Diacid Corrosion Inhibitors for Water-Based Systems

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Rust 101

- Oxidation of Iron and Its Alloys
  
  \[ 4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 \]

- Contributing Factors
  
  - pH Excursions
  - Agitation (Oxygen Entrainment)
  - Microbial Contamination

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Diacid Corrosion Inhibitors

- Used as amine salt for solubility and pH control.
- Protection by forming a molecular film.
- May be used in conjunction with borates and/or triazoles.
Uses For Diacid Inhibitors

- Water-based metalworking fluids.
- Water-based hydraulic fluids.
- Long-life antifreeze. (Aluminum and alloys)
Established Technology

- US 3,981,780 (9/21/76); UOP/CFR – Distillation Columns
- US 4,382,008 (5/3/83); ICI – Antifreeze
- US 4,390,440 (6/28/83); BASF – Hydraulic Fluids
- US 4,426,208 (1/17/84); Ethyl Corp. – Gasoline/Alcohol Blends
- US 4,533,481 (8/6/85); Lubrizol – Aqueous Systems
- US 4,647,392 (3/3/87); Texaco - Antifreeze
Scope of Study

Compare diacid corrosion inhibitors, specifically two new grades of azelaic acid with enhanced undecanedioic acid ($C_{11}$) using the iron-chip corrosion test ASTM D4627.
# Diacids Studied & Compositions

<table>
<thead>
<tr>
<th>Diacid (Wt%)</th>
<th>Azelaic Acid Tech Grade</th>
<th>Azelaic Acid CI Grade</th>
<th>Azelaic Acid CI+</th>
<th>Sebacic Acid</th>
<th>Corfree® M1</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;C&lt;sub&gt;9&lt;/sub&gt;</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;9&lt;/sub&gt;</td>
<td>85</td>
<td>70</td>
<td>45</td>
<td>&lt;10 (C&lt;sub&gt;4&lt;/sub&gt;-C&lt;sub&gt;9&lt;/sub&gt;)</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;10&lt;/sub&gt;</td>
<td></td>
<td></td>
<td>&gt;98</td>
<td>5-10</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;11&lt;/sub&gt;</td>
<td>15</td>
<td>40+</td>
<td></td>
<td>30-45</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;12&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td>30-45</td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>13 (&gt;C&lt;sub&gt;9&lt;/sub&gt;)</td>
<td>30 (Total &gt;C&lt;sub&gt;9&lt;/sub&gt;)</td>
<td>50 (Total &gt;C&lt;sub&gt;9&lt;/sub&gt;)</td>
<td>&lt;6</td>
<td></td>
</tr>
</tbody>
</table>
Previous Studies

Earlier work has shown that the efficacy of long chain diacids as corrosion inhibitors follows the order:

\[ C_{11} > C_{10} \approx C_{12} > C_{9} \]
An aqueous solution of the corrosion inhibitor is prepared. Standard iron chips (4g) are placed on a piece of clean filter paper in a petri dish and covered with 5g of the solution.

Cover the dish and allow it to stand for 20-24 hrs. After standing, the solution and chips are removed, the filter paper rinsed and examined for evidence of discoloration due to corrosion products. A clean filter paper is a “pass.”
A stepped series of inhibitor concentrations is run and the lowest concentration to pass is determined. Lower “pass” concentrations are indicative of more effective inhibition.
Stock Solution

94% Hard Water (304 mg/L CaCl$_2$ + 139 mg/L MgCl$_2$·6H$_2$O in distilled water)

2% MEA (Monoethanolamine)

2% TEA (Triethanolamine)

2% Diacid Inhibitor

Dilutions were prepared from the 2% inhibitor stock by adding hard water as above.

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Azelaic Acid – Emerox® 1112

TEST METHOD: ASTM D-4627 Iron Chip Corrosion Test
2%, 1.5%, 1%, 0.7%, 0.5%, 0.4%, 0.3%, 0.2%, 0.1% and 0.05% diacid
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2%, 1.5%, 1%, 0.7%, 0.5%, 0.4%, 0.3%, 0.2%, 0.1% and 0.05% diacid
Azelaic Acid – Emerox® 1185

Test Method ASTM D-4627 Iron Chip Corrosion Test
0.14%, 0.16%, 0.18% Diacid Concentrations

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Sebacic Acid

TEST METHOD: ASTM D-4627 Iron Chip Corrosion Test
2%, 1.5%, 1%, 0.7%, 0.5%, 0.4%, 0.3%, 0.2%, 0.1% and 0.05% diacid
Corfree® M1

TEST METHOD: ASTM D-4627 Iron Chip Corrosion Test
2%, 1.5%, 1%, 0.7%, 0.5%, 0.4%, 0.3%, 0.2%, 0.1% and 0.05% diacid
# Summary of Results

<table>
<thead>
<tr>
<th>Diacid (Wt%)</th>
<th>Azelaic Acid Emerox 1112</th>
<th>Azelaic Acid Emerox 1175</th>
<th>Azelaic Acid Emerox 1185</th>
<th>Sebacic Acid</th>
<th>Corfree® M1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 (A)</td>
<td>Rust</td>
<td>Rust</td>
<td>Rust</td>
<td>Rust</td>
<td>Rust</td>
</tr>
<tr>
<td>0.1 (B)</td>
<td>Rust</td>
<td>Rust</td>
<td>Rust</td>
<td>Rust</td>
<td>Rust</td>
</tr>
<tr>
<td>0.2 (C)</td>
<td>Rust</td>
<td>Rust</td>
<td>Pass</td>
<td>Rust</td>
<td>Pass</td>
</tr>
<tr>
<td>0.3 (D)</td>
<td>Rust</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>0.5 (E)</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>0.7 (F)</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>1.0 (G)</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>1.5 (H)</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>2.0 (I)</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
</tbody>
</table>
Conclusion

As expected, each of the diacids studied proved to be an effective corrosion inhibitor at concentrations $\geq 0.5\%$ wt. Enhancing the C$_{11}$ content of azelaic acid to 15% improves its corrosion-inhibiting properties to be comparable to sebacic acid. Raising the C$_{11}$ level to 45% improves the performance to be equivalent to Corfree$^\text{®}$ M1.