BIODEGRADABLE AND RENEWABLE RAW MATERIALS IN A NEW GENERATION OF WATER-TREATMENT PRODUCTS

B.A. Miksic, Dr. M. Kharshon, Dr. A. Furman
Cortec Corporation
St. Paul, Minnesota, USA

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New “Green” Inhibitors

“Green” chemistry is not an absolute goal or destination, but a dedication to the process for continual improvement, wherein the environment is considered along with the chemistry.
New “Green” Inhibitors (cont.)
The Principal Criteria for Inhibitors’ Acceptance

North Sea (UK, Norway, Denmark, The Netherlands)

Biodegradability: > 60% in 28 days

Marine toxicity: Effective Concentration,
50% (EC$_{50}$)/Lethal Concentration,
50% (LC$_{50}$)>10 mg/L to North Sea species

Bioaccumulation: Log Octanol/Water Partition Coefficient
(Pow)<3
The Products

S-10-F Additive for the condensate line

- Non-Toxic “green” filming corrosion inhibitor for boiler condensate
- Base: salts of aminoacids, produced from renewable resources
- Effective against corrosion caused by carbon dioxide and oxygen
- Resistant to oxidation and has high salt tolerance
- Outstanding film persistency in a wide temperature range
- Excellent replacement for film-forming amines (steam line)
- Compatible with the majority of ingredients used in boiler and condensate line treatment programs
- Can be used as a continuous and/or batch treatment
The Products

S-14 Bio-Antiscalant / corrosion inhibitor

- Unique “green” building block, natural polymer based (soy protein)
- Rare combination of a powerful scale inhibition and excellent multi-metal corrosion protection
- Readily biodegradable
- GRAS (Generally Recognized As Safe by CFR) approved
- Easy to formulate in variety of open formulations
- Compatible with common water treatment programs
- Economical
To Achieve the Desired Properties:

- Choice of biobased raw materials
- Environmental aspects
- Corrosion testing
- Antiscalant properties
Additive to the condensate line

Choice of materials, Environmental aspect

\[ \text{O} \]
\[ \text{R} - \overset{\text{O}}{\text{C}} - \overset{\text{N}}{\text{N}} - \text{CH}_2 - \text{COO}^- \text{M}^+ \]
\[ \text{CH}_3 \]

R-fatty acid hydrocarbon
M-metal

Salts of fatty amino acids
S-10 F
Additive to the condensate line (cont.)

- Rapid biodegradability
- Made from the RM based on renewable resources
- LD$_{50}$, mg/kg – 5000 oral rats (table salt-3000)
- Acceptable aquatic toxicity Per European Protocol: 96 hours 50% (LC$_{50}$)-56 ppm
- Based on NOEC and LOEC, S-10 F could be discharged into the sea in concentrations greater than 1200ppm
- Outstanding mildness to skin and eyes
- Excellent corrosion inhibition

(NOEC-No observable effect concentration)
(LOEC-Lowest observable effect concentration)
Corrosion Testing

○ **Immersion Corrosion Test**
  Concentration-300 ppm
  Carrier-DI water
  Conditions: **Static** - 95-100°C, 10 days
  **Dynamic** – 75-85°C, 48 hours, 200 rpm

○ **Electrochemical test**
  Equipment:
  Potentiostat/Galvanostat “Versastat”
  Working electrode: Carbon Steel SAE1018
  Conditions: **Dynamic** – 72°C, 200 rpm
### Protective Properties of S-10 F (Additive for Condensate Lines)

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass Loss</th>
<th>Protective Power, Z%*</th>
<th>Corrosion Rate, (mpy)</th>
<th>Protective Power, Z%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-10 F, 300 ppm</td>
<td>0.0970 (No visible corrosion)</td>
<td>91.49</td>
<td>0.233</td>
<td>87.01</td>
</tr>
<tr>
<td>Control*</td>
<td>0.1269 (Corrosion after 0.5 Hr.)</td>
<td>-</td>
<td>1.794</td>
<td>-</td>
</tr>
</tbody>
</table>

\[
Z = \frac{CR_i - CR_c}{CR_c} \times 100\% , \text{ where } \quad *\text{DI water; CR}_c = \text{Corrosion rate in DI water; CR}_i = \text{Corrosion rate in presence of inhibitor}
\]

**Tafel plots:**
1. 300 ppm S-10 F in de-ionized water
2. De-ionized water
The choice of materials

- Current products: phosphonates, acrylates
- Natural polymers as antiscalants
  - Polyaspartates
  - Soy polymer (protein part of soy beans)
  - Casein (from milk)
  - Polysaccharide (from sea weeds)
S-14 Bio
Antiscalant/Corrosion Inhibitor
The choice of materials

- Soy polymer (protein)
  Amide-linked polymers composed of amino acids

\[
\begin{align*}
R - CH - C - NH - CH - C - O^\ominus \\
\quad \quad \quad | \quad \quad \quad | \\
\quad \quad \quad NH_3 \quad O \quad \quad \quad R' \quad O \\
\quad \quad \quad +
\end{align*}
\]

Molecular weight range: 3,000 – 1,000,000
Corrosion testing

- Half-immersion corrosion test
  - Materials: Carbon Steel, Galvanized Steel, Aluminum, Copper
  - Testing Conditions: 72 hours, Room Temperature

- Pilot Cooling Tower Test
  - The real life test in cooling tower
  - Coupons: Carbon Steel SAE 1010, Copper CDA12, Hot-dipped galvanized steel
# S-14 Bio Antiscalant/Corrosion Inhibitor

## Results of Corrosion Tests

### Half immersion corrosion test

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon Steel</th>
<th>Galvanized Steel</th>
<th>Aluminum</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organophosphonate</td>
<td>Corrosion</td>
<td>Corrosion</td>
<td>Corrosion</td>
<td>Corrosion</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>Corrosion</td>
<td>Corrosion</td>
<td>Severe Corrosion</td>
<td>Severe Corrosion</td>
</tr>
<tr>
<td>Soy-based polymer (S-14 Bio)</td>
<td>No visible corrosion</td>
<td>No Visible Corrosion</td>
<td>No Visible Corrosion</td>
<td>No Visible Corrosion</td>
</tr>
<tr>
<td>Polysaccharide based</td>
<td>Slight Corrosion</td>
<td>Slight Corrosion</td>
<td>Slight Corrosion</td>
<td>No Visible Corrosion</td>
</tr>
<tr>
<td>Polyaspartic acid based</td>
<td>Corrosion</td>
<td>Severe Corrosion</td>
<td>Slight Corrosion</td>
<td>Slight Corrosion</td>
</tr>
<tr>
<td>Control</td>
<td>Corrosion</td>
<td>Corrosion</td>
<td>Corrosion</td>
<td>Corrosion</td>
</tr>
</tbody>
</table>
## S-14 Bio Antiscalant/Corrosion Inhibitor

### Results of Corrosion Tests

#### Pilot Cooling Tower Test Results

<table>
<thead>
<tr>
<th>Material</th>
<th>Presence of Scales</th>
<th>Corrosion Rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>On Steel Coupon</td>
<td>Carbon Steel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Galvanized Steel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Copper</td>
</tr>
<tr>
<td>Organophosphonate/ Polyacrylates/ Molybdate/ Triazole, 25 ppm</td>
<td>Not visible</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.056</td>
</tr>
<tr>
<td>S-14 Bio, 25 ppm</td>
<td>Not visible</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.026</td>
</tr>
<tr>
<td>Control</td>
<td>Visible</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>-----</td>
</tr>
</tbody>
</table>
S-14 Bio
Antiscalant/Corrosion Inhibitor

Evaluation of antiscaling properties
(NACE Standard TM-0374-2001)

- Conditions:
  - Brines, containing Calcium Sulfate and Calcium Carbonate
  - Concentration of the inhibitor: 10 ppm
  - Temperature 70-72°C
  - Time – 24 hours
# S-14 Bio

**Antiscalant/Corrosion Inhibitor**

**Antiscaling Properties**

## Results

<table>
<thead>
<tr>
<th>Materials</th>
<th>( \text{CaCO}_3, \text{ppm} )</th>
<th>% of inhibition*</th>
<th>( \text{CaSO}_4, \text{ppm} )</th>
<th>% of inhibition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organophosphonate</td>
<td>4050</td>
<td>95.5</td>
<td>3950</td>
<td>76.9</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>3100</td>
<td>16.7</td>
<td>4250</td>
<td>92.3</td>
</tr>
<tr>
<td>Polysaccharide based</td>
<td>3100</td>
<td>16.7</td>
<td>4200</td>
<td>89.7</td>
</tr>
<tr>
<td>Soy-based polymer (S-14 Bio)</td>
<td>4070</td>
<td>96.7</td>
<td>4250</td>
<td>92.3</td>
</tr>
<tr>
<td>Polyaspartic acid based</td>
<td>3000</td>
<td>6.6</td>
<td>4000</td>
<td>79.5</td>
</tr>
<tr>
<td>Control (w/o scale inhibitor)</td>
<td>2900</td>
<td>-</td>
<td>2450</td>
<td>-</td>
</tr>
<tr>
<td>Initial</td>
<td>4100</td>
<td>-</td>
<td>4400</td>
<td>-</td>
</tr>
</tbody>
</table>

*\% of scale inhibition = \((\text{Ca-Cb})/(\text{Cc-Cb})\)*100, where

- \(\text{Ca}\)-\(\text{Ca}^2+\) concentration in the treated sample after precipitation
- \(\text{Cb}\)-\(\text{Ca}^2+\) concentration in the blank after precipitation
- \(\text{Cc}\)-\(\text{Ca}^2+\) concentration in the blank before precipitation
## BIOBASED CONTENT

<table>
<thead>
<tr>
<th>Sample</th>
<th>C14 content, % modern carbon</th>
<th>Biobased content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive to Condensate (S-10 F)</td>
<td>88.5</td>
<td>84.3</td>
</tr>
<tr>
<td>Antiscalant/Corrosion Inhibitor (S-14 Bio)</td>
<td>95.6</td>
<td>91.5</td>
</tr>
</tbody>
</table>
Conclusion

- “Green” product S-10 F inhibits corrosion as well or better than its more toxic traditional counterparts used in boilers.
- “Green” S-14 Bio is a natural polymer-based antiscalant/corrosion inhibitor that is a very effective fully biodegradable multifunctional building block for water-treatment applications.
- The new “Green” products meet the legal requirements.
- Usage of “Green” products shows environmental awareness and concern.

Thank you!