Enhanced High Acid Corrosion Control with Innovative Chemical Additive

A Presentation by: Mr. James Ondyak

Authors: Dr. Mahesh Subramaniyam, Mr. James Ondyak, Mr. James Noland, Mr. P. N. Ramaswamy and Mr. Parag Shah.
<table>
<thead>
<tr>
<th>Present Affiliation</th>
<th>Dorf Ketal, Executive Vice President Marketing &amp; Business Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>Academic Qualifications</td>
<td>MS Chemical Engineering, Illinois Institute of Technology MBA Harvard Business School</td>
</tr>
<tr>
<td>Areas of Specialization</td>
<td>New Technology Introductions Business Development</td>
</tr>
</tbody>
</table>
| Achievements / Awards | Dorf Ketal Executive Board Member Previous Experience:  
  • Division President Nalco  
  • Corporate VP of Marketing for all Nalco  
  • Board Member of Nalco-Saudi  
  • General Manager European Business Unit  
  • District Manager of the Year  
  • District Representative of the Year |
Outline

• High TAN Opportunity Crudes
• Innovation Summary
• Risk of Fouling with Conventional Chemical Additives
• Key Technology Differentiator and Test Results
• Operational Benefits of “P-Efficient” HTCI
• Case Study
• Conclusion
Old Ways vs. New Ways

phone circa 1979

phone circa 2014
High TAN Opportunity Crudes

High TAN Crudes: Discounted Price: Higher Profit Margins

Naphthenic Acids = High Temp Corrosion = Corrosion $ Control

**CORROSION MITIGATION**

<table>
<thead>
<tr>
<th>Crude</th>
<th>Origin</th>
<th>API Gravity °API</th>
<th>Total Sulfur wt %</th>
<th>TAN mg KOH/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doba</td>
<td>Chad</td>
<td>21.1</td>
<td>0.12</td>
<td>5.18</td>
</tr>
<tr>
<td>Merey16</td>
<td>Venezuela</td>
<td>17.9</td>
<td>2.15</td>
<td>1.46</td>
</tr>
<tr>
<td>Dar</td>
<td>Sudan</td>
<td>24.5</td>
<td>0.11</td>
<td>4.1</td>
</tr>
<tr>
<td>Albacora</td>
<td>Brazil</td>
<td>19.4</td>
<td>0.55</td>
<td>2.37</td>
</tr>
</tbody>
</table>

**PRODUCTION ESTIMATES**

1.2 MM BPD in 2000 to 4.5 MM BPD in 2020
CONVENTIONAL PHOSPHATE ESTER MECHANISM

- Inefficient phosphorus delivery due to low “P-efficiency”
- Low “P-efficiency”: Potential fouling problem
- Innovative TANscient™ LP additive with improved “P-efficiency”
- Requires 50% to 80% less phosphorus for equivalent protection
- Superior TANscient™ LP additive: new benchmark for refinery HTCI
Innovation isn't just what we do. It's who we are.

A Responsible Care® Company

Risk of Fouling from Conventional HTCI

Low “P-Efficiency” = Degradation & Phosphorus Fouling

- Exchanger Fouling from Dislodged Scale
- Column Fouling from Residual Product
- Coking from Iron Pick Up due to Acidic Nature
- Catalyst Impairment and Fouling, Reduced Run Length
### Risk of Fouling from Conventional HTCI

<table>
<thead>
<tr>
<th>CONVENTIONAL PHOSPHATE ESTER CHEMISTRY</th>
<th>INNOVATIVE TANscient™ LP CHEMISTRY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traditional phosphate esters</td>
<td>Breakthrough additive</td>
</tr>
<tr>
<td>(mixed mono- &amp; di-alkyl esters) with 7-8% P</td>
<td>mainly tri-esters with ≤ 1.2% P</td>
</tr>
<tr>
<td>Decompose to phosphoric acid below 290 °C</td>
<td>Low corrosivity</td>
</tr>
<tr>
<td>Low “P-efficiency”</td>
<td>Enhanced “P-Efficiency”</td>
</tr>
<tr>
<td>Needs reactive sulfur to generate iron sulfide layer</td>
<td>Effective without reactive sulfur</td>
</tr>
<tr>
<td>Poor iron polyphosphate stability</td>
<td>Stable iron polyphosphate film</td>
</tr>
</tbody>
</table>
### Key Technology Differentiator

**TEST CONTAINS 1% OF EACH PRODUCT AT 290 °C**

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Phosphorus Content (%)</th>
<th>% P Converted to Precipitate</th>
<th>Photo</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Innovative TANscient LP</td>
<td>1.2</td>
<td>4.2</td>
<td><img src="image" alt="TANscient LP" /></td>
<td>No adherence to the wall</td>
</tr>
<tr>
<td>Conventional phosphate ester additive</td>
<td>7.5</td>
<td>97.3</td>
<td><img src="image" alt="Phosphate Ester" /></td>
<td>Blackish deposit adhered to the wall</td>
</tr>
<tr>
<td>Low phosphorus thio-phosphate ester additive</td>
<td>2</td>
<td>74.4</td>
<td><img src="image" alt="Thio-Phosphate Ester" /></td>
<td>Blackish deposit adhered to the wall</td>
</tr>
</tbody>
</table>

*Cleanliness of the flask indicates higher soluble phosphorus and better thermal stability*
Differences in P Required for Equal Corrosion Rates

**UNTREATED CORROSION RATE = 463 MPY, STATIC TEST**

Sample ................. D130 (Distilled Residue)
Nap Acid ............... Commercial
Tan ....................... 1.3 mg KOH/g
Temp..................... 290 °C (Passivation & Test)
Time (Passivation) .... 1 hr 30 min
Time (Test) ............. 4 hrs
Purging............... Nitrogen (110 ml/min)
Operational Benefits of “P-Efficient” TANscient™ LP HTCI

- Less risk of fouling and deposits
- More effective at all critical temperatures, down to 200 °C.
- No slipstream cooling required for chemical injection
- Less complex quill design required for low acidity HTCI
- Effective passivation at far lower dosages
- More flexibility to respond to TAN upsets
Operational Benefits of “P-Efficient” TANscient™ LP HTCI

**PROBE - Mass Loss**

- Atmospheric residue with TAN 0.7-1.6 mg KOH/g
- Corrosion-susceptible areas: Vacuum furnace inlet, furnace tubes and furnace outlet
- TANscient™ LP additive reduced the rate of mass loss
- Benefit: Flexibility in processing high TAN crude
Conclusions

• Conventional inhibitors have serious drawbacks and limitations
• Current HTCI users now have a much better alternative
• This new corrosion control chemistry is easy to substitute without risk
• Advantages are easily demonstrated in the lab and in the field
• No chemical supplier “black box”

We have a strong IP position and we can fully explain the chemistry under NDA.
Discounted High Acid Crudes are Increasingly Available

- Superior Corrosion Control
- Reduces Risk of Fouling
- Sustains Unit Reliability
- Flexibility in Crude Blend Slates
- Enhanced Profit Margins

CAPTURE THAT DISCOUNT WITH TANscient™ LP HTCI CHEMISTRY!