Improving Refinery Flexibility and Margins with High TAN Crudes

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Agenda

• The opportunity in high acid crudes
• Processing issues with HA crudes
• The right chemistry matters
Why process HAC crudes?

• **True opportunity crudes:**
  – Offered at lower cost/bbl
  – Generally increasing supply
  – Product yield balance

• **It’s about improving profitability:**
  – 100 mbpd crude unit
  – Change from a 0.7 to 1.0 TAN limit
  – At $5/bbl discount... **$50,000/day lower cost**

Why the discount?

• High nap. acids
• High sulfur
• Low API Gravity
• High solids
• High viscosity
• Tramp Amines
But...what’s the catch?

- There are processing challenges with HAC’s:
  - Tank Farm (emulsions, dewatering concerns)
  - Desalting Issues
  - Corrosion Potentials
  - Downstream Impacts
HAC properties impact desalting

- Slower oil/water resolution
- Increased rag formation
- Significant oil under-carry potential
- Poor removal efficiencies
- Can limit throughput

Can increase downstream fouling and corrosion potentials
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A Responsible Care® Company

The Right Chemistry Matters in Desalting

• Dorf Ketal proprietary, multi-functional resins for high pH, high solids
• Formulated for today’s opportunity crude challenges (2010 and 2012)
• Patent-pending, Reactive Adjunct technologies that accelerate emulsion resolution (by up to 80%)

Desalter Brine from a <18° High TAN Crude Blend

Existing Program

35ppm of a 30yr old EB

Dorf Ketal Program Performance

DK EB/RA Program

15ppm EB / 2ppm Reactive Adjunct

24 hours later
Differentiated Desalting Technologies

- **Desalter Adequacy Test** – Proprietary software used to assess desalting capability of a specific desalting asset against industry standards for a given crude slate and operating conditions.

- **Crude Compatibility Assessment** – Tool to study crude blending compatibility issues in tankage and during processing.

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**Crude Name**

<table>
<thead>
<tr>
<th>Crude Name</th>
<th>Density</th>
<th>Solubility</th>
<th>Insolubility</th>
<th>% of Crude in Blend</th>
<th>% of Crude in Blend</th>
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<tbody>
<tr>
<td>Arab Heavy</td>
<td>0.890</td>
<td>62.2</td>
<td>30.2</td>
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<td>Arabian Light</td>
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<td>18.8</td>
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<td>Arab XL</td>
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<td>15.2</td>
<td>5.0</td>
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<td>Eocene</td>
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<td>Iran Heavy</td>
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<tr>
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<td>Rhuff Condensate</td>
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<td>92.7</td>
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</table>

**Output from Compatibility Software**

- **Compatible**
- **Incompatible**
HAC Corrosion Attack in the CDU

Location Conditions:
- High Acidity
- High Temperature (200-400°C / 400-750°F)
- High Shear
- Low to high Sulfur

Sulfidic and naphthenic acid attack occur simultaneously in crude unit operations.
What about metallurgy?

- Can provide ultimate protection (with proper selection)
- High Capital Option
- Delayed ROI (only if running HAC’s)
- Every component in a circuit must be upgraded alloy
- Requires a shutdown to implement (2 or more years away)

A high temperature corrosion inhibitors can provide the needed corrosion protection, either short or long term.
What about HTCI’s?

- Provides protection where metallurgy is insufficient
- Reduces the porosity of the weak iron sulfide scale
- Reduces naphthenic acid access to the base metal
- Phosphorus is the critical chemical reactant that changes the iron sulfide scale
- Common delivery forms for crude unit applications:
  - Phosphate esters
  - Thiophosphate esters

All phosphate esters will work...if dosage is high enough.
What are partial phosphate esters?

How are partial phosphate esters made?

4 ROH + $\text{O} \equiv \text{P} = \text{O}$ → $\text{PO}_3\text{OH}$ + $\text{PO}_3\text{OH}$ + $\text{R} \text{O}_2\text{PO}_2\text{OH}$

Alcohol  Phosphorus Pentoxide  Mono-ester One “R” Group  Di-ester Two “R” Groups
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Issues with Conventional Partial Esters

- Highly acidic at process temperatures
- Thermally unstable, producing insoluble phosphorus (not beneficial)
- Requires much higher dosages to maintain protective scale
- Higher fouling potential / greater P to poison downstream catalysts

Partial ester comes to the FeS scale as mostly insoluble P

Insoluble P and iron loss to downstream units

Weak protective scale development
The Right Chemistry Matters in HAC Corrosion

**TANSCIENT™ HTCI Tri-esters**

- Patented technology (within the last 8 years)
- Fully engineered molecules for improved thermal stability
- Made by ethoxylating to full esterification (tri-esters)
- Improved oil solubility with no acidity potential

![Chemical Reaction](image)
Benefits of TANSCIENT™ HTCI Technology

- Delivers more soluble phosphorus to fortify the iron sulfide scale
- Builds a more tenacious iron polyphosphate scale
- Requires much lower P dosage to maintain protection
- As much as $1/7$ the amount of phosphorus injected vs partial ester products

TANSCIENT comes to the FeS scale as mostly soluble P

Minimal P and iron loss to downstream units

Robust protective scale development
# TANSCIENT™ in Lab Testing

<table>
<thead>
<tr>
<th>Test</th>
<th>Measure</th>
<th>TANSCIENT™</th>
<th>Phosphate Ester</th>
<th>Thiophosphate Ester</th>
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<tr>
<td><strong>Thermal Stability</strong></td>
<td><strong>Soluble P Remaining @ 2hr</strong></td>
<td>90%</td>
<td>23%</td>
<td>40%</td>
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<td>@ 550°F, 1.0 TAN</td>
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<tr>
<td><strong>Static Test @ 550°F</strong></td>
<td><strong>Relative P for equal mpy</strong></td>
<td>1.0</td>
<td>3.9</td>
<td>1.4</td>
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<tr>
<td>@ 11 TAN</td>
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<tr>
<td><strong>Dynamic Test @ 650°F</strong></td>
<td><strong>mpy @ Relative P</strong></td>
<td>4 @ 1</td>
<td>13 @ 6.3</td>
<td>14.5 @ 1.7</td>
</tr>
<tr>
<td>@ 1.6 TAN, 2K rpm</td>
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<td></td>
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</tr>
</tbody>
</table>
TANSCIENT™ in Field Applications

• Multiple International Applications and ongoing USA trials
• Results:
  – Comparable performance to conventional phosphate and thiophosphate esters
  – Dosages as high as \( \frac{1}{6} \)th the \( \text{P} \) of other programs
  – Reduced P and Fe loading to downstream catalytic units
  – No fouling issues
TANSCIENT™ HTCI Implementation Methodology

1) Gather Information
- Crude Assays
- Corrosion Inspection Date
- P&IDs, PFDs, ISOs, etc...
- Interviews

2) Define Current State / Limitations
- Analyze Metallurgy & System Data
- Understand current corrosion activity
- Identify current and desired crude blends
- Calculate TAN Distributions per different crude blend scenarios
- Perform Risk Analysis

3) Physical Walkthrough
- All lines of concern
- Identify sampling, & injection locations
- Develop short and long term monitoring plans
- Understand “Intangibles”

4) Develop Test Plan
- Model & Calculate to constraints
- Identify limits and prioritize streams with and w/o chemistry
- Define step approach and chemistry

5) Solidify Crude State & Timing
- Gain agreement with site on plan
- Work with Econ & Planning on crude timing and step wise addition of crude(s)
- Order equipment and install

6) Execute & Monitor
- Baseline and step testing
- Data driven decisions on increasing TAN
- Initiate injections and iterative monitoring
- Quantify data and hold gains

Keys to Success
- Integrated work team with representation from all key stakeholder disciplines
- Task team leadership and formation that can remove hurdles to allow project to develop
What is the HAC margin benefit?

• **100 mbpd Charge:**
  - TAN Δ +0.3 (0.7 to 1.0)
  - Typical crude unit treat locations & dosages
  - $5/bbl cost benefit

• **Δ Chemical Costs:**
  - Desalting - +$0.04/bbl
  - HTCI - +$0.11/bbl

• **Overall +$0.15/ HAC bbl**

Great ROE - $0.15 yields $5
High Acid Crude Processing Summary

- HAC’s can provide significant incremental margin improvements.
- But there are processing issues to consider and manage:
  - Desalting impacts
  - High Temperature Corrosion potential
  - Up & downstream impacts.
- The right chemical technologies absolutely matter!