MIST Technology for Delayed Cokers

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A Subsidiary of

C³ International
A NanoTechnology Licensing Company
Who is Coker Coaters?

- Utilizes C3’s “MIST” ceramic coatings for petrochemical applications such as delayed coking, ethylene cracking, and other processes where inorganic materials are attacked by the harsh nature of their environments.

- MIST technology is already used commercially & proven in harsh environments outside of the petrochemical industry.
What can **MIST** Technology do for Delayed Cokers?

- Stabilize Coke Formation
- Eliminate Metal Sulfidation
- Flow Assurance
- Lower Heater Duty
- Reduction in Greenhouse Gases
- Extended Run Lengths
- Extended Equipment Life
What is *MIST* Technology?

- Ultra-thin, ceramic film anchored to an inorganic surface at the molecular level—a Surface Modification and a Coating.
- Film remains anchored despite “hostile” environments (sulfur, acid, heat, hydrocarbons, liquid metal, etc.).
- Film is versatile: Harnesses properties of 79 elements to impart customized properties.
What is **MIST** Technology?

- Winner of 2006 R&D 100 Award
- Winner of 2007 Micro/Nano 25 Award
How do we know *MIST* is thin & anchored at the molecular level?

**TEM of MIST**

TEM Image by Dr. Jane Howe, Oak Ridge National Laboratory

**SAM of MIST**

SAM Profile by Dr. Harry Meyer, Oak Ridge National Laboratory

Sputter rate~20nm/min

-C-
-Zr-
-Fe-
How do we know *MIST* is stable and will not spall off?

- **Laboratory Data**
  - Scanning Auger Microscopy, Oak Ridge National Laboratory
  - Wallace Dunker Test, Case Western Reserve
  - Thermogravimetric Analysis, Fouling and Coking Technology
  - Physical Nature of Oxides Present
  - Internal Testing: Aqua Regia and High Temp Salt Spray

- **Commercial Application Data**
  - Aluminum Die Casting
  - Hot Rolled Steel
Thermogravimetric Analysis

- Fouling and Coking Technology determined the thermal stability of the MIST coating in air and nitrogen from 68°F to 1832°F
  - Found coating is thermally stable at 1832°F in both air and nitrogen
  - Thermal properties were similar to diamonds
Aqua Regia Test

- Sample exposed to specific volume of 3 parts HCl to 1 part HNO3 for 1 hour

*MIST Die Casting Coating*  
*MIST Coker Coating*
High Temperature Salt Spray Test

- Samples heated to 1652°F in air, then sprayed with 10% salt water solution for 1 hour. Test recommended by Alberta Research Council.

*MIST* Die Casting Coating

*MIST* Coker Coating
Aluminum Die Casting

- Liquid Aluminum (1292°F) is poured into the shot sleeve
- A plunger then ejects the liquid Aluminum into a die mold cavity
- 1 cycle takes <3 minutes. During this period the shot sleeve is exposed to temperatures from 600°F to 1292°F
- With MIST coating total cycles went from 19,000 to 98,309 (2 months to 9 months)*

*Sleeve was pulled because production run was finished, not because MIST failed
Hot Rolled Steel Application

- Hot Steel moving at 1000 feet/minute rolls down conveyor belts as its thickness is being decreased
- Guide Rollers (seen at right) keep this steel on track on the conveyor and experience significant wear scarring
- Untreated rollers last 1 week while MIST treated rollers last 10 weeks and still have 5 times less mass loss than the untreated roller
- This is a 50x improvement in wear resistance*

*As determined by Dr. Peter Blau, Tribologist, Oak Ridge National Laboratory, using a Coordinate Measuring Machine to analyze depth profile of scars
How is MIST Applied?

- A patented precursor liquid is mixed with the salts of the desired metals to form a solution.
- The solution is then applied to the inorganic surface to be treated. The solution is non-toxic and can be applied by brushing, spraying, dipping, spinning, pigging, etc.
- Once solution is applied, heat material to ~830°F. Heating rate does not affect the coating. Can be done instantaneous with pulsed plasma method or slowly in a conventional furnace.
- Once temperature is reached, the MIST coating and surface modification is formed.
Bench Testing conducted by Dr. Ghaz Dickakian of Fouling and Coking Technology, Inc. (F.A.C.T.)

- Dr. Dickakian worked for Exxon for 35 years in carbon technology & fouling and coking mitigation
- Testing equipment acquired from Exxon
- Expert in South American Heavy and Sour Feeds
- Extensive Library of Testing Data for Comparative Results
- Please refer to Paper for details
F.A.C.T.'s Thermal Fouling Test Setup
First, F.A.C.T. determines optimum fouling temperature of a given crude on an uncoated heat exchanger (heat exchanger simulates delayed coker furnace conditions).

<table>
<thead>
<tr>
<th>Test Operating Conditions</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchanger metal temp. (°F)</td>
<td>800</td>
<td>900</td>
<td>1010</td>
</tr>
<tr>
<td>Unit pressure (psig)</td>
<td>950</td>
<td>950</td>
<td>950</td>
</tr>
<tr>
<td>Unit atmosphere</td>
<td>Nitrogen</td>
<td>Nitrogen</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Test time (minutes)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Thermal Fouling</td>
<td>18</td>
<td>28</td>
<td>90</td>
</tr>
</tbody>
</table>

Exchanger metal temperature of 1010°F was selected for testing the coated exchanger test tubes as this temperature is within the coker furnace metal operation.
Second, F.A.C.T. tests coated heat exchangers with same parameters for optimum fouling

<table>
<thead>
<tr>
<th>Exchanger Heater</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchanger temp (°F)</td>
<td>1010</td>
<td>1010</td>
<td>1010</td>
</tr>
<tr>
<td>Unit pressure (psig)</td>
<td>950</td>
<td>950</td>
<td>950</td>
</tr>
<tr>
<td>Unit Atmosphere</td>
<td>Nitrogen</td>
<td>Nitrogen</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Oil flow rate (cc/min)</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Test time (minutes)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>Thermal Fouling Measurements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 minutes</td>
<td>5</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>30 minutes</td>
<td>22</td>
<td>21</td>
<td>30</td>
</tr>
<tr>
<td>45 minutes</td>
<td>33</td>
<td>32</td>
<td>36</td>
</tr>
<tr>
<td>60 minutes</td>
<td>41</td>
<td>45</td>
<td>36</td>
</tr>
<tr>
<td>75 minutes</td>
<td>45</td>
<td>45</td>
<td>36</td>
</tr>
<tr>
<td>90 minutes</td>
<td>47</td>
<td>45</td>
<td>36</td>
</tr>
<tr>
<td><strong>Effectiveness (%)</strong></td>
<td>52.0</td>
<td>53.0</td>
<td>62.0</td>
</tr>
</tbody>
</table>
Graph of data from previous slide on fouling results

Time (minutes)

Fouling (°T, °F)

C/S 1018  Coated 1  Coated 2  Coated 3
F.A.C.T. Conclusions

- *MIST* Stabilizes Temperature Increase
- *MIST* Retards Coke Formation
- *MIST* Prevents Metal Sulfidation
- *MIST* is Stable at Delayed Coker Furnace Operating Temperatures
- *MIST* does not Spall off and Contaminate the Product
- Calculated Effectiveness of 52% - 62% are exceptional and never been seen before using the Thermal Fouling Method
Questions (so far)?
MIST Benefits for Delayed Cokers

- Stabilizes Coke Formation
- Eliminates Metal Sulfidation
- Flow Assurance
- Lower Heater Duty
- Reduction in Greenhouse gases
- Extended Run Lengths
- Extended Equipment Life
Stabilizes Coke Formation
Eliminates Metal Sulfidation
Flow Assurance

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Lower Heater Duty
Reduction in Greenhouse gases

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Extended Run Lengths

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Extended Equipment Life

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Questions (so far)?
What is the Procedure for Coating a Delayed Coker Furnace?
Application Procedure for Delayed Coker

1. DDT does mechanical cleaning of the tubes
2. DDT finishes this with their standard polishing procedure
3. DDT uses Fullkote techniques to ensure the tube ID is dry
4. DDT uses compressed Nitrogen to propel a pig train carrying the *MIST* solution through the furnace, wetting the tube ID with the liquid
5. Equipment is removed, and heaters are fired so that tube ID reaches a temperature greater than 830°F
6. *MIST* Coating and Surface Modification is now in place
7. In field tests, steps 4 and 5 are repeated 6-8 times to ensure full coverage
MIST Solution Application with Pig Train

- Pig Train Direction
- Furnace Tube
- N2
- Solution Reservoir
- Coating
Requirements of Refinery

- Allow DDT’s trucks and personnel access to the refinery with DDT’s standard requirements for cleaning projects
- Provide Compressed Nitrogen
- Provide the personnel and energy to follow refinery procedure for heating up furnace tube ID to greater than 830°F and then cooling the tubes down
- In addition to the cleaning procedure, the extra time needed for coating is estimated at 4 days
Common Questions about MIST

- Will MIST spall off?
  - MIST technology is used commercially in harsh environments around products that cannot be contaminated and has proven it is stable and does not spall off.

- Will MIST adversely affect the metal integrity or structure?
  - The thinness of MIST ensures that it will not adversely affect product flow or metal structure.

- Will MIST affect the product coming into contact with it?
  - The inert nature of the oxides ensure that it will not adversely affect the product coming into contact with it.

- What are the hazards associated with MIST application?
  - MIST is applied by the Trained Professionals at DDT who are familiar with Delayed Cokers.
  - Project oversight will be provided by Evan Hyde of Becht Engineering, a safety and process expert.
  - Coating by product is a small amount of C02.
Summary: *MIST* is a **Low Risk/High Reward** Proposition, providing:

- Longer Runs
- Flow Assurance
- Lower Heater Duty
- Lower Emissions
- Extended Equipment Life
- One Less Variable for the Refinery to Worry About
Questions?
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