Crude Oil Compatibility

Irwin (Irv) Wiehe
Soluble Solutions

COQG Meeting
Houston, Texas
October 2, 2003

Irvin@SolubleSolutions.com
www.SolubleSolutions.com
Including Fouling Tendency in Crude Oil Purchase Decisions

Irwin (Irv) Wiehe
Soluble Solutions

MUG 36
Haverly Technical Conference

Newport, Rhode Island
September 28 to October 1, 2003

Irv@SolubleSolutions.com
www.SolubleSolutions.com
<table>
<thead>
<tr>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble Solutions</td>
</tr>
<tr>
<td>Incentives to Minimize Fouling</td>
</tr>
<tr>
<td>Causes of Asphaltene Fouling</td>
</tr>
<tr>
<td>Solution: Oil Compatibility Model &amp; Tests</td>
</tr>
<tr>
<td>Services Provided by Soluble Solutions</td>
</tr>
<tr>
<td>How to Apply Results</td>
</tr>
</tbody>
</table>
22 Years at Exxon Corporate Research and 5 Years at Soluble Solutions
Fouling Common in Crude Preheat Train

- Stable Emulsions
- Atmospheric Distillation Unit
- Coking
- Heat Exchanger Fouling

Crude Feed

Desalter 250-300°F

Furnace

Stripping Steam

Stable Emulsions

Coking

To Gas Plant

Water Gasoline

5 psig 110°F

Naphtha

Distillate

Gas Oil

To Vacuum Tower
Large Incentives for Minimizing Fouling of Crude Preheat Train

- Decreased Maintenance Costs
- Reduced Energy Costs
- Increased Capacity (Days on Stream)
- Confidence to Purchase Opportunity Crudes

First Three: 3 Billion $ / Year for US Refining (C. B. Panchal of Argonne National Labs)

- Needs to be Estimated for Each Refinery
Causes of Crude Preheat Train Fouling

- Iron Sulfide / Iron Oxide: Corrosion
- Sea Salts & Clays: Desalter Operation (Emulsions)
- Asphaltenes: Crude Oil Selection / Blending Order
  - Insoluble: Incompatibility or Self-Incompatibility
  - Soluble: Nearly Incompatible: Adsorption (Slower)
Physical Model of Petroleum

Asphaltenes Held in Oil in Delicate Balance

- Balance Upset by Adding Saturates
- Balance Upset by Reducing Aromatics and/or Resins
- Mixing Oils Can Upset Balance and Precipitate Asphaltenes: Incompatibility

A = Asphaltenes (Solute)
R = Resins (Dispersant)
a = Aromatics (Solvent)
s = Saturates (Nonsolvent)
Avoiding Asphaltene Sediments is not Sufficient

- **Self-Incompatible**
  - Deposit

- **Incompatible on Blending**
  - Mix
  - Deposit

- **Nearly Incompatible**
  - Mix
  - Adsorb

- **Thermal Conversion at Heated Wall**
**Oil Compatibility Model**

- **Measure Solvency and Insolubility of Oils**
  - Toluene: Model Solvent
  - n-Heptane: Model Nonsolvent

- **Predict Compatibility and Incompatibility**
  - Proportions of Blend
  - Order of Blending
  - Self-Incompatible

- **Nearly Incompatible Oils**
  - Fouling by Adsorption
  - Stable Oil-Water Emulsions
Oil Compatibility Model

**Insolubility Number** $\equiv I_N$

Measures Degree of Asphaltene Insolubility

**Solubility Blending Number** $\equiv S_{BN}$

Measures Ability of Oil to Dissolve Asphaltenes

**Criterion of Compatibility:** $S_{BN} > I_N$

Measurement of $I_N$ and $S_{BN}$

- Blend Oil with Test Liquid (Toluene and n-Heptane)
- Determine Flocculation Points for Oil / Test Liquid Ratios

Test Liquid + Oil = Mix Oil and Test Liquid

See if Insoluble Chain Agglomerates of Asphaltenes Under Optical Microscope
Data Verifies Linear Relation
Compatibility Numbers Calculated from Intercepts

Least Square Line: \( y = 29.5 - 0.200 \times \); \( R = 0.998 \)

\( I_N = 29.5 \)

\( S_{BN} = (1 + 100/HD) I_N \)

\( S_{BN} = (1 + 100/147) 29.5 = 50 \)

Arab Light Crude

% Toluene in Test Liquid
100 Volume Oil / Volume Test Liquid
Oil Compatibility Tests

- **Heptane Dilution Test**
  Determine maximum ml. of n-heptane that can be blended with 5 ml. of oil without precipitating asphaltenes.

- **Toluene Equivalence Test**
  Blend in separate bottles 10 ml. of test liquid and 2 grams of oil. By varying the vol. % toluene mixed with n-heptane in the test liquid, determine the minimum % toluene required to keep the asphaltenes soluble.

- **Other Tests for Oils Without Asphaltenes**
Mixtures of Oils: Compatibility Criterion*

Solubility Blending Number for a Mixture of n Oils

\[ S_{BN_{mix}} = \frac{V_1 S_{BN_1} + V_2 S_{BN_2} + V_3 S_{BN_3} + \ldots + V_n S_{BN_n}}{V_1 + V_2 + V_3 + \ldots + V_n} \]

Compatibility Criterion

\[ S_{BN_{mix}} > I_{N_{max}} = \text{Maximum } I_N \text{ in Mixture} \]

Order of Mixing is Important

Slow Kinetics for Redissolving Requires to Mix in Order that Never Precipitate Asphaltenes (Add Low \( S_{BN} \) to High \( S_{BN} \))

* Process for Blending Potentially Incompatible Oils
US Patent 5,871,634 (1999), Assigned to Exxon
Incompatible Blends: Volume Average $S_{BN} < I_N$ of Any Oil

Blends of Souedie and Forties

Forties: $S_{BN} = 27$, $I_N = 11$
Souedie: $S_{BN} = 63$, $I_N = 39$

$S_{BN} < I_N$ for Souedie

$I_N = 39$ for Souedie
Self-Incompatible Crude Oil
Soluble in 1 Volume of Toluene but not n-Heptane

Yme Crude Oil*

$\text{I}_N = S_{BN} = 13 = \text{TE}$

*Thanks to Statoil for permission to present data

More than 10 Self-Incompatible Crudes (12 < $\text{I}_N$ < 58)
More Than 100 Incompatible Pairs Of Crudes

Prediction Is Conservative

- Incompatible Pairs of Crudes
- Compatible Pairs of Crudes

Higher Insolubility Number

Lower Solubility Blending Number
Alcor Hot Liquid Process Simulator*

* Done by G. Dickakian of F.A.C.T.
Nearly Incompatible Oils are Moderately Fouling

1999 US Patent 5,997,723 by Wiehe & Kennedy, Assigned to Exxon
Causes of Stable Water in Oil Emulsions in Desalters (Rag Layer)

- Iron Sulfide: Additives to Make Water Wet
- Clays: Additives to Make Water Wet
- Naphthenic Acids: Limit TAN of Crude Blends
- Asphaltenes: Crude Oil Selection / Blending Order

- Insoluble: Incompatibility or Self-Incompatibility
- Soluble: Nearly Incompatible - Most Stable
Emulsions Most Stable by Nearly Incompatible Asphaltenes

Asphaltene – Toluene - Heptane - Water Mixtures

Stability of Emulsion

% Toluene in Heptane – Toluene (Solubility Blending Number)

% Water Resolved

Water Droplets Stabilized by Rigid Interface of Asphaltenes

Mclean and Kilpatrick (1997)
Services Offered by Soluble Solutions

- Train Your Lab to Run Oil Compatibility Tests
- Run Tests at DNV Petroleum Services, NJ ($500 per Crude Oil)
- Coordinate Crude Compatibility Exchange
  - Companies Pool Results and Cost of Running Tests
  - Best Results at Lowest Price
- Advise on Crude Purchasing, Scheduling, Blending Decisions with Respect to Fouling
How to Apply Without Violating Patents

- Do Not Purchase Self-Incompatible Crudes
- Do Not Blend Crude Oils that Are Predicted to be Incompatible in Any Proportion
- Do Not Blend Crude Oils that Are Predicted to be Nearly Incompatible in Any Proportion
- Soluble Solutions Available for Consulting