introduction of peaks other than those relating to the aliphatic carbons comprising the simpler as-applied film. C1s peaks indicating compounds with S, Cl, or ether type (R’ – O – R chemical configuration) were identified in stages c, e, and f, while peaks related to carbonates were identified in stages e and f. O1s peaks, shown in Figure 74, indicated the addition of peaks from corrosion product, identified as Fe2O3 and more generally as metal...
oxides in stages c, e, and f. Hydroxyl groups or chlorates, as well as carbonates, were identified in stages f for the O1s component. The hydroxyl groups or chlorates are possibly from water absorption of the film or found along with the corrosion product. The Si2p component was identified as an organic silicone-type that is found in petroleum oils; the chemical state of the silicone, shown in Figure 75, did not change with the formation on corrosion, but it did decrease in intensity. In Figure 75, the chemical states for S were narrowed, but not definitively determined due to the presence of sulfur-components in the CPC film and the electrolyte. There simply was not enough information from these spectra regarding the sulfur-based peaks to make conclusions.

High resolution peaks for Ca, Na, Ba, and Fe were more difficult to identify in terms of chemical states due to interference from the corrosion product and remnants of the sea-salt from the electrolyte. The calcium-based components, shown in Figure 76, were not originally detected in the Red CPC type; therefore, they originated from the sea-salt electrolyte. Peaks relating to both CaCl2 and CaSO4 were identified, and both were possibilities found within the corrosion product. The sodium-based peaks in the high resolution spectra in Figure 76 were identified as Na2SO4 for the as-applied film and stage c, and NaCl for stages e and f. The Na2SO4 component from stage c, as well as the NaCl component from stages e and f, originated from the sea-salt electrolyte that was not rinsed off of the substrate prior to measurements. The peaks representing Ba3d were measured but not identified in either the survey or high resolution survey scans due to the fact that the Fe LMM peaks overwhelmed their signature region, shown in Figure 77 for stages e and f. The high resolution scan of the binding energy region for Ba3d is show in Figure 77; the Ba3d peaks are identified in the as-applied film, but not in stage c. Other Fe-related peaks overwhelmed the same regions where other Ba-related peaks would have also appeared. The presence of barium-related corrosion inhibitors on the surface after immersion in the artificial seawater solution was uncertain, due to the inability to identify the peaks. Doublet peaks representing Fe2p, shown in Figure 77, were identified in stages c, e, and f, as corrosion product formed on the surface. The spectrum in stage f is likely representative of corrosion product and electrolyte remnant components only and no CPC film.
Figure 74. High resolution XPS spectra of the degradation stages c, e, and f (corresponding to IR-spectra in Figure 72) for a) C1s and b) O1s on a 1018 steel surface treated with the Red CPC type and immersed in ¼-strength artificial seawater. In the C1s spectra group, the y-axis scale for stages c, e, and f is narrower than for the as-applied film so that all of the peaks could be compared in the same figure.
Figure 75. High resolution XPS spectra of the degradation stages c, e, and f (corresponding to IR-spectra in Figure 72) for a) Si2p and b) S2p on a 1018 steel surface treated with the Red CPC type and immersed in ¼-strength artificial seawater. In the Si2p spectra group, the y-axis scale for stages c, e, and f is narrower than for the as-applied film so that all of the peaks could be compared in the same figure.
Figure 76. High resolution XPS spectra of the degradation stages c, e, and f (corresponding to IR-spectra in Figure 72) for a) Ca2p and b) Na1s on a 1018 steel surface treated with the Red CPC type and immersed in ¼-strength artificial seawater.
Figure 77. High resolution XPS spectra of the degradation stages c, e, and f (corresponding to IR-spectra in Figure 72) for a) Ba3d and b) Fe2p on a 1018 steel surface treated with the Red CPC type and immersed in ¼-strength artificial seawater.
4.3 Application of CPC to 1018 Steel Substrate: Dip versus Spray

The dip and spray CPC application techniques offered different degrees of protection from the formation of corrosion product, but the same conclusions could be made regarding the CPCs in terms of their general behavior. The coupons used the dipping application for the Red and Blue CPC types seemed to not degrade as quickly as the coupons in which the spray application was used, as shown in Figures 78 and 79. In both cases, the corrosion potential and corrosion rates for the dipped coupons were characteristic of a more protective CPC film. Corrosion product formed less quickly on the dipped coupons; however, the manner in which the coupons corroded (quickly after the initial formation of corrosion product) remained the same. In the case of the Brown CPC, the results for the dipped vs. sprayed techniques were indistinguishable and are shown in Figure 80; these results led to the consideration of other factors that may have contributed to differences in the application techniques, such as initial CPC dwell time.

![Figure 78](image.png)

Figure 78. Plots of a) corrosion potential and b) corrosion rate for the two different CPC application techniques, spraying(—) and dipping (—−−), using the Blue CPC type. While the lines are shown as continuous, the measurements were not. Measurements were made each 24 hours and are labeled by immersion day. The control results (—−−−−) are included for comparison. The solid straight line for b) indicates the failure criteria.
The results comparing the dipping and spraying applications were distinct and less likely to be related to application method than to the fact that the corrosion inhibitors were given more time to adsorb onto the metal substrate when immersed in the bulk CPC during the dip application. This assumption about dwell time is based on the results from a subsequent sprayed-on application test set that underwent the same electrochemical evaluation as the previous electrochemical results reported in Figures 36, 37, and 38;
however, the coupons were only given a limited time to lay flat before being hung vertically to cure. During the spraying application of CPCs for the electrochemical results previously reported in this study, the treated coupons were allowed to lie flat for between 30 and 120 minutes prior to being hung vertically for curing. This dwell time was based on the amount of time needed to transport the freshly-treated coupons to the laboratory for the vertical hang curing. In the additional spray application procedure, the freshly-cured coupons were stored at a 35-45° angle during transport and then hung vertically to cure; this procedure essentially allowed for a dwell time of 0 minutes. When the subsequent electrochemical evaluation began, results displayed in Figure 81, all of the coupons corroded quicker and at a higher rate than previous test sets (results from Figures 36-38 and the spray results in Figures 78-80). The assumption based on results in Figure 81 is that the longer dwell time for the CPCs on the metal substrate relates directly to the formation of a more protective film.

A closer examination of the dwell times between the sprayed and dipped application techniques needs to be made. In the specific case of the dipped vs. sprayed application, the dipped application allowed the coupons to be fully immersed in the bulk CPC for about 3 minutes and then the thickly-coated metal coupons were hung vertically to cure. The thick CPC film remained on the coupon surface to slowly drip off over 48 hours as it also cured. During spraying, a much thinner and more evenly distributed coating of the bulk CPC was initially sprayed onto the metal surface. While the horizontal dwell time was much
longer for the sprayed coupons (30-120 minutes versus 3 minutes), the amount of CPC left to cure on the surface was considerably less than for the dipped coupons. Excess CPC dripped off the sprayed coupons, but in a much smaller quantity. The Brown results may not have been able to be differentiated between the application techniques, shown in Figure 80, because that CPC type may require less time for the protective film to form on the substrate as compared to the Red and Blue CPC types. This last statement is only a supposition, and not proved in this study. These application factors leave unanswered questions that are possible areas for further study, but beyond the scope of this work.
Chapter 5

5.0 Discussion

Several key points can be made based on the results of this study of Corrosion Preventative Compounds applied to 1018 steel surfaces and their corresponding immersion in ¼-strength artificial seawater solution.

1) The components comprising the CPC film that provided protection to the 1018 steel surface after immersion in artificial seawater could be identified, but the structure of the inhibitor compounds remained somewhat unknown due to the complexity in composition of both the CPC and the sea-salt-based electrolyte.

Surface analysis of both the as-applied CPC films and the immersed films lead to generalizations about the protective nature of the films:

a) The degree of protection (or length of continuous immersion time during which the CPC provided protection) seemed to be directly-related to the presence of the CPC’s oil-based components on the substrate surface. Regardless of the presence of corrosion inhibitor additives, the role that the mixture of oils played in controlling corrosion at the substrate surface could not be discounted. Even amidst a visually-corroded surface, especially in the case of the Brown CPC type, the 1018 steel substrate remained protected from failure with the addition of the oil-based CPC surface film. IR measurements proved that the oil-based film remained on the substrate surface, likely intermixed with the corrosion product, to provide an intermediate stage of surface protection in the static immersion environment. In the case of the Blue and Red CPC types, this intermediate stage was short-lived; however, the stage was long-lasting for the Brown CPC type. The intermediate stage had the consistency of an oily-rust type of corrosion product; where the CPC and corrosion product no longer co-existed as two separate components, but instead commingled and seemed to act as a single rather protective film. For IR analysis, the CPC films were detected via the presence of C-H vibrations within the different
stages of the degrading surface films as a function of extended immersion time (in some cases, 10 days). For XPS measurements, the CPC films were detected using the presence of C1s (aliphatic hydrocarbon) and Si2p (silicone oil) components across the coupon surface within areas identified as intact film, degrading film, and corrosion. These components were chosen because they comprised the majority of oil-based constituents within the bulk and as-applied CPC films.

b) Corrosion inhibitive additives, such as barium, calcium, and sodium sulfonates, may have been components of the CPCs, but their identification as the primary source of corrosion protection is questionable. Peak-fitting of high resolution XPS results revealed the presence of BaSO₄ or CaSO₄-based components in the as-applied films (depending on the CPC type), which could be translated into barium and calcium sulfonate components within the oil-based CPC film. Na1s, in the form of NaSO₄, was identified and seemed to also be an additive to the oil-based mixture. Barium, calcium, and sodium sulfates and sulfonates have high solubility in oil solutions (and low solubility in aqueous solutions) and are known additives to oil-based mixtures to prevent corrosion[124-127]. In general, their chemical structure consists of a functional group (usually an alky group), attached to an aromatic ring, followed by the sulfonate group and calcium, barium, or sodium component: \((R-\text{O})\text{-SO}_3\text{Ca}\), for example. Identification of these possible components at the substrate surface after the substrates were immersed became difficult due to the fact that 1) the components were originally detected at low concentrations (less than 1 atomic percent), 2) the corrosion product formed a thick layer that blocked the metal/film interface, and 3) sea-salt contains Na, S, and Ca constituents that made identification of any of these intact sulfonate-based components within the corrosion layer inconclusive when deconvoluting from the sea-salt component-based signature peaks. In the case of barium, the peaks were overwhelmed by peaks for Fe LMM; therefore it was unknown whether barium was detected via XPS on the corroded substrate surface. Suggestions regarding methods to eliminate these unknowns are included in a following section within this research.
2) The Blue and Red CPC types did not offer sustainable protection of the 1018 steel surface in ¼-strength artificial seawater. Both films tended to degrade and were finally replaced by corrosion product. The corrosion behavior of 1018 steel coupons treated with both the Blue and Red CPC types were very similar when immersed in ¼-strength artificial seawater; therefore, the discussion for these two types will be combined. Both CPC film types tended to completely degrade relatively quickly (within 24 to 72 hours) after immersion. The \( E_{\text{CORR}} \) values, shown in Figure 82 for ~75% of the replicates, were nearly identical to the corresponding values for the control coupon (~ -730mV vs. SCE), indicating that the protective film actually degraded and no longer remained on the surface. A Nyquist plot in Figure 83 shows that only the mass transfer time constant appeared on days 1 and 2 of immersion relating to both CPCs Blue and Red. The mass transfer reaction related to likely penetration of the corrosive ions in the seawater through the film to the metal surface, which in turn caused corrosion product formation on the surface.
IR spectra correlated with the electrochemistry results that indicated that the film types were replaced with corrosion product as they formed on the surface. Overall, both CPC types exhibited relatively simple stages (that can be referred to in Table 8, shown again below for ease of comparison) of film degradation and failure including, a) intact film (lasted briefly), b) open areas with sparse CPC, c) initial film degradation (with CPC-related peaks that decreased in intensity) d) medium corrosion with CPC film incorporated (lasted only briefly), and f) corrosion with no CPC film incorporated (as film was replaced with corrosion product).

Degradation stages b, c, d, and f are described specifically for the case of the Red and Blue CPC types. Explanation of these stages using examples from Red and Blue CPC-treated coupons are highlighted:

**Stage b**: Areas existed across the coupon surfaces where nearly no CPC was adsorbed, physically or chemically, to the substrate surface prior to and after the initial immersion into the electrolyte solution. These “holes” in the CPC film created areas of vulnerability for the formation of corrosion due to the lack of a protective CPC layer. Figure 84 displays an example of a hole in the CPC film (labeled as Blue 1), where the film is vulnerable. In addition, areas of bare metal existed within larger areas corrosion product that had formed on the bare metal, labeled as Blue 2 in Figure 84. The spectra for each exposed area is pictured in Figure 84 for the Blue and Red CPC types, where the absorbance units have been exaggerated to indicate that only trace amounts of the CPC were detected.

![Figure 84](image)

*Figure 84. a) Pictures (representing Stage 2) of areas on the Blue (left and center) and Red (right) CPC-treated surfaces, within the film (left and right) and within the corrosion product (center), where nearly no CPC was detected (via FT-IR). b) The corresponding IR-spectra are included with exaggerated intensity units that identify only trace amounts of the CPCs. Spectra from bottom to top represent the pictures from left to right.*
Table 8. Representative Surface Stages Existing on the 1018 Steel Surfaces with Corresponding Visual and IR-Spectral Illustrations.

<table>
<thead>
<tr>
<th>Description of CPC Film Stages</th>
<th>Visual Representation of CPC Film Stages</th>
<th>IR Spectral Representation with Peak Identification of CPC Film Stages</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Intact CPC film</td>
<td><img src="image1" alt="Visual Representation" /></td>
<td><img src="image2" alt="IR Spectral Representation" /></td>
</tr>
<tr>
<td>b) Exposed area with no CPC or sparse CPC film (bare metal)</td>
<td><img src="image3" alt="Visual Representation" /></td>
<td><img src="image4" alt="IR Spectral Representation" /></td>
</tr>
<tr>
<td>c) Initial CPC film degradation (initial or light corrosion)</td>
<td><img src="image5" alt="Visual Representation" /></td>
<td><img src="image6" alt="IR Spectral Representation" /></td>
</tr>
<tr>
<td>d) Medium corrosion with CPC film incorporated</td>
<td><img src="image7" alt="Visual Representation" /></td>
<td><img src="image8" alt="IR Spectral Representation" /></td>
</tr>
<tr>
<td>e) Heavy or dense corrosion with CPC film incorporated</td>
<td><img src="image9" alt="Visual Representation" /></td>
<td><img src="image10" alt="IR Spectral Representation" /></td>
</tr>
<tr>
<td>f) Corrosion with no CPC incorporated</td>
<td><img src="image11" alt="Visual Representation" /></td>
<td><img src="image12" alt="IR Spectral Representation" /></td>
</tr>
</tbody>
</table>
Stages c and d: When areas of corrosion product were measured via IR spectroscopy, a definitive decrease in CPC film intensity was also measured. This phase lasted briefly (until the CPC film washed away and was replaced with the corrosion product), because some of the intact CPC film was intermixed with corrosion product. The CPC film and corrosion product were not part of the same phase (meaning that the CPC film and corrosion product are considered two different types of phases); instead, the two phases existed simultaneously on the same measured area. Images showing examples of the two phases, CPC and corrosion product, are shown in Figure 85; the IR spectra show that the CPC films and corrosion product do not exist on the metal surface mutually exclusive of each other.

![Image](124x434 to 170x474)

![Image](186x434 to 233x476)

![Image](124x358 to 171x403)

![Image](185x358 to 232x402)

Figure 85. a) Pictures (representing Stages 3 & 4) of areas on 1018 steel coupons treated with the Blue (top) and Red (bottom) CPC types where the CPC film and corrosion product co-existed simultaneously on the surface. b) The corresponding IR-spectra (labeled based on pictures in a)) show the presence of both CPC and corrosion product, where the CPC intensity is greatly reduced as compared to the representative as-applied film spectrum (bottom peak).

Stage f: This stage existed across much of the surface area where progressive or thick corrosion product had formed on the substrate surface. Peaks for the CPC film (C-H) were not detected along with the corrosion product. The IR spectra for the Blue and Red CPCs were very similar to the spectra for the control coupon, shown in Figure 86, in which only corrosion product existed.
3) The Brown CPC type did offer some *sustainable* protection of the 1018 steel surface in 1/4-strength artificial seawater. The CPC film tended to combine with the corrosion product as it formed and progressed, and offered an intermediate layer of protection from advanced stages of corrosion.

The surface of the 1018 steel coupons treated with the Brown CPC type remained protected from failure via corrosion for a more extended time (up to 23 days of continuous immersion in some cases) likely due to the formation of an intermediate protective stage (film) that contained both CPC film and corrosion product. The Brown CPC type provided protection for the longest amount of time during the existence of an intermediate stage between when the CPC film was fully intact to when it later degraded. Figure 87 displays the electrochemical behavior of the surface of the Brown CPC-treated 1018 steel substrate (for one representative replicate), where the primary degradation stages relating to the corrosion rate and potential are highlighted.

The intermediate stage is the focus of this discussion and consisted of the intact CPC film with newly-formed corrosion product incorporated into it; the intermediate stage is considered to be a single surface film rather than two un-related phases (CPC and corrosion product). The resulting intermediate stage can be best described as an *oily rust*, where the corrosion product could be wiped away in the same manner as the oil and left
an oily (to the touch) FeOOH-based residue. Underneath this oily rust layer, the 1018 steel surface remained nearly fully-protected across the entire area exposed to the corrosive electrolyte (artificial seawater).

The existence of the intermediate stage was most noticeable from the IR-spectral results, which indicated that the CPC film might be incorporated with the corrosion product into a single film phase rather than co-existing as stand-alone phases. For a film that was degraded and replaced by corrosion product (as in the case for the Red and Blue CPC types), the intensity of the C-H peaks (primary indicator of the presence of the CPC film) decreased as the intensity of the O-H peaks (indicative of corrosion product) increased. For the case of the Brown CPC shown in Figure 88, as the intensity of the O-H peaks increased, the intensity of the C-H peaks did not necessarily decrease in turn. In general, the C-H peak intensity remained similar to that of the as-applied CPC. This observation lead to the determination that the CPC film was not washed away after immersion, but remained intact and commingled with the corrosion product to produce an intermediate protective film. The intermediate film is defined as the CPC component co-mingling with the corrosion product, where each stage type cannot be easily distinguished.

Present in all of the IR spectra in Figure 88 for the Brown CPC type were peaks that represented both the CPC and corrosion product, regardless of the degree to which corrosion products formed on the steel surface. The IR spectral pattern for the intermediate degradation stage consisted of O-H stretching (2500-3500 cm⁻¹) and oxygenated functionalities (900-1800 cm⁻¹ – possibly C-O) representing the corrosion product, as well as C-H vibrations (at 2840-3000 cm⁻¹ and 1375-1470 cm⁻¹) representing Figure 87. Plot of corrosion rate (dotted lines) and potential (solid line) as a function of immersion time (in ¼-strength artificial seawater) for one representative Brown CPC type-treated 1018 steel coupon. The primary CPC degradation stages are highlighted.
the CPC film. After the thicker corrosion products formed on the coupon surface, the CPC film remained protective and intact, as is dictated by the strong C-H peaks (2840-3000 cm\(^{-1}\) and 1375-1470 cm\(^{-1}\)) that changed only nominally in intensity (shown in Figure 88) during seemingly progressive film degradation. Despite the visually unaesthetic appearance of the coupon surface (covered with rust-colored corrosion product) that may have otherwise indicated failure of the film, this intermediate stage actually provided protection to the substrate underneath the oily intermediate film stage.

![Figure 88. IR spectra and photographs of a series of measured points 1-5 that display a progression of corrosion product formation without the degradation of the CPC film components. This 1018 coupon was treated with the Brown CPC type and immersed in ¼-strength artificial seawater for 3 days.](image)

The protection that the oily corrosion product film provided to the substrate surface can be shown in several examples, where the CPC film remained intact and active despite the appearance of a degraded film and surface. Underneath the oily corrosion-product film displayed in Figure 89, the 1018 steel substrate remained un-corroded. Figure 89 shows that a small portion of the film was removed to determine if the intermediate stage was providing ongoing protection despite the visual appearance of failure via corrosion. Another example using Figure 90 shows that once the initial
intermediate protective layer formed, it seemed to provide ongoing protection to the metal substrate surface. Even cases where the corrosion product visually appeared to overcome the substrate surface proved to be misleading, as the intermediate stage appeared highly degraded but still provided protection to the surface. The photographs, included in Figure 90 along with the corresponding IR spectra, show that the CPC film remained fully intact despite the appearance of a degraded film. In these examples, highlighted in Figure 90, corrosion products appeared dense or similar to the fully-degraded surface of the control coupon. The IR spectrum for the photograph in Figure 90 was also included in Figure 90, where the high intensity of the CPC-based peaks (relating to the C-H vibrations) indicated a fully intact CPC film amidst the corrosion product (which is also represented by the low intensity O-H peaks at 3500-2500 cm\(^{-1}\)). Regardless of the state of visual degradation of the 1018 steel surface treated with the Brown CPC type, the CPC remained incorporated into the corrosion product. Eventually, the 1018 steel surface was considered to have failed using electrochemical criteria (a corrosion rate above 0.04 mm/yr and corrosion potential near \(-725\) mV vs. SCE). The electrochemical methods could not take into account the intermediate phase that remained on the innermost surface of the coupon, likely due to the overwhelming influence that the corrosion product had on \(i_{\text{CORR}}\) and \(E_{\text{CORR}}\) values.
The electrochemical-based results corresponded to IR results relatively well as further evidence of an intermediate protective stage. Shown in Figure 87 above, the intermediate stage (CPC film intermingled with corrosion product) caused the corrosion rate to be consistently low and the potential values significantly higher than values typical for a corroded 1018 steel surface (~730mV vs. SCE). Identification of the intermediate stage that included intact CPC film and corrosion product was made using EIS results presented in the form of Nyquist plots, where the existence of two time constants, charge and mass transfer, is easier to observe than on the Bode plots. Figure 91 shows that, for the entire immersion time (23 days) and most notably after corrosion product had incorporated into the CPC film, the two time constants, charge and mass transfer, were present. The Nyquist plots represented diffusion occurring through the film to the metal interface (mass transport), along with a definite degree of protection that still existed (presence of charge transfer). Although the coupons visually appeared to be

Figure 90. Photographs and corresponding IR spectra of heavily-corroded areas on the surface of a 1018 steel coupon treated with the Brown CPC type and immersed in ¼-strength artificial seawater for up to 10 days. The CPC film is indicated on the IR spectra via the C-H vibration peaks (2840-3000cm⁻¹ and 1375-1470cm⁻¹) amidst peaks corresponding to the corrosion product (3500-2500cm⁻¹). The photograph outside of the spectra represents a common and fully-corroded surface from the control coupon.
failing due to corrosion product formation, they were actually being protected by the intermediate film stage.

![Nyquist plot](image.png)

**Figure 91.** Nyquist plots of one 1018 steel replicate (■) treated with the Brown CPC type and immersed for 23 days in 1/4-strength artificial seawater compared to the control (■ ■). The plot indicates the charge and mass transfer components that represent the intermediate stage (CPC combined with corrosion product) of the protective film.

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4) The method of application and corresponding dwell time for a CPC on a metal surface during curing heavily influenced the length of protection provided by the CPC film.

When any of the CPC types were applied to the 1018 steel coupon surface, the amount of time that the CPC was allowed to dwell on the surface prior to vertical suspension for curing seemed to have the most impact on the effectiveness of the CPC in mitigating corrosion. The corresponding electrochemical results for the CPCs that were applied via the dipping method were all relatively consistent between replicates and between test sets, as the same procedure and dwell time was used for each application. The electrochemical results varied greatly when the CPCs were applied via the spray method due primarily to the differences in horizontal dwell time that occurred prior to the vertical suspension step for curing.

The amount of dwell time prior to curing directly related to the overall success that the cured CPC film had for slowing corrosion in the 1/4-strength artificial seawater environment. Figure 92 displays electrochemical results from polarization measurements.
of three different test sets using the spray application. Figure 92 showed that the
replicates within each set were similar, but the results between test sets were drastically
different. In Figure 92, the 45° dwell position related to zero minutes of horizontal dwell
time. The only variable that changed between the rest sets was the dwell time; therefore,
it is surmised that the dwell time had the most impact on the behavior of the CPC film on
the coupon surface. The method of application (dipping or spraying) does not necessarily
indicate the effectiveness of protection, although the 1018 steel coupons that used the
dipping method for CPC application did appear to have improved protection against
protection. In fact, the dwell time again was the primary cause of this increase in
protection since the CPC was allowed to “dwell” longer at the surface during the vertical
cure as dipping resulted in a thick coating on the coupon surface that slowly dropped off
over time. The thickness of each coating on the 1018 steel substrate surface was not able
to be obtained consistently for reasons stated in the Results section and relations to film
thickness and degree of protection from corrosion could not be explored. The
preliminary thickness data for the Brown CPC type, when related to the electrochemical
results between CPC application methods, indicated that although the film was at least 10
times thicker in general (~21μm) for the dipped method versus the spray method (~2-3
μm), electrochemical data did not support a consistent difference between the
performance of the CPC in mitigating the onset of corrosion. This conclusion, although
not examined in detail, leads to further agreement that the dwell time has the most impact
on the ability of a CPC to inhibit corrosion.
Figure 92. Corrosion rate plot comparing three different test sets that used the spraying CPC application, with varying dwell times and scenarios: horizontal angle dwelled for ~0 minutes (---) and ~120 minutes(-----), and a vertical dwell position for ~0 minutes(-----). Plot uses data from 1018 steel treated with the Brown CPC type and immersed in ¼-strength artificial seawater for 3 days.
Chapter 6

6.0 Conclusion and Recommendations for Future Work

6.1 Conclusion

1) The oil-based components comprising the CPCs do not function just to carry corrosion inhibiting compounds to the substrate surface, but rather also remain on the 1018 substrate surface as a barrier for protection, even after corrosion product forms. The corrosion inhibiting additives appear to be barium, calcium, and sodium-containing species, likely in the form of sulfates or sulfonates.

2) The Blue and Red CPC types do not offer sustainable protection of the 1018 steel surface in ¼-strength artificial seawater. Both films tend to degrade, become removed from the surface after immersion, and become replaced by corrosion product.

3) The Brown CPC type does offer some sustainable protection of the 1018 steel surface in ¼-strength artificial seawater. The film type tends to combine with the corrosion product as it initiates and progresses, and offers an intermediate layer of protection from advanced stages of corrosion in a static type of immersion condition.

4) The dwell time, rather than method of application, for a CPC on a metal surface during curing heavily influences the length of protection provided by the CPC film. In general, the spray application produces a less-effective protective layer than the dip application against the corrosive artificial seawater environment, largely due to the length of time the CPC is allowed to dwell on the surface prior to curing and immersion. The thickness of the cured CPC film, at least up to the film thicknesses in this study (estimated between 2µm to 20µm), did not impact the inhibiting properties of the CPC.
6.2 Recommendations for Future Work

Based on the results obtained in this research using oil-based corrosion preventative compounds on 1018 steel, several suggestions for future work include:

- Study the different stages of CPC degradation and corrosion formation found across the substrate surface using a droplet cell or Scanning Electrochemical Microscopy. Because the CPC film degraded in-homogeneously across the substrate surface after immersion into the artificial seawater environment, electrochemical tests designed for this research were limited to providing results for the sum of the different electrochemical reactions occurring across the entire surface. The ability to more locally monitor the state of the CPC film and substrate surface would aid in better determining how the CPC film provides protection from corrosion. Either of these techniques is suggested to be run in tandem with a surface chemistry study using FT-IR.

- Study the cross-section of the CPC film and corrosion stages via X-ray Photoelectron Spectroscopy, using the ion-milling technique. This technique would possibly reveal whether or not components of the CPC film remains on the surface interface after a layer of corrosion product has become onset on the surface. This approach may not be straight-forward, as the CPC film remains in an oily liquid form on the substrate surface even after immersion.

- Obtain a non-destructive method to measure film thickness that does not require coating or other surface modifications and can measure the larger surface area of the immersion cell (approximately 5cm²). Ideally, an optical profilometry method
would be used to measure the thickness of the as-applied film as well as of the film during different stages of immersion. The CPC film was visually shown to increase in thickness, possibly due to water take-up. This possibility could be explored with reliable thickness measurements and further surface chemistry analysis.

- Determine definitively the inorganic components, if any, comprising the oil mixture. Bulk chemical analysis of the separated components could be applied. An electrochemical study of the neat oil mixture could determine the role that both the organic and any inorganic components play in inhibiting corrosion.
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Appendix A

CPC Application Procedures

Procedure for Applying Oil-based Corrosion Preventative Compounds onto a Metal Substrate: Dipping

Materials:
CPC of choice
Metal substrate
Container for immersing substrate in CPC (suggestion is a shallow glass container, but plastic cup for individual immersion is fine)
Stand with attached rod or other apparatus to hang substrate clamps
Clamps to allow substrates to hang vertically after immersion (suggestion are binder clips from an office supply store)

Procedure:
1) Pour CPC into the immersion container, making sure to have enough to completely cover the substrate on both sides once immersed.
2) After degreasing the substrate, immerse the substrate into the immersion container on one side for 1.5 minutes.
3) Using a glass rod or wooden stick, maneuver the substrate so that it flips to fully coat the other side for 1.5 minutes. (Both sides will be fully immersed during steps 2 and 3).
4) Using the same maneuvering stick, carefully bring the immersed coupon out of the bulk CPC and attach a clamp to the metal substrate.
5) Attach clamps to the rod on the stand and allow to cure for 48 hours.
6) Place a container below substrates to collect excess CPC as it drips off of substrates.
7) Rinse the substrates with attached clamps in deionized water to remove excess CPC.
8) Allow to hang dry completely before evaluation.
Procedure for Applying Oil-based Corrosion Preventative Compounds onto a Metal Substrate: Spraying

Materials:
CPC of choice
Metal substrate
Spray nozzle (Spray Systems Co. #62240-60°) and attached arm (see Figure 1)
Spray paint bulk storage container (see Figure 1)
Air compressor or compressed-air source
Solvent for cleaning spray nozzle (suggestion is paint thinner)
Stand with attached rod or other apparatus to hang substrate clamps
Clamps to allow substrates to hang vertically during and after application (suggestion are binder clips from an office supply store)

Procedure:
1) Attach clamps to metal substrates and hang vertically onto stand
2) Attach air source to paint storage container and spray the metal substrates, keeping approximately a 12 inch distance for about 3 seconds or until substrate is fully coated. (Suggestion, use a spray paint chamber with proper ventilation for spraying CPC and cleaning with solvent).
3) Completely rinse the CPC out of the nozzle using a solvent.
4) Allow the treated substrates to hang vertically to cure for 48 hours.
5) Rinse the substrates with attached clamps in deionized water to remove excess CPC.
6) Allow to hang dry completely before evaluation.
Appendix B

Electrochemical Study of Polished and Grit-Blasted 1018 Steel Surfaces Treated with Three Commercially Available Oil-Based CPCs

Introduction:

When surface chemistry techniques, namely FTIR and XPS, are applied to the steel coupons, the surface roughness needs to be relatively low to reduce source beam scattering. The effect that a polished surface may have on the electrochemical results relates directly to the conclusions made by surface chemistry techniques concerning the evolution of the CPC film and the gradual onset of corrosion products. The electrochemical results for the grit-blasted surface must be compared to electrochemical results for the polished surface under the same conditions to verify that the conditions and results used for corrosion monitoring and surface chemistry are comparable.

Experimental:

Open circuit potential was measured until the CPC/steel system reached equilibrium in ¼-strength artificial seawater electrolyte solution each day until failure, i.e. when the corresponding corrosion rate results reached levels at or near the untreated steel control results. Polarization resistance measurements were run at ±0.015V vs E_{CORR} immediately after the potential measurements were determined. The polarization resistance values were determined using the Stearn-Geary equation, \( R_p = \frac{B}{I_{CORR}} = \frac{(\Delta E)/(\Delta I)_{E \to 0}}{b_a + b_c} \), where \( B = (b_a b_c)/2.3(b_a + b_c) \), with \( b_a \) and \( b_c \) values of 0.10. The counter electrode chosen for all electrochemical experiments was a graphite rod. The electrochemical measurements were recorded using the PC4 family of potentiostats and corresponding software from Gamry Instruments, Warminster, PA. The grit-blasted surface used 600-grit aluminum oxide to create the rough finish. The polished surface was formed using up to a 1200-grit silicon carbide wet paper.
Results and Discussion:

Some differences existed for corrosion potential and results between the polished and unpolished or grit-blasted surface finishes. The corrosion potential, shown in Figure 1, for the control with a polished surface finish was slightly more negative, -750mV from -725mV vs. SCE, than for the unpolished control. The corrosion potentials for all of the CPC types, except for some replicates for CPC Red, reached a steady-state corrosion potential sooner for the polished surfaces. Overall, the corrosion potentials were very similar for either surface finish. The polarization resistance values, $R_p$, shown in Figure 2, followed the same trend as the corrosion potential, in that the values were similar between the two surface types.

![Figure 1. Potential as a function on immersion time in ¼-strength artificial seawater for 1018 steel coupons treated with three CPC types: a) Brown, b) Blue, and c) Red. The grit-blasted surface finish is compared to the polished surface finish for all CPC types and the control (black lines).](image-url)
For purposes of this body of work, the general performance trends between the CPCs remained the same, with the Brown CPC providing the longest and most consistent protection from corrosion, while the Red CPC provided similar but more mediocre protection, and the Blue CPC provided little or no protection even after initial immersion into the electrolyte. From this portion of the study, it is acceptable to relate polished coupons necessary for surface chemistry techniques to the unpolished coupons used in general corrosion evaluations.

Figure 2. Potential as a function on immersion time in ¼-strength artificial seawater for 1018 steel coupons treated with three CPC types: a) Brown, b) Blue, and c) Red. The grit-blasted surface finish is compared to the polished surface finish for all CPC types and the control (black lines)
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