EVALUATION OF PROPOSED NATURAL CORROSION INHIBITORS FOR X-52 CARBON STEEL IN ETHANOL MEDIA

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

Rafael F. Oliveira

December, 2015
EVALUATION OF PROPOSED NATURAL CORROSION INHIBITORS FOR X-52 CARBON STEEL IN ETHANOL MEDIA

Rafael F. Oliveira

Thesis

Approved: 

Advisor
Dr. Homero Castaneda-Lopez

Interim Dean of the College
Dr. Mario Ricardo Garzia

Faculty Reader
Dr. Hongbo Cong

Dean of the Graduate School
Dr. Chand Midha

Faculty Reader
Dr. Qixin Zhou

Date

Department Chair
Dr. Michael Cheung
ABSTRACT

This work describes the testing performed for corrosion control actions for X-52 carbon steel in ethanol media by using inhibitors, the following compounds were included: linalyl formate, linalyl acetate, linalyl butyrate, citronellyl acetate and 1-pentylallyl acetate. The experiments were performed in an electrochemical 3 electrode system with an X-52 steel rotating cylinder electrode (RCE) with rotational speed adjusted to 130 RPM. The system was deaerated by bubbling nitrogen gas into the ethanol solution. The Electrochemical Impedance Spectroscopy (EIS) technique was used to characterize the metal/electrolyte interface. Experimental testing was performed in anhydrous ethanol solution with 5 mM or 10 mM of one inhibitor. Surface analyses for the corroded surfaces were obtained by scanning electron microscopy (SEM) and White light interferometry (WLI). The results suggest that linalyl formate promotes the highest corrosion inhibition efficiency at 10 mM, followed by citronellyl acetate and linalyl butyrate. At this concentration, 1-pentylallyl acetate and linalyl acetate have not promoted corrosion inhibition. At a concentration of 5 mM, linalyl formate, linalyl acetate and linalyl butyrate promoted high inhibition efficiencies during the first hours but none was able to promote a longer protection than one day, possibly due to chemical degradation, chemical reactions and/or reduced surface coverage. The linalyl formate is considered the best chemical for inhibition purposes, especially at the concentration of 10 mM.
ACKNOWLEDGEMENTS

I would like to thank my thesis advisor, Dr. Homero Castaneda-Lopez, for all the guidance during the research activities, and CAPES Foundation, Ministry of Education of Brazil, Brasilia – DF, Zip Code 70.040-020 for the graduate scholarship provided by the Brazil Scientific Mobility program.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF FIGURES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vii</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>xii</td>
</tr>
</tbody>
</table>

## CHAPTER

### I. INTRODUCTION AND BACKGROUND

- Steel corrosion in ethanol solutions ................................................................. 1
- Corrosion Inhibitors ............................................................................................... 3
- Flow systems effects on corrosion ......................................................................... 5
- Electrochemical techniques used to characterize corrosion processes ............... 7
- Electrical equivalent circuits to the corrosion system ........................................ 9
- Surface imaging techniques .................................................................................. 13
- Research objectives .............................................................................................. 15
- Hypothesis .............................................................................................................. 16

### II. MATERIALS AND METHODS

- Samples preparation and experimental setup ....................................................... 18
- Electrochemical Impedance Spectroscopy (EIS) .................................................. 21
- Equivalent circuit parameters and corrosion inhibition efficiencies calculation .. 22
- Surface characterization techniques ...................................................................... 23

### III. RESULTS AND DISCUSSION

.............................................................. 25
EIS Impedance profiles ................................................................. 25
Equivalent circuit parameters fitting ........................................... 28
Corrosion Inhibition Efficiencies ............................................... 33
White light interferometry results ............................................. 36
Scanning electron microscopy images ....................................... 40

IV. CONCLUSIONS ........................................................................ 45
Future Work ................................................................................ 46

REFERENCES ................................................................................ 47

APPENDICES .................................................................................. 50

APPENDIX A. EIS NYQUIST PLOTS ............................................. 51
APPENDIX B. EIS BODE PLOTS ................................................... 84
APPENDIX C. WLI SURFACE IMAGES ....................................... 117
APPENDIX D. WLI ROUGHNESS PROFILES ............................... 123
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Equivalent circuit to the inhibited corrosion process</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>Chemical structures of linalyl acetate (A), linalyl butyrate (B), linalyl formate (C), citronellyl acetate (D) and 1-Pentylallyl acetate (E)</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>Experimental setup sketch with graphite rod counter electrode (A), rotating cylinder electrode shaft (B), API 5L X52 steel working electrode (C), saturated calomel reference electrode (D), gas dispersion tube (E), N₂ inlet (F) and gas outlet (G)</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>Charge transfer resistance profiles for blank test and 10 mM experiments</td>
<td>29</td>
</tr>
<tr>
<td>5</td>
<td>Charge transfer resistance profiles for blank test and 5 mM experiments</td>
<td>29</td>
</tr>
<tr>
<td>6</td>
<td>Double layer capacitance profiles for blank test and 10 mM experiments</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>Double layer capacitance profiles for blank test and 5 mM experiments</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>Corrosion inhibition efficiency profiles for each inhibitor at 10 mM</td>
<td>34</td>
</tr>
<tr>
<td>9</td>
<td>Corrosion inhibition efficiency profiles for each inhibitor at 5 mM</td>
<td>34</td>
</tr>
<tr>
<td>10</td>
<td>Cylinder electrode SEM surface images from blank test (A) and the tests with 10 mM of linalyl formate (B), linalyl acetate (C), linalyl butyrate (D), citronellyl acetate (E) and 1-Pentylallyl acetate (F)</td>
<td>43</td>
</tr>
<tr>
<td>11</td>
<td>Cylinder electrode SEM surface images from polished sample (A) and the tests with 5 mM of linalyl formate (B), linalyl acetate (C), linalyl butyrate (D), citronellyl acetate (E) and 1-Pentylallyl acetate (F)</td>
<td>44</td>
</tr>
<tr>
<td>12</td>
<td>EIS Nyquist plot - Blank test - Day 1</td>
<td>51</td>
</tr>
<tr>
<td>13</td>
<td>EIS Nyquist plot - Blank test - Day 2</td>
<td>52</td>
</tr>
<tr>
<td>14</td>
<td>EIS Nyquist plot - Blank test - Day 3</td>
<td>53</td>
</tr>
<tr>
<td>15</td>
<td>EIS Nyquist plot - Test with linalyl formate at concentration of 10 mM - Day 1</td>
<td>54</td>
</tr>
</tbody>
</table>
EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 10 mM - Day 1
EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 10 mM - Day 2
EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 10 mM - Day 3
EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 5 mM - Day 1
EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 5 mM - Day 2
EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 5 mM - Day 3
EIS Bode plot - Blank test - Day 1
EIS Bode plot - Blank test - Day 2
EIS Bode plot - Blank test - Day 3
EIS Bode plot - Test with linalyl formate at concentration of 10 mM - Day 1
EIS Bode plot - Test with linalyl formate at concentration of 10 mM - Day 2
EIS Bode plot - Test with linalyl formate at concentration of 10 mM - Day 3
EIS Bode plot - Test with linalyl formate at concentration of 5 mM - Day 1
EIS Bode plot - Test with linalyl formate at concentration of 5 mM - Day 2
EIS Bode plot - Test with linalyl formate at concentration of 5 mM - Day 3
EIS Bode plot - Test with linalyl acetate at concentration of 10 mM - Day 1
EIS Bode plot - Test with linalyl acetate at concentration of 10 mM - Day 2
EIS Bode plot - Test with linalyl acetate at concentration of 10 mM - Day 3
EIS Bode plot - Test with linalyl acetate at concentration of 5 mM - Day 1
EIS Bode plot - Test with linalyl acetate at concentration of 5 mM - Day 2
EIS Bode plot - Test with linalyl acetate at concentration of 5 mM - Day 3
EIS Bode plot - Test with linalyl butyrate at concentration of 10 mM - Day 1
WLI surface image – Test with linalyl acetate at concentration of 10 mM

WLI surface image – Test with linalyl acetate at concentration of 5 mM

WLI surface image – Test with linalyl butyrate at concentration of 10 mM

WLI surface image – Test with linalyl butyrate at concentration of 5 mM

WLI surface image – Test with citronellyl acetate at concentration of 10 mM

WLI surface image – Test with citronellyl acetate at concentration of 5 mM

WLI surface image – Test with 1-Pentylallyl acetate at concentration of 10 mM

WLI surface image – Test with 1-Pentylallyl acetate at concentration of 5 mM

WLI roughness profile – Polished electrode

WLI roughness profile – Blank test

WLI roughness profile – Test with linalyl formate at concentration of 10 mM

WLI roughness profile – Test with linalyl formate at concentration of 5 mM

WLI roughness profile – Test with linalyl acetate at concentration of 10 mM

WLI roughness profile – Test with linalyl acetate at concentration of 5 mM

WLI roughness profile – Test with linalyl butyrate at concentration of 10 mM

WLI roughness profile – Test with linalyl butyrate at concentration of 5 mM

WLI roughness profile – Test with citronellyl acetate at concentration of 10 mM

WLI roughness profile – Test with citronellyl acetate at concentration of 5 mM

WLI roughness profile – Test with 1-Pentylallyl acetate at concentration of 10 mM

WLI roughness profile – Test with 1-Pentylallyl acetate at concentration of 5 mM
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Input and output parameters of the semi empirical correlations between linear and rotational flow</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>Average line roughness ($R_a$) and root mean square line roughness ($R_q$) from each experiment</td>
<td>40</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION AND BACKGROUND

Steel corrosion in ethanol solutions

Although the ethanol molecule does not cause corrosion in steel directly, it is a strong scouring agent, so it can remove deposited corrosion products at the surface, exposing the bare metal to corrosive contaminants in solution. The steel substrate interface in ethanol media is complex and highly depended on the solutions contaminants. It is known that an electrical double layer is formed at the bare metal interface and water molecules tend to adsorb preferentially in the steel surface even in ethanol solutions with small water content. An increase in the double layer thickness is usually associated with a decrease in corrosion rates as the corrosive species diffusion process becomes slower. In addition, the formation of stable corrosion products films may impose a physical barrier, also slowing down the species diffusion process [1]. Therefore, steel corrosion in ethanol solutions is depended on the concentration of these contaminants, specially water, dissolved oxygen and ions, such as chloride. The main corrosion mechanisms in this environment are denominated wet, dry, electrolytic and galvanic corrosion and stress corrosion cracking (SCC) [2].

Wet corrosion happens even at small concentrations of dissolved water in ethanol. The water molecules adsorb in the steel substrate and react with the metallic iron, generating iron oxides, most of which are dissolved in the ethanol solution or create a
porous corrosion product layer, which usually does not protect the steel surface from further corrosion. In addition, an increase in water content also increases the solution conductivity, accelerating the ions movements. This mechanism is represented by the cathodic reaction 1 and the desorption reaction 2 [3].

\[ Fe + H_2O(ads) \rightarrow Fe - O_{ads} + 2H^+ + 2e^- \]  

\[ n \: Fe - O_{ads} \rightarrow Fe_2O_3 \text{ or } Fe_3O_4 \]  

Dry corrosion occurs when the dissolved oxygen causes the cathodic reduction of ethanol and the oxidation of metallic iron according to the reactions 3 and 4. It is the main mechanism in ethanol solutions with low water content. The formed adsorbed iron oxide can also desorb according to the reaction 2, previously shown. As this dry mechanism generates water, it also enhances the wet corrosion mechanism [2].

\[ \frac{1}{2}O_2 + C_2H_5OH + 2e^- \rightarrow OH^- + C_2H_5O^- \]  

\[ Fe + OH^- + C_2H_5O^- \rightarrow Fe - O_{ads} + C_2H_4 + H_2O + 2e^- \]  

Anhydrous ethanol is very hygroscopic and it easily absorbs water moisture from the atmosphere. It also presents higher oxygen solubility than in aqueous solutions, so it is very difficult to experimentally maintain a completely dry ethanol solution in contact with an active metal. As both water content and dissolved oxygen concentration interfere in the corrosion rates significantly, in this work, nitrogen bubbling was employed in the ethanol solutions during all experiments in order to maintain a constant dissolved oxygen concentration similar in all tests. This also restricted the ethanol access to atmospheric moisture, so that the water content increase during the immersion time was slow, linear
and similar in all experiments. Although the anhydrous ethanol solution submitted to nitrogen purge is much less corrosive than fuel grade ethanol, which contains higher water content, oxygen concentration and other impurities, the corrosion experiments in this deaerated condition are preferred to achieve good reproducibility of the corrosive media in all tests.

When another kind of metal is also present in solution and in contact with the steel, galvanic corrosion is also an important issue to consider as the solution conductivity can increase significantly depending on the water content. In addition, increased solution conductivity enhances the electrolytic corrosion mechanisms kinetics [2].

Stress corrosion cracking (SCC) is a corrosion mechanism that only occurs in metallic regions with accumulated tensile stress in specific environment conditions. Although being relatively rare, it poses a significant threat when it does occur, as it can cause significant damages to assets in the field, such as buried pipelines, due to its detection difficulty and the deterioration of the steel mechanical properties in the affected regions. In ethanol media the presence and concentration of dissolved oxygen is the most crucial parameter, and there is no evidence of SCC in deaerated ethanol solutions with the dissolved oxygen concentration minimized by nitrogen purging [4].

Corrosion Inhibitors

Corrosion inhibitors are generally defined as chemical substances or mixtures that can be added in small amounts to a corrosive environment and reduce the corrosion rate of an exposed metallic surface. In general, the mechanisms of inhibition are divided into three major categories defined as chemical adsorption, physical adsorption and chemical
complex formation. An inhibitor can promote one or more of these mechanisms at the same time. Chemical adsorption is defined as the creation of a chemical bond between the adsorbed molecule or ion and the surface substrate, promoting a strong chemical interaction and the formation of a thin film covering the surface. Physical adsorption occurs when the adsorbed specie remains at the surface due to electrostatic attraction, therefore creating a much weaker interaction with the surface than chemisorption. The third major mechanism occurs when the inhibitor reacts vigorously with potential corrosive species in the bulk phase, creating a stable chemical complex, preventing these species to reach the metallic surface. The inhibitors that follows this last mechanism are usually called scavengers [5].

The corrosion inhibitors are also classified according to their chemical nature and main mechanism of inhibition. They can be organic or inorganic and natural or synthetic. The adsorption inorganic inhibitors are divided into anodic or cathodic categories. Anodic inhibitors act by preferential adsorption in the anodic areas of the surface, reducing the anodic corrosion reactions kinetics, and cathodic inhibitors act in a similar way in the cathodic regions, reducing the cathodic corrosion reactions. Although some inorganic inhibitors present both anodic and cathodic effects, most of them cause preferentially one of these actions. However, organic inhibitors, in most cases, tend to chemically adsorb more uniformly, presenting both anodic and cathodic inhibition [5].

The use of adsorption corrosion inhibitors in liquid media for surface modification is a common approach as a corrosion control action in closed flow systems, such as pipelines. However, each corrosion inhibitor presents different efficiencies highly
dependent on its chemical composition, the fluid media physicochemical properties, and the solid surface features [6].

Grosser, F. N. et al [7] verified through electrochemical and weight loss experiments that the use of linalyl acetate (LA) in ethanol media can lead to good corrosion inhibition efficiencies for low carbon steel, as it was determined by 24 hours weight loss tests. It was also suggested that the inhibition effect is caused by LA preferential adsorption in the metal surface, significantly increasing the charge transfer resistance. However, as the weight loss measurements were just performed at 24 hours of immersion, the protective film stability, which is an important information to decide the inhibitor’s industrial applications viability, was not clearly evaluated. At the same time, structurally similar chemicals should be tested in order to better understand the relationship between the adsorption phenomena and the inhibitor chemical structure and possibly determine a more adequate inhibitor.

**Flow systems effects on corrosion**

The flow velocity profile near the metal surface in flow systems can considerably change the diffusion process, which is usually the controlling step in several corrosion mechanisms. There are two major cases of fluid flow effects on corrosion. The first case occurs when there is no significant protective film or scale covering the metal surface, typically in low pH solutions and in the absence of corrosion inhibitors. In this scenario, an increase in flow speed leads to faster transport of the species diffusing to the bare metal surface and those moving away from it, causing a significant increase in the corrosion rates. The second case happens when there are protective films or scales, which are not
easily removed by the flow, typically in high pH conditions and in the presence of adsorption corrosion inhibitors. In this situation, the corrosion phenomena is controlled by the species transport through the protective film, therefore, there is no significant change in the corrosion rate as flow speed increases, as long as, the protective film remains intact. In addition, temperature, local pH, the composition and physical properties of the steel, the presence and concentration of contaminants, such as organic acids, and corrosion inhibitors are also key important parameters of the corrosion process in flow systems, whose effects are mainly depended on which solution corrosion is occurring [8].

It is important to perform corrosion laboratory tests trying to simulate a similar environment as in the field. One major difference is that most industrial process flows are open systems while most of the laboratory tests are performed in closed batch systems, for simplicity in apparatus and techniques, leading to the accumulation of soluble corrosion products, which modify the medium corrosivity, especially for corrosion susceptible alloys, such as carbon steels, in aggressive media. Fortunately, this corrosivity change can be reduced by performing the tests in a short period of time relatively to the speed the solution physicochemical properties change.

So a rotating cylinder electrode (RCE) is commonly used to mimic this effect in a static fluid. Silverman, D. C. [9] proposed a correlation between the RCE rotational speed and the average flow speed in the pipe so that the mass transfer coefficients of the corrosion reagents diffusing to the bare metal surface in both systems are close. This method uses as input the steel cylinder electrode outer diameter (d_{cyl}) in cm, the ethanol solution density (\rho) in g/cm³, the solution dynamic viscosity (\mu) in g.cm⁻¹.s⁻¹, the
diffusivity coefficient of water in ethanol (D) in cm$^2$/s, the diameter of the pipe (d$_p$) in cm and the flow rate through the pipe (U$_p$) in cm/s. The Schmidt number (Sc) is calculated according to Equation I. The linear speed of the cylinder electrode surface (U$_{cyl}$) that present approximately the same mass transport conditions of the flow system is calculated in cm/s in Equation II and the RCE rotational speed (F), in RPM, to promote this linear speed at the steel surface is calculated in Equation III [10].

$$Sc = \frac{\mu}{\rho \times D} \quad \text{(I)}$$

$$U_{cyl} = 0.1185 \left(\frac{\rho}{\mu}\right)^{1/4} \left(\frac{d_{cyl}^{3/7}}{d_p^{5/28}}\right) Sc^{-0.0857} U_p^{5/4} \quad \text{(II)}$$

$$F = \frac{60 \times U_{cyl}}{\pi \times d_{cyl}} \quad \text{(III)}$$

Electrochemical techniques used to characterize corrosion processes

Traditionally, corrosion rates are determined by direct methods, such as weight loss measurements, however, this classical approach demands significant time of sample exposure to the corrosive environment and it only gives average corrosion rates. So, they cannot provide much information about the ongoing corrosion mechanisms and the corrosion rate time profile. As corrosion is an electrochemical process, it became a common practice to apply electrochemical techniques for corrosion characterization, which can give high accuracy results in a short period of time and monitor the corrosion time evolution. These indirect techniques cause an electrical perturbation in the corrosion
system using direct current (DC) or alternate current (AC) in order to relate the system response to the ongoing corrosion process [11].

The most employed electrochemical techniques in corrosion inhibitors research are Tafel lines extrapolation, polarization resistance determinations and electrochemical impedance spectroscopy (EIS). In order to employ the Tafel extrapolation DC method, it is usually performed a potentiodynamic polarization sweep in the working electrode by imposing a potential sufficiently below the open circuit potential (OCP) until one sufficiently above it, while measuring the passing electrical current. This allows the creation of the polarization plot, which relates the imposed electrode potential with its surface current density in absolute values. The OCP is continuously changing with time and it corresponds to the potential at which the working electrode naturally stay while undergoing the corrosion process in the studied system, so it is necessary to measure it before each polarization sweep. The anodic and cathodic Tafel lines are obtained by fitting the linear regions in the polarization plot located above and below the OCP. As these lines represent the anodic and cathodic reactions kinetics, their intersections occur at the corrosion potential and the corrosion current density, which is directly related to the corrosion rate at the moment [12].

The polarization resistance DC method also relies on the potentiodynamic polarization, but the sweep range is much shorter, usually between 10 mV above and below the OCP. The polarization resistance ($R_p$) is defined as the derivative of potential with respect to current density at the corrosion potential. Close to this potential, the
polarization curve resemble a straight line, allowing an easy determination of $R_p$, which is inversely related to the corrosion rate [11].

EIS is an alternate current analysis technique mostly employed to determine equivalents electrical circuit models to the corrosion phenomena. It measures the current response to an imposed alternate potential signal around a specified initial potential at different frequencies, allowing the impedance profile of the system to be calculated. In this present work, the EIS technique was employed, because it can generate reliable results in very low conductivity media, such as in ethanol solutions, where the ions transport restrictions make the DC technique results unreliable. In addition, EIS impedance results can provide more mechanistic information about the processes occurring at the metal surface [13].

Electrical equivalent circuits to the corrosion system

Electrical equivalent circuits are theoretical electrical circuits considered to demonstrate the same electrical response of a specific physical system when submitted to a potential perturbation. They are combinations of classical electrical elements, such as resistors, capacitors and inductors, and non-ideal distributed elements, such as constant phase elements, which generally does not exist in real electrical circuits. These circuits are commonly used as a methodological tool in corrosion inhibitors research as their elements can be related to specific processes occurring at the metal surface in the corrosion system, such as ions diffusion through a protective thin film, providing a greater comprehension of the ongoing changes in the studied system [14]. It has been previously shown that an adsorption and electrochemical process can be represented by different electrical equivalent circuits, which present the same EIS impedance response in
the considered frequency range [13]. Therefore, an adequate equivalent circuit model should be chosen based on mechanistic knowledge of the corrosion process rather than from purely mathematical treatment of the EIS data, so that each circuit element is related to a specific real phenomenon as precisely as possible.

The equivalent circuit shown in Figure 1 is generally considered suitable to represent the corrosion inhibition process in a metallic substrate as each circuit element represents an analog to a specific mechanism or electrochemical process [15–18]. The circuit is composed of the solution resistance ($R_s$), film resistance ($R_f$), charge transfer resistance ($R_{ct}$), film constant phase element (CPE$_f$) and double layer constant phase element (CPE$_{dl}$). Ideal capacitors can be used to represent the corrosion system capacitive behavior when the formation of the double layer is mostly uniform in a smooth surface, and when the protective film at the surface is homogeneous and presents high surface coverage. However, in systems with irregular surfaces and nonhomogeneous films, the EIS response cannot be well fitted in an equivalent circuit containing only classical ideal elements. In such cases, it is usual to employ distributed electrical elements, whose impedances are determined by more than one parameter, which makes possible the simulation of non-ideal behaviors. Although the impedance signal presents capacitive characteristics, the constant phase elements are employed, instead of pure capacitors, in order to simulate the non-ideal capacitive behavior that can be present due to film failures and incomplete surface coverage, which allow an increase in the corrosion current. The constant phase element is the most adopted distributed circuit element to replace ideal capacitors, as it can also provide a measurement of how much non-ideal the system is, based on the CPE exponential coefficient [17]. The CPE impedance ($Z_{CPE}$) is calculated
through Equation IV where \( f \) is the frequency, \( Y \) is the CPE magnitude, \( n \) is the CPE exponential coefficient related to its phase shift response and \( i \) is the imaginary number. It is noticed that the CPE's can behave as ideal capacitors, resistors or inductors if \( n \) is set equal to 1, 0 or -1, respectively.

The effective double layer capacitance (\( C_{dl} \)) can be empirically determined through Equation V where \( f_{\text{max}} \) is the frequency that causes the highest absolute value of the impedance imaginary component in the high frequency semicircle in the Nyquist plot [19]. Although less suitable to empirical \( C_{dl} \) determinations, the Helmholtz model, shown in equation VI, is useful to explain its physical meaning as a decrease in its value can be caused by an increase in the protective layer thickness (\( \delta \)) [20]. The others parameters are the dielectric constant of the local medium (\( \varepsilon \)), the vacuum permittivity (\( \varepsilon_0 \)) and the electrode surface area (A).

\[
Z_{CPE} = Y^{-1}(i2\pi f)^{-n} \quad (IV)
\]

\[
C_{dl} = \frac{1}{2\pi f_{\text{max}}R_{ct}} \quad (V)
\]

\[
C_{dl} = \frac{\varepsilon\varepsilon_0 A}{\delta} \quad (VI)
\]
The solution resistance ($R_s$) is related to the solution electrolytes diffusion process in the fluid bulk phase and represents the transport limitations of the corrosive species from the bulk phase until the film-solution interface. Therefore, solutions with low conductivity, such as anhydrous ethanol, are expected to present high solution resistances as the movement freedom of the ions in the bulk phase are more restricted than in more conductive media. In the EIS Nyquist plot, the solution resistance controls the maximum speed the system can react to the imposed electrical perturbation, which is what cause the EIS absolute impedance response tends to zero as the perturbation frequency is increased indefinitely. In the EIS Nyquist plot, the solution resistance value is usually determined by manually prolonging the capacitive semicircle to the high frequency region until it reaches the real impedance axis. The solution resistance value is equal to the impedance of this intersection point with the horizontal axis [19]. Similarly, the film resistance ($R_f$) is related to the electrolytes diffusion process through the protective film covering the metal surface, so thicker and less porous films are expected to present a high film resistance. Its value is usually calculated in the EIS fitting process to the equivalent circuit, rather than by direct visual inspection of the EIS plots.

The charge transfer resistance ($R_{ct}$) is related to the kinetics of the redox reactions occurring at the bare metal surface and represents the restrictions that control how fast the electrons are changing between the corrosive species and the bare metal. As thicker and more protective films reduce the amount of corrosive species that reach the bare metal interface at the same time, an increase in the $R_{ct}$ value can be caused by the formation of a protective film, while film failures cause $R_{ct}$ drops. So, the changes in $R_{ct}$ are intrinsically related to the corrosion inhibition process. Therefore, the charge transfer
resistance is the most important equivalent circuit element in the study of corrosion inhibitors and it is the focus of the EIS analysis in this work. In the EIS Nyquist plot, the charge transfer resistance value appears as the difference between the impedance of the two points where the capacitive semicircle would intersect the real impedance axis if manually prolonged, which is usually the diameter of the semicircle [19].

The film (CPE$_{f}$) and double layer (CPE$_{dl}$) constant phase elements represent the capacitive behavior created by the accumulation of opposing electrical charges at the bulk-film and film-metal interfaces, respectively. Each CPE presents the magnitude (Y) and the exponential (n) coefficients, as previously shown in Equation IV, which are both obtained in the fitting process of the EIS impedance data. In the case of CPE$_{dl}$, the magnitude coefficient is related to the effective double layer capacitance, but its relation is also depended on the value of the exponential coefficient.

Surface imaging techniques

Scanning white light interferometry (WLI) and scanning electron microscopy (SEM) are among the most commonly used techniques to study the surface physical characteristics following an exposure of a surface to the corrosion phenomena. In the interferometry, a white light coherent beam is split in two by a system of lenses. One part is directed to the sample and the other to a very smooth reference surface. After reflection, both beams are recombined and detected by the microscope camera. If the sample surface area where the light reflects is at a specific height, the light gets in focus, generating an image of black and white lines that represents the surface at this specific height. The microscope is then slowly moved in the vertical direction, allowing all
horizontal plans to get in focus, therefore, performing a surface vertical scan. The combination of all these data creates a 3D image of the scanned area with high vertical resolution, which allows the characterization of the surface features even if they present high angles [21].

In this work, WLI measurements were performed to generate a 3D image and a 2D roughness profile of the corroded surfaces after the experiments. This information is useful to check possible signs of localized corrosion, such as pits, indicating if the formed inhibitor film presented failures in certain areas. The surface average roughness parameters were also calculated from these profiles, allowing a quantitative roughness comparison between surfaces from different experiments. The average roughness is expected to increase if intense localized corrosion occurs but may not change as much if a more generalized corrosion path is predominant, therefore, these measurements can also provide information about the predominant corrosion morphology in the system, corroborating the EIS analysis.

For the SEM, the imposed radiation is an electron beam, which presents significant advantages due to its high intensity, small wavelength and also for being mono-energetic. The sample is inserted in a closed chamber and the air inside it is sucked by a pumping system, creating the necessary vacuum to avoid the interferences from interactions between the atmospheric gases and the imposing beam. Then, a mono-energetic electrons beam is emitted to the sample surface, colliding with the electrons of the atoms in a very small volume close to the sample surface. The electrons high intensity causes the ejection of the electrons in the most external orbitals of these superficial
atoms. These secondary atoms are detected by the microscope, allowing the construction of the surface image in the scale of few micrometers. In addition, the imposed high intensity electron beam can also cause the ejection of electrons from an inner atomic orbital. In order to stabilize the electrosphere, an electron from the outer orbital migrate to this inner orbital, releasing energy in the form of X-ray whose intensity is characteristic of the kind of atom the X-ray came from. Therefore, an energy-dispersive X-ray spectrometer (EDS), present in the equipment, can analyze the X-ray spectra and determine the local atomic mass composition of the few surface atomic layers in specific surface regions [22].

In this work, SEM images were used for qualitative comparison between the corroded surfaces. The main purpose is to check for areas where corrosion products remained adhered to the metal surface and determine the atomic mass composition of such areas through EDS. If corrosion products were still covering many regions in the metal surface after the experiments, it may suggests that a stable protective film, or at least a physical barrier, was formed, potentially reducing the corrosion rates. Therefore, this information can be useful to reinforce EIS conclusions about the presence of thick protective barriers.

Research objectives

The general objective for this research was to characterize qualitatively and quantitatively by means of electrochemical and high resolution techniques, such as, electrochemical impedance spectroscopy (EIS), white light interferometry (WLI) and scanning electron microscopy (SEM), the ability of linalyl acetate and some similar
compounds, namely linalyl formate, linalyl butyrate, citronellyl acetate and 1-Pentylallyl acetate, to inhibit corrosion in X-52 carbon steel in ethanol media.

The particular objectives were:

- Evaluate each chemical that will act as inhibitor in different concentrations and with respect to time
- Compare the performance of each chemical by assuming the same environmental conditions at different concentrations
- Analyze the interfacial mechanism occurring at the substrate/electrolyte interface level

Hypothesis

Few articles concerning the adsorption mechanism of organic inhibitors to carbon steel in ethanol media have been published, but its relationship in aqueous solutions to their chemical structures is explained by several authors. The polar functions of nitrogen, oxygen or sulfur, \( \pi \)-bonds and heterocycles atoms are considered to create strong interactions with the carbon steel substrate, increasing surface coverage and inhibition efficiencies [23–28].

It is assumed that these chemical structures influence the adsorption mechanism in ethanol media, thus the four similar compounds to linalyl acetate were chosen to test how the molecules ramifications can facilitate the exposure of these polar groups and \( \pi \)-bonds to the surface active sites, leading to an increase in inhibition efficiency and protective film stability. We assume that electrochemical techniques can characterize the influence of
these chemicals in the corrosion/dissolution properties. So, EIS is employed regularly during the corrosion tests in order to determine the evolution of the corrosion inhibition efficiency of each chemical at the same molar concentration. These results can be used to quantitatively determine how much the protective film, promoted by each chemical, mitigated the corrosion process and for how long it remained sufficiently stable and protective. As the inhibitors chemical structures are very similar, differing only by the presence or length of a ramification, it is reasonable to say that their differences in inhibition efficiencies are caused by the presence or absence of the considered ramification. Therefore, this approach aims at getting more insight about the relationship between the inhibitors chemical structures and their efficiencies in ethanol media.
CHAPTER II
MATERIALS AND METHODS

Samples preparation and experimental setup

The five chemicals linalyl formate, linalyl acetate, linalyl butyrate, citronellyl acetate and 1-pentylallyl acetate, whose chemical structures are shown in Figure 2, were experimentally evaluated as corrosion inhibitors in the 5 mM and 10 mM concentrations. These two concentrations were chosen based on the studies of Grosser, F. N. et al [7] that demonstrated that linalyl acetate was able to promote high corrosion inhibition efficiencies, above 60%, for low carbon steel immersed in aerated ethanol solution. Although in this study, the studied corrosive media is a deaerated ethanol solution with less dissolved oxygen, the corrosion tests in these two concentrations were considered adequate to compare the inhibition efficiencies of the five tested chemicals. Each experiment was performed in a glass cell containing 250 ml of anhydrous ethanol and one of the considered chemicals during a total immersion time of three days. The blank tests were performed in the same conditions but without any corrosion inhibitor. This immersion time was considered sufficient to test the stability of the protective inhibitor film in the steel surface during the initial stages of the corrosion process of a clean steel surface as it was verified that the acceleration of the corrosion process occurs mostly until the third day of immersion.
The used rotating cylinder electrode (RCE) was made of API 5L X52 carbon steel with the following composition (wt.%): 1.07% Mn, 0.23% Si, 0.16% C, 0.14% Cu, 0.09% Ni, 0.07% Cr, 0.03% Mo, 0.026% Al, 0.02% V, 0.012% P, 0.004% S, 0.002% Ti, 0.001% Ca, 0.0003% B and the remaining being Fe. Its exposed area was of 3 cm².

Before each new experiment, the RCE were manually polished by using 240, 400 and 600 grit sandpapers in sequence to remove any previous corrosion products and deposits in the metal surface. It was also cleaned and degreased with ethanol after the polishing. The RCE was connected to a speed adjuster and set to operate at constant 130 RPM during all its immersion time. This value was calculated using the previously explained semi empirical correlations, shown in Equations I, II and III, proposed by Silverman, D. C. [9] to simulate, in a rotating system, the mass transport phenomena inside a linear pipe. The used model input values, the calculated Schmidt number, linear speed at electrode surface and required RCE rotational speed are displayed in Table 1.
Table 1: Input and output parameters of the semi empirical correlations between linear and rotational flow

<table>
<thead>
<tr>
<th>$d_{cy}$ (cm)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$\mu$ (g.cm$^{-1}$.s$^{-1}$)</th>
<th>$D$ (cm$^2$/s)</th>
<th>$d_p$ (cm)</th>
<th>$U_p$ (cm/s)</th>
<th>$Sc$</th>
<th>$U_{cy}$ (cm/s)</th>
<th>$F$ (RPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>0.9165</td>
<td>1.80</td>
<td>0.00001</td>
<td>30.48</td>
<td>122</td>
<td>196399</td>
<td>8.38</td>
<td>130</td>
</tr>
</tbody>
</table>

All experiments were performed in a deaerated solution to keep low and similar oxygen concentration in all cases, as it is expected the corrosion phenomena to be highly depended on the dissolved oxygen concentration in the ethanol. The deaerated solutions were obtained by injecting nitrogen gas from a compressed nitrogen cylinder to the bottom of the glass cell using a simple gas dispersion tube. The cell was not completely sealed, allowing the nitrogen to escape to the atmosphere, purging the oxygen from the ethanol solution. The bubbling process started one hour before the RCE immersion, so the solution was well deaerated since the experiments beginning.

In each experiment, the chemical to be tested was added from its analytical concentrated solution, considered pure for all purposes, to the ethanol solution only once immediately before the immersion of the working electrode. The precise inhibitor volume, necessary to produce the intended inhibitor concentration, was measured and added using a micropipette with adjustable volume. The experimental setup in the glass cell is shown in Figure 3.
Figure 3: Experimental setup sketch with graphite rod counter electrode (A), rotating cylinder electrode shaft (B), API 5L X52 steel working electrode (C), saturated calomel reference electrode (D), gas dispersion tube (E), N₂ inlet (F) and gas outlet (G)

Electrochemical Impedance Spectroscopy (EIS)

All EIS experiments were performed with a Solartron® Analytical Modulab potentiostat by imposing in the RCE, which is the working electrode, a sinusoidal potential wave with peak-to-peak amplitude of 10 mV around the open circuit potential (OCP), determined just before each EIS measurement, and its frequency varying from 10 Hz to 100 KHz. A graphite rod and a saturated calomel electrode (SCE) were employed as counter and reference electrodes, respectively. All the reported potentials use the SCE potential as the zero reference. The first EIS measurement started one hour after the steel sample immersion in the solution, which was performed in order to verify the initial effects of the inhibitor’s film after it has been properly formed at the metal surface. The
others measurements were performed every three hours following immersion during a period of exposure time of 72 hours.

The results are expressed through the Nyquist and Bode plots. The Nyquist graph shows the imaginary part of the impedance in the vertical axis and the real part in the horizontal, while the Bode plots are expressed as two combined plots showing the impedance magnitude and its phase shift, both as a function of the potential frequency. Through these plots, a comparison between the blank test and the tests with inhibitors at different periods of time after the samples immersion can be made in order to determine the inhibition efficiencies profile throughout the experiments duration, indicating for how long each inhibitor efficiently protects the steel in ethanol media.

Equivalent circuit parameters and corrosion inhibition efficiencies calculation

The considered equivalent circuit model was the one previously shown in Figure 1. The circuit elements parameters were fitted to the experimental data using Zview® software fitting tool set with the weighted sum of squares data weighting method. Only the frequency range from 100 Hz to 4000 Hz was considered to be fitted as at very high frequencies there is significant divergence from the capacitive semicircle.

Although the corrosion inhibition efficiency is traditionally calculated based on measured corrosion rates, this approach is not practical in this work, as the corrosion rates are expected to be very low and difficult to be directly determine in weight loss tests. Therefore, as the increase in charge transfer resistance ($R_{ct}$) is related to the inhibition of the corrosion reactions, it was used to calculate the inhibition efficiency ($\eta(\%)$) through
Equation VII where (i) and (B) stands for the experiment with the considered corrosion inhibitor and the blank test, respectively.

$$\eta(\%) = \frac{R_{ct(i)} - R_{ct(B)}}{R_{ct(i)}} \times 100 \quad (VII)$$

Surface characterization techniques

After the end of each immersion test, the X-52 steel cylinder electrode was carefully removed from solution and dried at room temperature. The corroded surface was analyzed using the scanning white light interferometric (WLI) microscope model Bruker® Contour GT. The used magnification factor was 1000 and the image represented an area of approximately 1 mm². The 2D roughness profile along the vertical axis of the cylinder electrode was also obtained. For each profile, the 2D parameters called average line roughness ($R_a$) and root mean square line roughness ($R_q$) were determined by the analysis software. These parameters are defined in the Equations VIII and IX, where $L$ is total length of the roughness profile and $Z(x)$ is the height at the location $x$ above the profile mean height value [29].

$$R_a = \frac{1}{L} \int_0^L |Z(x)| \, dx \quad (VIII)$$

$$R_q = \frac{1}{\sqrt{L}} \int_0^L |Z^2(x)| \, dx \quad (IX)$$

The other employed characterization analysis was the Scanning Electron Microscopy (SEM). As this technique uses a radiation source with a much smaller wavelength than visible light, the image resolution was bigger than in the optical
microscopy. Then, it was possible to obtain 2D surface images with a magnification factor of 3000 for each corroded electrode, providing a clear image of the surface in the micrometers scale. The EDS analysis was also conducted in the regions with accumulated corrosion products, which can be seen as the black regions in the SEM images.
CHAPTER III
RESULTS AND DISCUSSION

EIS Impedance profiles

All EIS results were displayed in the form of Nyquist plots in the Appendix A, and in the form of Bode plots in Appendix B. As there are many EIS measurements for each experiment, the results are displayed separately for each day after the electrodes immersion for visual convenience. It was noticed that, in all cases, the Nyquist plots presented two semicircles. The first semicircle, in the frequency range from around 4 KHz to 100 KHz, is actually considered to be a strong deviation of the capacitive semicircle caused by frequency dispersion in the system. As it is not related to the studied corrosion phenomena, this frequency range was excluded from the EIS plots. The second semicircle, which appears in the frequency range from 100 Hz to 4000 Hz, is consistently related to the corrosion reactions kinetics and its diameter is directly proportional to the fitted value of the charge transfer resistance [11].

The intended purpose to inject these chemicals in ethanol was to cause their preferential adsorption in the metal surface, reducing the bulk phase corrosive species access to the bare metal, significantly slowing the corrosion kinetics. This inhibitive effect could be verified by the increase in the capacitive semicircle diameter in the experiments with effective inhibitors when compared with the blank test at the same immersion time.
The Nyquist plots from the blank test, shown in Figures 12 to 14, indicate that, in the absence of inhibitors, the corrosion rate continuously accelerated, mainly during the first day of immersion, as the reduction of the capacitive semicircle diameter also corresponded to a reduction in the charge transfer resistance ($R_{ct}$) and an increase in the double layer capacitance ($C_{dl}$). Therefore, in the impedance Nyquist plot of each chemical and concentration, their inhibition efficiencies were qualitatively compared according to the size of the capacitive semicircle when compared with the blank test at the same immersion time. In addition, the created film stability could be compared by how fast the semicircle decreased in size in each experiment as a protective film failure is expected to accelerate the corrosion rates, reducing the capacitive semicircle diameter in the Nyquist plot.

The Nyquist plots for linalyl formate at the concentration of 10 mM, shown in Figures 15 to 17, clearly indicate a bigger capacitive semicircle than the blank test during the whole experiment. Although the semicircle diameter decreased with time, as it is expected for organic inhibitors subjected to degradation processes, the reduction pace was sufficiently slow to keep the semicircle bigger than in the absence of inhibitors. It suggests that a stable protective film was formed in the first hour, remaining sufficiently undamaged at least for three days. At the concentration of 5 mM of linalyl formate, a big capacitive semicircle was also present in the Nyquist plot of the first hour, shown in Figure 18, but it quickly decreased during the first day, remaining similar to the no inhibitors case. This suggests that, although a protective film was initially present, it was not stable enough at the interface to prevent significant failures. Therefore, the use of linalyl formate as a corrosion inhibitor is recommended at the concentration of 10 mM.
In the case of the Nyquist plots of linalyl acetate at the concentration of 10 mM, shown in Figures 21 to 23, there was no evidence that a consistent protective film was formed, as the capacitive semicircle in the Nyquist plot remained practically the same as in the blank tests at all times. It suggests that the film created at the interface was allowing the corrosive species to easily reach the bare metal. The Nyquist plot in Figure 24 indicates that, at the concentration of 5 mM of linalyl acetate, the capacitive semicircle presented a bigger diameter during the first day, suggesting the presence of an unstable film in the first day. One possible explanation for the better results at 5 mM than at 10 mM is that adsorbed linalyl acetate molecules may cause lateral repulsion on each other, reducing the films cohesion more at a higher concentration, however this hypothesis needs further investigations.

Linalyl butyrate presented similar tendencies to linalyl formate at the concentration of 10 mM, as its Nyquist plots, shown in Figures 27 to 29, also presented a bigger capacitive semicircle than in the blank test during the three days. However, the semicircle diameter was smaller for linalyl butyrate than for linalyl formate. Therefore, the linalyl butyrate film may have allowed the passage of more corrosive species to the bare metal than in the case of linalyl formate. At the concentration of 5 mM of linalyl butyrate, the Nyquist plots in Figures 30 to 32 indicated that the capacitive semicircle decreased fast, remaining similar to the blank test after the first day. This suggests the formation of an unstable protective film, which deteriorated during the first day.

Citronellyl acetate at the concentration of 10 mM also promoted a bigger capacitive semicircle in the Nyquist plots, shown in Figures 33 to 35, than in the blank
test, but still smaller than in linalyl formate experiment at the same concentration. However, at the concentration of 5 mM of citronellyl acetate, the Nyquist plots in Figures 36 to 38 have shown that the capacitive semicircle diameter was similar to the blank test since the experiment beginning, indicating no increase in corrosion protection. Therefore, citronellyl acetate is not the most recommended corrosion inhibitor for carbon steel in ethanol.

In the case of 1-pentylallyl acetate at the concentration of 10 mM, the Nyquist plots in Figures 39 to 41 clearly show that the capacitive semicircle diameter was smaller than in the blank test at all times. This effect could also be visualized in its Bode plots, shown in Figures 72 to 74, as the impedance absolute values in the experiment with 10 mM of 1-pentylallyl acetate remained smaller than in the blank test. However, at the concentration of 5 mM of 1-pentylallyl acetate, the Nyquist plots in Figures 42 to 44 indicated that the capacitive semicircle size remained similar to the blank test. This suggests that 1-pentylallyl acetate may have increased the steel corrosion rates when present at the concentration of 10 mM. One possible explanation is that 1-pentylallyl acetate may react with corrosion products, removing them from the surface and exposing the bare metal to continue the corrosion process. Therefore, 1-pentylallyl acetate cannot be used as a corrosion inhibitor for carbon steel in ethanol.

Equivalent circuit parameters fitting

Only the EIS data in the frequency range from 100 Hz to 4000 Hz were considered in the equivalent circuit parameters fitting process because the high frequency region does not represent the corrosion process adequately, as it was previously discussed. The charge transfer resistances ($R_{ct}$) are displayed in Figures 4 and 5 and the
double layer capacitances \((C_{dl})\) are shown in Figures 6 and 7 for the experiments with concentrations of 5 mM and 10 mM, respectively. The \(C_{dl}\) values were obtained by using the previously shown Equation V.
Figure 6: Double layer capacitance profiles for blank test and 10 mM experiments

Figure 7: Double layer capacitance profiles for blank test and 5 mM experiments
Linalyl formate promoted the greatest $R_{ct}$ values at the concentration of 10 mM among all tested chemicals, as it was expected due to its big capacitive semicircle in the Nyquist plot. Its $R_{ct}$ values also decreased slowly. In addition, its $C_{dl}$ values were smaller than in the blank test and this difference increased with time. This confirms that less corrosive species reached the bare metal surface than in the others experiments, due to the presence of a stable and more protective film. However, at the concentration of 5 mM, its $R_{ct}$ values decreased much faster and the $C_{dl}$ remained close to its values in the blank test, indicating film failures. Therefore, this reinforces the previous conclusion from the EIS results that linalyl formate is the most efficient chemical as corrosion inhibitor in ethanol and its application is recommended at the concentration of 10 mM.

Linalyl acetate at the concentration of 10 mM promoted $R_{ct}$ and $C_{dl}$ values similar to their values in the absence of inhibitors at all times. At the concentration of 5 mM, its $R_{ct}$ values were initially bigger than in the blank test but it quickly decreased during the first day, while the $C_{dl}$ remained close to its blank test values. This indicates that linalyl acetate could not promote a consistent and stable protective film, confirming that its use as a corrosion inhibitor is not recommended in ethanol.

Linalyl butyrate at the concentration of 10 mM presented $R_{ct}$ values slightly greater than in the blank test but much smaller than in the linalyl formate experiment at the same concentration. As the $C_{dl}$ values in the linalyl butyrate and linalyl formate tests at the concentration of 10 mM were close, it can be said that the film thickness was also similar for both inhibitors. So, their difference in $R_{ct}$ values may be related to the physical properties of the protective film, such as its porosity, suggesting that linalyl butyrate
promoted a less protective film than linalyl formate. At the concentration of 5 mM of linalyl butyrate, the $R_{ct}$ values declined much faster, remaining similar to its values in the blank test after the first day. At the same time, the $C_{dl}$ values increased with time, suggesting the loss of the protective film during the first day, as it was previously suggested in the analysis of the Nyquist plots.

Citronellyl acetate at the concentration of 10 mM caused greater $R_{ct}$ values than in the blank test, but still smaller than in the linalyl formate experiment at the same concentration. Its $C_{dl}$ values were smaller than in the blank test. This confirms the presence of a film that provides less protection than the film formed by linalyl formate. At the concentration of 5 mM of citronellyl acetate, the $R_{ct}$ remained close to its blank test values. In addition, its $C_{dl}$ values were much higher than in the absence of inhibitors, indicating a thinner and more porous film at the metal interface. This suggests that, at a low concentration, the film promoted by citronellyl acetate may present significant failures, allowing a small intensification of a localized corrosion process by creating preferential regions for the corrosion reactions. Therefore, citronellyl acetate is not the most recommended chemical as a corrosion inhibitor for carbon steel in ethanol.

The chemical 1-pentylallyl acetate at the concentration of 10 mM promoted much lower $R_{ct}$ values than in the blank test throughout the whole experiment. In addition, the $C_{dl}$ values continuously increased, becoming bigger than its values from the blank test. At the concentration of 5 mM of 1-pentylallyl acetate, the $R_{ct}$ values were high in the first hour but they quickly decreased to remain close to the values from the blank test. At the same time, the $C_{dl}$ values also increased during the experiment with the concentration of
5 mM of 1-pentylallyl acetate, becoming much larger than the values from the blank test. This suggests that a thinner and less protective barrier was created at the surface than in the blank test, especially at the higher concentration of 10 mM of 1-pentylallyl acetate, corroborating the conclusions from the analysis of the EIS plots that 1-pentylallyl acetate caused an increase in corrosion rates.

**Corrosion Inhibition Efficiencies**

In all experiments, it can be seen in the EIS Nyquist plots that the differences between an EIS measurement and its previous one became more negligible as the experiment approached its end at 72 hours after the electrodes immersion in ethanol. This stabilizing effect could also be verified in the fitted values of the charge transfer resistance, which have not changed significantly during the third day of immersion. This means that after three days, the corrosion process became mostly depended on the properties of the protective film that had already been formed. Therefore, the EIS data from the three days experiments are sufficient to develop a comprehensive analysis about the evolution of the corrosion inhibition efficiencies of each tested chemical. The $R_{ct}$ values from each EIS measurement were used to calculate the inhibition efficiency through equation VII, so that an efficiency profile was obtained for each inhibitor and concentration, as shown in Figures 8 and 9.
Figure 8: Corrosion inhibition efficiency profiles for each inhibitor at 10 mM

Figure 9: Corrosion inhibition efficiency profiles for each inhibitor at 5 mM
In the concentration of 10 mM, linalyl formate presented the highest and most stable efficiency during the experiment, followed by citronellyl acetate and linalyl butyrate. As previously discussed, linalyl acetate and 1-pentylallyl acetate have not promoted a stable corrosion protection at this concentration. These results suggest that the ramifications in the chemical structures of the inhibitors presented a big influence in their ability to promote protective films at the surface. A smaller carbon chain bonded to the carbonyl group increased the chemical inhibition efficiency, as linalyl formate presented much higher inhibition efficiency than linalyl acetate and linalyl butyrate. At the same time, the ramification and double bond in the carbon chain extremity close to the carbonyl group may hamper the adsorption mechanism, explaining why citronellyl acetate presented higher inhibition efficiency than linalyl acetate. As 1-pentylallyl acetate is the only tested chemical that does not contain a ramification and double bond in the extremity of the carbon chain opposite to the carbonyl group in its chemical structure, it can also be suggested that this ramification and double bond are very important to promote the formation of a stable protective film.

In the concentration of 5 mM, all chemicals, except citronellyl acetate, presented high inhibition efficiencies in the first hour but it quickly dropped to zero during the first day, suggesting that there might have been inhibitors losses or degradation. It is also noticed that linalyl acetate and linalyl butyrate achieved higher efficiencies in the first hours than they could promote in the experiments with 10 mM, reinforcing the hypothesis that lateral repulsions between the adsorbed inhibitors molecules might occur at higher concentrations. Therefore, for these two chemicals, an increase in concentration may have reduced the stability of the formed protective film.
Finally, as linalyl formate promoted the highest corrosion inhibition efficiencies in the concentration of 10 mM and their values were significantly raised by an increase in its concentration from 5 mM to 10 mM, it can be safely said that, among the considered chemicals, linalyl formate is the most suitable one to be used as a corrosion inhibitor for X-52 steel in ethanol media. This is also in accordance with the previous discussed analyses of the EIS results.

White light interferometry results

The interferometric 3D surface images of the X52 steel electrode after each experiment and also of a polished unused electrode are shown in Appendix C, and their roughness profiles in the cylinder electrode vertical axis are shown in the Appendix D. It can be seen in Figure 78 that, before immersion in ethanol, the steel surface was very smooth due to the rigorous polishing procedure it had been submitted. This characteristic can also be verified in the surface depth profile, presented in Figure 90, as the peaks and valley in the plot were small. In Figures 79 and 91, it is shown that in the absence of inhibitors, the corrosion process slightly increased the surface irregularity, but it was still mostly smooth, suggesting that the steel did not suffered a severe localized corrosion process, and few corrosion products deposits were formed, probably because most of them were dissolved in the solution, as ethanol is a strong scouring agent. This means, that if a high surface irregularity was present in an experiment with a corrosion inhibitor, a thick protective barrier might have covered the bare metal interface. Therefore, the increase in the apparent surface irregularity after each experiment was caused mostly by the formation of protective barriers and corrosion products deposits at the steel surface,
allowing a qualitative comparison of the morphology changes that occurred at the steel surface under each condition.

In Figures 80 and 92, it can be seen that in the presence of linalyl formate at the concentration of 10 mM, the surface became more irregular than in the blank test, suggesting the presence of a protective barrier. This corroborates the analyses of its EIS results, as the low $C_{dl}$ and high $R_{ct}$ values obtained in this experiment also indicated the presence of such barrier. In addition, at the concentration of 5 mM of linalyl formate, the surface image and roughness profile, shown in Figures 81 and 93, presented a very similar irregularity to the steel surface from the blank test, suggesting that no significant protective film remained at the surface after the three days of immersion, which is also in good agreement with the higher $C_{dl}$ and lower $R_{ct}$ values previously calculated for this experiment.

In Figures 82 and 83, it is shown that the steel surfaces from the experiments with 10 mM and 5 mM of linalyl acetate remained similar in roughness to the surface from the blank test, what can also be verified in their roughness profiles, shown in Figures 94 and 95. This suggests the absence of a consistent protective film in both experiments, and it also supports the previous analysis of the EIS data from the experiments with this chemical, which has indicated that linalyl acetate could not promote a significant corrosion protection.

In Figures 84 and 96, it can be clearly seen that the surface from the experiment with linalyl butyrate at the concentration of 10 mM became more irregular than the surface from the blank test, but still less irregular than in the experiment with linalyl
formate at the same concentration. So, in accordance with the previous EIS analysis, which indicated that, in this experiment, the $R_{ct}$ values were just slightly greater and the $C_{dl}$ values were smaller than in the blank test, it is reasonable to propose that a film was present at the surface but it could not prevent the passage of corrosive species as efficiently as the film in the experiment with linalyl formate. In Figures 85 and 97, it is shown that in the experiment with the concentration of 5 mM of linalyl butyrate, the surface remained smooth, indicating the absence of such film. Therefore, these results reinforce the conclusion that linalyl butyrate is not an efficient corrosion inhibitor in ethanol media.

In the experiment with citronellyl acetate at the concentration of 10 mM, the surface image and roughness profile, shown in Figures 86 and 98, indicate that the surface became slightly more irregular than in the blank test but still less irregular than in the experiment with linalyl formate at the same concentration. This result reinforces the conclusion from the EIS analyses that a less protective film was formed in the presence of citronellyl acetate than in the presence of linalyl formate. In the test with the concentration of 5 mM of citronellyl acetate, the surface image and roughness profile, shown in Figures 87 and 99, indicated the presence of several sharp peaks. In agreement with the previous discussion about $R_{ct}$ and $C_{dl}$ values in this experiment, it suggest a small intensification of a localized corrosion mechanism, which created these corrosion products deposits in the preferential regions for the corrosion reactions, confirming that citronellyl acetate is not recommended to be employed as a corrosion inhibitor in ethanol media.
In Figures 88 and 100, it is shown that in the experiment with the concentration of 10 mM of 1-pentylallyl acetate, the surface became very irregular. However, as the roughness increase was very high and the EIS results have shown a strong decrease in $R_{ct}$ values and an increase in $C_{dl}$ values, it is reasonable to suggest that the increase in surface roughness was caused by an intensification of the corrosion process rather than the formation of a protective film. In the test with the concentration of 5 mM of 1-pentylallyl acetate, the surface image and roughness profile, shown in Figures 89 and 101, indicated a smooth surface, suggesting that, at this lower concentration, 1-pentylallyl acetate did not cause a significant increase in corrosion rates, but it has not promoted a protective film either, which confirms the previous conclusions from the EIS analysis.

The average line roughness ($R_a$) and the root mean square line roughness ($R_q$) parameters calculated from the roughness profiles in Appendix D are displayed in Table 2. As the steel surface was polished following the same procedure in all cases, it can be considered that the roughness parameters of the steel electrodes before immersion in ethanol were approximately the same in all cases. It is noticed that both parameters did not changed much between all experiments. As they represent average roughness per unit length, $R_a$ and $R_q$ are not very sensible to the presence of few thin peaks and valleys, which can justify these similar values. In addition, it is noticed that the high $R_a$ value calculated for the blank test was overestimated, as its roughness profile, shown in Figure 91, is tilted, due to a bad positioning of the steel surface in the interferometer during this measurement. Nevertheless, it can still be verified that the $R_a$ and $R_q$ values were higher in the surface from the experiment with 10 mM of linalyl formate than in the surfaces
from the experiments with the others chemicals at this same concentration, as it was expected from the previous discussions.

Table 2: Average line roughness (Ra) and root mean square line roughness (Rq) from each experiment

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Ra (µm)</th>
<th>Rq (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished sample</td>
<td>6.177</td>
<td>7.453</td>
</tr>
<tr>
<td>Blank test</td>
<td>6.537</td>
<td>7.813</td>
</tr>
<tr>
<td>Linalyl formate 10 mM</td>
<td>6.418</td>
<td>7.582</td>
</tr>
<tr>
<td>Linalyl acetate 10 mM</td>
<td>6.060</td>
<td>7.364</td>
</tr>
<tr>
<td>Linalyl butyrate 10 mM</td>
<td>6.219</td>
<td>7.445</td>
</tr>
<tr>
<td>Citronellyl acetate 10 mM</td>
<td>6.017</td>
<td>7.301</td>
</tr>
<tr>
<td>1-Pentylallyl acetate 10 mM</td>
<td>6.283</td>
<td>7.532</td>
</tr>
<tr>
<td>Linalyl formate 5 mM</td>
<td>5.887</td>
<td>7.284</td>
</tr>
<tr>
<td>Linalyl acetate 5 mM</td>
<td>6.302</td>
<td>7.567</td>
</tr>
<tr>
<td>Linalyl butyrate 5 mM</td>
<td>6.248</td>
<td>7.545</td>
</tr>
<tr>
<td>Citronellyl acetate 5 mM</td>
<td>6.380</td>
<td>7.591</td>
</tr>
<tr>
<td>1-Pentylallyl acetate 5 mM</td>
<td>6.216</td>
<td>7.494</td>
</tr>
</tbody>
</table>

Scanning electron microscopy images

The SEM images are displayed in Figures 10 and 11 below. The higher magnification and definition of these images when compared with the interferometry images allowed the visualization of the surface features in richer details. The EDS analysis of the black areas, which were present specially in the experiment with the
concentration of 10 mM of citronellyl acetate, indicated a high carbon mass concentration above 50%. It was also verified in all images that in the lighter areas, the carbon mass concentration was below 10%. As the iron oxidation occurred during the corrosion process, many of the corrosion products were dissolved in the ethanol solution, reducing the local iron concentration and increasing the local concentration of the non-corroded chemical elements present in the X-52 steel, such as carbon. Therefore, it is reasonable to consider that these black areas represented remnants of a corrosion product film.

In the SEM image from the blank test, shown in Figure 10, it can be seen that almost no corrosion products film remained at the surface, confirming the absence of a protective barrier. The same can be said in the images from the experiments with the concentration of 10 mM of linalyl acetate, linalyl butyrate and 1-pentylallyl acetate, also shown in Figure 10, confirming the previous conclusions that these three chemicals could not promote a stable protective film. The SEM images from the experiments with linalyl formate and citronellyl acetate at the concentration of 10 mM, shown in Figure 10, indicated evidences of a corrosion product film as expected from the EIS and interferometry results. However, the protectiveness of such films cannot be compared just with the SEM images.

It can be seen that the SEM image of the polished unused surface, shown in Figure 11, presented some black regions. However, in this case, as the surface had been polished just before its SEM measurement, these regions were considered to represent a contamination from the sandpapers used in the polishing process. This contamination was not present in the steel surfaces after the experiments because it was easily removed by the ethanol solution after the electrodes immersion. In all SEM images from the
experiments with concentration of 5 mM, shown in Figure 11, there were no clear evidences of a protective film. This confirms that no tested chemical, in the concentration of 5 mM, could promote a stable corrosion protection during the whole three days of steel immersion in ethanol.
Figure 10: Cylinder electrode SEM surface images from blank test (A) and the tests with 10 mM of linalyl formate (B), linalyl acetate (C), linalyl butyrate (D), citronellyl acetate (E) and 1-Pentylallyl acetate (F)
Figure 11: Cylinder electrode SEM surface images from polished sample (A) and the tests with 5 mM of linalyl formate (B), linalyl acetate (C), linalyl butyrate (D), citronellyl acetate (E) and 1-Pentylallyl acetate (F)
CHAPTER IV
CONCLUSIONS

Among the five evaluated chemicals at the concentration of 10 mM, linalyl formate promoted the best corrosion protection in ethanol media with a stable inhibition efficiency of approximately 50% during the experiments duration of three days. Citronellyl acetate and linalyl butyrate also favored the steel protection with smaller inhibition efficiencies, but linalyl acetate has not promoted inhibition consistently at this concentration. The chemical 1-pentylallyl acetate caused an increase in the corrosion rates by probably favoring a localized corrosion mechanism. The chemicals whose chemical structures contain fewer and smaller ramifications bonded to the carbonyl group presented bigger inhibition efficiencies. In addition, the presence of the ramification and double bond in the carbon chain close to the carbonyl group has reduced the inhibition efficiency and the presence of those far from the carbonyl group was indispensable to promote a stable protective film. At the concentration of 5 mM, 1-pentylallyl acetate and citronellyl acetate have not promoted a significant change in the corrosion rates. At this same concentration, linalyl formate, linalyl acetate and linalyl butyrate promoted high inhibition efficiencies during the first hours, but no tested chemical could promote a stable corrosion protection during three days, suggesting possible inhibitors losses or degradation during the tests. Finally, the most efficient chemical for corrosion inhibition purposes is linalyl formate in the concentration of 10 mM.
Future Work

Future corrosion experiments in higher concentrations above 10 mM of linalyl butyrate, citronellyl acetate and specially linalyl formate can be performed to check how much their corrosion inhibition efficiencies can still be increased. In addition, the synergy between these three chemicals in the adsorption process in the steel surface can be analyzed with experiments containing their mixtures at different concentrations. As in this work, the chemicals were tested in a relatively less corrosive environment due to the low water and dissolved oxygen concentrations, further experiments in controlled aerated conditions, higher water concentrations and in different pH and temperatures can provide more information about the relation between these important parameters and the properties of the inhibitors protective films created at the steel substrate-electrolyte interface.
REFERENCES


APPENDICES
APPENDIX A

EIS NYQUIST PLOTS

Figure 12: EIS Nyquist plot - Blank test - Day 1
Figure 13: EIS Nyquist plot - Blank test - Day 2
Figure 14: EIS Nyquist plot - Blank test - Day 3
Figure 15: EIS Nyquist plot - Test with linalyl formate at concentration of 10 mM - Day 1
Figure 16: EIS Nyquist plot - Test with linalyl formate at concentration of 10 mM - Day 2
Figure 17: EIS Nyquist plot - Test with linalyl formate at concentration of 10 mM - Day 3
Figure 18: EIS Nyquist plot - Test with linalyl formate at concentration of 5 mM - Day 1
Figure 19: EIS Nyquist plot - Test with linalyl formate at concentration of 5 mM - Day 2

Nyquist plot - Linalyl formate 5 mM - Day 2

Z'' (KΩ cm²) vs Z' (KΩ cm²)

-600
-500
-400
-300
-200
-100
0
100
200
300
400
500
600

27 h
30 h
33 h
36 h
39 h
42 h
45 h
48 h
Figure 20: EIS Nyquist plot - Test with linalyl formate at concentration of 5 mM - Day 3
Figure 21: EIS Nyquist plot - Test with linalyl acetate at concentration of 10 mM - Day 1
Figure 22: EIS Nyquist plot - Test with linalyl acetate at concentration of 10 mM - Day 2
Figure 23: EIS Nyquist plot - Test with linalyl acetate at concentration of 10 mM - Day 3
Figure 24: EIS Nyquist plot - Test with linalyl acetate at concentration of 5 mM - Day 1
Figure 25: EIS Nyquist plot - Test with linalyl acetate at concentration of 5 mM - Day 2
Figure 26: EIS Nyquist plot - Test with linalyl acetate at concentration of 5 mM - Day 3
Figure 27: EIS Nyquist plot - Test with linalyl butyrate at concentration of 10 mM - Day 1
Figure 28: EIS Nyquist plot - Test with linalyl butyrate at concentration of 10 mM - Day 2
Figure 29: EIS Nyquist plot - Test with linalyl butyrate at concentration of 10 mM - Day 3
Figure 30: EIS Nyquist plot - Test with linalyl butyrate at concentration of 5 mM - Day 1
Figure 31: EIS Nyquist plot - Test with linalyl butyrate at concentration of 5 mM - Day 2
Figure 32: EIS Nyquist plot - Test with linalyl butyrate at concentration of 5 mM - Day 3
Figure 33: EIS Nyquist plot - Test with citronellyl acetate at concentration of 10 mM - Day 1
Figure 34: EIS Nyquist plot - Test with citronellyl acetate at concentration of 10 mM - Day 2
Figure 35: EIS Nyquist plot - Test with citronellyl acetate at concentration of 10 mM - Day 3
Figure 36: EIS Nyquist plot - Test with citronellyl acetate at concentration of 5 mM - Day 1
Figure 37: EIS Nyquist plot - Test with citronellyl acetate at concentration of 5 mM - Day 2
Figure 38: EIS Nyquist plot - Test with citronellyl acetate at concentration of 5 mM - Day 3
Figure 39: EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 10 mM - Day 1
Figure 40: EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 10 mM - Day 2
Figure 41: EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 10 mM - Day 3
Figure 42: EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 5 mM - Day 1
Figure 43: EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 5 mM - Day 2
Figure 44: EIS Nyquist plot - Test with 1-Pentylallyl acetate at concentration of 5 mM - Day 3
APPENDIX B

EIS BODE PLOTS

Bode plot - No Inhibitors - Day 1

Figure 45: EIS Bode plot - Blank test - Day 1
Figure 46: EIS Bode plot - Blank test - Day 2
Figure 47: EIS Bode plot - Blank test - Day 3
Figure 48: EIS Bode plot - Test with linalyl formate at concentration of 10 mM - Day 1
Figure 49: EIS Bode plot - Test with linalyl formate at concentration of 10 mM - Day 2
Figure 50: EIS Bode plot - Test with linalyl formate at concentration of 10 mM - Day 3
Figure 51: EIS Bode plot - Test with linalyl formate at concentration of 5 mM - Day 1
Figure 52: EIS Bode plot - Test with linalyl formate at concentration of 5 mM - Day 2
Figure 53: EIS Bode plot - Test with linalyl formate at concentration of 5 mM - Day 3
Figure 54: EIS Bode plot - Test with linalyl acetate at concentration of 10 mM - Day 1
Figure 55: EIS Bode plot - Test with linalyl acetate at concentration of 10 mM - Day 2
Figure 56: EIS Bode plot - Test with linalyl acetate at concentration of 10 mM - Day 3
Figure 57: EIS Bode plot - Test with linalyl acetate at concentration of 5 mM - Day 1
Figure 58: EIS Bode plot - Test with linalyl acetate at concentration of 5 mM - Day 2
Figure 59: EIS Bode plot - Test with linalyl acetate at concentration of 5 mM - Day 3
Figure 60: EIS Bode plot - Test with linalyl butyrate at concentration of 10 mM - Day 1
Figure 61: EIS Bode plot - Test with linalyl butyrate at concentration of 10 mM - Day 2
Figure 62: EIS Bode plot - Test with linalyl butyrate at concentration of 10 mM - Day 3
Figure 63: EIS Bode plot - Test with linalyl butyrate at concentration of 5 mM - Day 1
Figure 64: EIS Bode plot - Test with linalyl butyrate at concentration of 5 mM - Day 2
Figure 65: EIS Bode plot - Test with linalyl butyrate at concentration of 5 mM - Day 3
Figure 66: EIS Bode plot - Test with citronellyl acetate at concentration of 10 mM - Day 1
Figure 67: EIS Bode plot - Test with citronellyl acetate at concentration of 10 mM - Day 2
Figure 68: EIS Bode plot - Test with citronellyl acetate at concentration of 10 mM - Day 3
Figure 69: EIS Bode plot - Test with citronellyl acetate at concentration of 5 mM - Day 1
Figure 70: EIS Bode plot - Test with citronellyl acetate at concentration of 5 mM - Day 2
Figure 71: EIS Bode plot - Test with citronellyl acetate at concentration of 5 mM - Day 3
Figure 72: EIS Bode plot - Test with 1-Pentylallyl acetate at concentration of 10 mM - Day 1
Figure 73: EIS Bode plot - Test with 1-Pentylallyl acetate at concentration of 10 mM - Day 2
Figure 74: EIS Bode plot - Test with 1-Pentylallyl acetate at concentration of 10 mM - Day 3
Figure 75: EIS Bode plot - Test with 1-Pentylallyl acetate at concentration of 5 mM - Day 1
Figure 76: EIS Bode plot - Test with 1-Pentyllalyl acetate at concentration of 5 mM - Day 2
Figure 77: EIS Bode plot - Test with 1-Pentylallyl acetate at concentration of 5 mM - Day 3
APPENDIX C

WLI SURFACE IMAGES

Figure 78: WLI surface image – Polished electrode

Figure 79: WLI surface image – Blank test
Figure 80: WLI surface image – Test with linalyl formate at concentration of 10 mM

Figure 81: WLI surface image – Test with linalyl formate at concentration of 5 mM
Figure 82: WLI surface image – Test with linalyl acetate at concentration of 10 mM

Figure 83: WLI surface image – Test with linalyl acetate at concentration of 5 mM
Figure 84: WLI surface image – Test with linalyl butyrate at concentration of 10 mM

Figure 85: WLI surface image – Test with linalyl butyrate at concentration of 5 mM
Figure 86: WLI surface image – Test with citronellyl acetate at concentration of 10 mM

Figure 87: WLI surface image – Test with citronellyl acetate at concentration of 5 mM
Figure 88: WLI surface image – Test with 1-Pentylallyl acetate at concentration of 10mM

Figure 89: WLI surface image – Test with 1-Pentylallyl acetate at concentration of 5 mM
APPENDIX D

WLI ROUGHNESS PROFILES

Figure 90: WLI roughness profile – Polished electrode

Figure 91: WLI roughness profile – Blank test

Figure 92: WLI roughness profile – Test with linalyl formate at concentration of 10 mM
Figure 93: WLI roughness profile – Test with linalyl formate at concentration of 5 mM

Figure 94: WLI roughness profile – Test with linalyl acetate at concentration of 10 mM

Figure 95: WLI roughness profile – Test with linalyl acetate at concentration of 5 mM
Figure 96: WLI roughness profile – Test with linalyl butyrate at concentration of 10 mM

Figure 97: WLI roughness profile – Test with linalyl butyrate at concentration of 5 mM

Figure 98: WLI roughness profile – Test with citronellyl acetate at concentration of 10 mM
Figure 99: WLI roughness profile – Test with citronellyl acetate at concentration of 5 mM

Figure 100: WLI roughness profile – Test with 1-Pentylallyl acetate at concentration of 10 mM

Figure 101: WLI roughness profile – Test with 1-Pentylallyl acetate at concentration of 5 mM