TUBACOCAT

ANTI-COKING SOLUTION FOR FIRED HEATERS
IN DELAYED COKER, VISBREAKER & VACUUM DISTILLATION UNITS

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Sanjay Lodha
Global Business Director
• Tubacex Group
• Tubacoat concept
• Product characterization
• Coke deposition in fired heater tubes
• Chemical Inertness and Coking Resistance Study
• Field applications/Case Studies- Fired Heaters and others
• Anti Corrosion Commercial Application
• Conclusion
Global Presence

- Sales: 700 million euros
- 2600 professionals
- Full Range of Seamless Stainless tubular Products
- 15 mills in Spain, USA, Austria, Italy, India, Thailand, Norway, UAE & Saudi
- Commercial presence in over 30 countries
- A Service Solutions Company, providing services and master distribution

A worldwide leading supplier of Seamless Stainless and High Nickel Alloy Tubes
Tubacoat – Key Advantages

Introduction

✓ Technology-based company
✓ 100% subsidiary of TUBACEX
✓ Engineering, industrial development and commercialization of tubular solutions based on advanced innovative coatings

Value-added products with...

• Outstanding corrosion resistance in different media and thermal conditions
• High abrasion resistance (64HRC hardness)
• Anti-adherent and anti-fouling properties
• Chemical inertness

Specifically developed to...

• Provide long term reliable & competitive solutions to industrial applications under severe working conditions and extreme environments
Tubacoat concept

Potential applications

- Furnaces
- Heat exchangers
- Condensers
- Boilers
- Reactors
Product Characterization

Key Properties

**MORPHOLOGICAL**
- **Roughness**
  Ra and Rz decrease \( \approx 97\% \) minimizing particle adhesion

**MECHANICAL**
- **Hardness & Elasticity**
  Coating is harder than substrate but less elastic
- **Abrasion resistance**
  \( \approx 94\% \) decrease in mass loss

**CHEMICAL**
- **High corrosion resistance**
  compared to base material under different conditions and standard tests
- **Chemical inertness**
  of the coated tube surface avoids reactions

**THERMAL**
- **Thermal resistance**
  Good performance under thermal cycling. No delamination & No cracks
- **Thermal conductivity**
  \( f(T) \) Average (reference) 6 W/mK
Product Characterization

Morphological

Continuous coating layer

**Thickness control** based on suspension parameters & rheological properties

![Coating Image](image)

Typical coating thickness range: **100-150 μm**
Product Characterization

Anti-adherence

**Roughness.** Ra and Rz decrease ≈ 97% minimizing particle adhesion

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ceramic coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra ≈ 1.5 µm and Rz ≈ 7.8 µm</td>
<td>Ra &lt; 0.04 µm and Rz ≈ 0.2 µm</td>
</tr>
</tbody>
</table>
Product Characterization

Mechanical

**Abrasion resistance**

≈ 94% decrease in mass loss

Mass loss for 10,000 cycles

\[ \Delta w_n = < w_0 > - < w_n > \]

- **Substrate**
  \[ \Delta w_{10000} = 94.783 - 94.725 \]
  \[ \Delta w_{10000} = 58 \text{ mg} \]

- **Ceramic coating (T153)**
  \[ \Delta w_{10000} = 119.377 - 119.373 \]
  \[ \Delta w_{10000} = 4 \text{ mg} \]
Hardness and elasticity properties can be improved by modifying structure and composition of ceramic compounds and process conditions.
Product Characterization

Thermal Resistance

Good performance under **thermal cycling**
No delamination – No crack

<table>
<thead>
<tr>
<th>n Cycles</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water cooled</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Different working temperature and thermal cycling resistance can be achieved by modifying structure and composition of ceramic compounds.

Thermal cycling (450° C / 10 min) + Rapid water cooling (15° C)

Thermal cycling (30 min) + Rapid water cooling (20° C)
Product Characterization

Characteristics

Tubacoat glass-finished layer will protect the inner or outer surface of the tubes.

- **Deposition Rate** will decrease due to its chemical inertness and smoothness of surface
- **Removal Rate** will increase due to its anti-adherence properties
- **Heat Transfer loss** will reduce due to lower fouling layer
- **Fluid Flow** will maintain/increase the stream
Product Characterization

Rate of fouling

High fouling avoidance & low adherence of coated tube compared to bare material

Results after 7 months in test rig @ crude oil at 240°C

Significantly higher fouling avoidance of coated sample, and the eventual deposition is not adhered to surface, being easily removable with pressurized water
Product Characterization

Chemical

High corrosion resistance compared to base material

**Acid corrosion test**
- **Conditions:**
  - Solution: 10% HCl at 22°C
  - Visual inspection

**Acid corrosion at boiling temperature**
- **Conditions:**
  - Solution: boiling H2SO4 (30%)
  - 18 h (UNE-EN ISO 28706-2)

<table>
<thead>
<tr>
<th>Acid Corrosion Test</th>
<th>Acid corrosion at boiling T</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
<td>Liquid Contact</td>
</tr>
<tr>
<td>1000 h</td>
<td>Vapour Contact</td>
</tr>
<tr>
<td>2000 h</td>
<td></td>
</tr>
</tbody>
</table>
The coating is vitrified above 800ºC/1470ºF which provides chemical bonding and “glass” properties, enhancing adherence between coating and substrate and increasing resistance to fouling, corrosion and abrasion at high temperature compared to in-situ coatings.
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Coke deposition in fired heater tubes

Delayed coker, Visbreaker & VDU fired heaters

DCU / VB / VDU

Example fired heater cell

Radiant section

Coke deposition

High value products

Low value feedstock
Coke deposition in fired heater tubes

Coke deposition problems

As coke layer grows....

- ↓ Heat transfer & ↑ Tube skin temp
- ↓ Effective area & ↑ Pressure drop

NEED FOR FREQUENT DECOCKING

Efficiency loss

Production loss

Higher OPEX
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Anti-coking Solution For Fired Heaters

When the coating is applied to the inner surface of heater tubes:

- Minimizes coke formation (chemical inertness)
- Minimizes coke deposition (anti-fouling)

Fired heater with coating applied will obtain:

- Longer run lengths
- Lower fuel consumption
- Increased safety and reliability
Coking Resistance Study

- DME cracks towards the equimolecular CO, H₂ and CH₄ (Eq. (1) depends on T)
- Parallel reactions of the gaseous products occur (Eqs. 2-4) depending on T and on the characteristics of the contact surface (active sites on the surface)

\[
\text{DME cracking: } \text{CH}_3\text{OCH}_3 \xrightarrow[A]{4} \text{CH}_4 + \text{CO} + \text{H}_2
\]

Boudouard reaction: \[ 2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C} \downarrow \]

Methane decomposition: \[ \text{CH}_4 \rightleftharpoons \text{H}_2 + \text{C} \downarrow \]

Reverse-Water Gas Shift: \[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \]
Chemical Inertness and Coking Resistance Study

Chemical inertia and reproducibility

- Temperature = 300-700°C/572-1290°F
- Residence time = 60s
- Time on stream: 80 min

### Degradation Temperatures

<table>
<thead>
<tr>
<th>Cycle</th>
<th>NON COATED</th>
<th>COATED</th>
</tr>
</thead>
<tbody>
<tr>
<td>T10 (ºC)</td>
<td>587 465</td>
<td>574 571</td>
</tr>
<tr>
<td>T50 (ºC)</td>
<td>641 518</td>
<td>631 632</td>
</tr>
<tr>
<td>T90 (ºC)</td>
<td>685 565</td>
<td>680 682</td>
</tr>
</tbody>
</table>

Without coating

With coating

- **COATED TUBES ARE CHEMICALLY INERT PREVENTING COKE FORMING REACTIONS**
Study of carbon formation

Calculation of carbon formed

$\text{(DME)}_{\text{in}} - (\text{DME} + \text{CO} + \text{CO}_2 + \text{CH}_4)_{\text{out}}$

Without coating

With coating

DME Conversion (%)
Temperature (ºC)
Cycle 1
Cycle 2

C$_{\text{formed}}$ (g)
Time on stream (min)
Cycle 1
Cycle 2

Study of carbon formation

Chemical Inertness and Coking Resistance Study
Combustion conditions:

- Temperature = 300-700°C/572-1290°F
- Residence time = 6 s
- Time on stream (700°C/1290°F): CO₂ < 0.1%

Carbon deposited

Integration of (CO+CO₂) curves

Without coating

With coating
Coke formation and coke deposition

Conclusions

• **Chemical inertness** of coated tube surface **avoids coking reactions** occurring in the active sites of non-coated tubes.

• **Carbon formed** is 10 times lower in coated tube vs non-coated tube.

• **Carbon deposited** is 100 times lower in coated tube vs non-coated tube.
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PROBLEM DESCRIPTION

Coke deposition inside the tubes causing:

- **Fired heaters** frequent shutdown for pigging → **Huge loss of production cost**
- **Preheat exchangers** constantly taken out of service due to coke accumulation → **Tube deformation related to hot spots**
- Poor **Heat transfer efficiency** due to coke layer → **High fuel consumption in the furnace**

TUBACOAT TRIAL

ID coated tubes, bends and flanges installed at the furnace outlet line to prove anti-fouling properties.

Dimensions: OD 4”, Sch. 80 - 317L SS

450 ºC/842 ºF, 10 bar
TRIAL RESULTS (after 9 months)

Coke deposition inside the tubes causing:

• **Very thin coke layer** - not detected by Radiographic test - 75% reduction in coke deposition.

• **Coke was much easier to remove** - 3 times lower water pressure than before was enough to remove all the coke.

• **Decoking services** - may use softer pigs and cleaning will be less frequent

CONCLUSIONS

• **Run lengths without decoking/online spalling** can be increased between 3 and 4 times

• **Savings** by Customer 1.5 Million USD per year
  - 1.1 M$ higher throughput (reduced shutdown time 7days/yr)
  - 0.15 M$ furnace online spalling/pigging,
  - 0.15 M$ fuel consumption,
  - 0.10 M$ Heat Exchanger cleaning
• Refinery operates 1 Delayed Coker, with normal capacity 124,000 barrel/day.
• Delayed Coker has 3 furnaces. Each furnace 6 passes. Each pass 30 radiant tubes
• Heater tube material: P9
Anti-coking solution – Case Study – Asia Refinery #1

Decoking Problem

- Frequent decoking is required due to coke layer build up leading to:
  - High pressure drop
  - Increase in tube metal skin temperature

- Each furnace requires pigging every 3 months and online spalling every 30-45 days in 2 passes/furnace

- During pigging, one full furnace is out of service for 3-4 days → unit running at 70% capacity. During Online Spalling, reduced capacity to 93% for one day/pass.

Every time one furnace is taken out of service for pigging, the cost due to reduced throughput is approximately 3.6 MM USD/furnace

Every time online spalling is performed in 2 passes of 1 furnace, the cost due to reduced throughput is approximately 125 KUSD/furnace
Cost: Tube cost (year 1) + cost due to reduced throughput during decoking + cost due to higher fuel consumption

By extending Run Length without decoking by 3 times, estimated incremental benefit of 10 million USD/year.
Coating Integrity during spalling/pigging

Anti-coking solution – Coating during spalling/pigging

Online spalling:

➢ Coating designed to withstand online spalling (high temperature and thermal shock).

Mechanical pigging:

➢ Pigs of 64 Rockwell C (RHC) can be used without damage to coating.
Problem Description

- Heater tube material: 9 Cr 1 Mo
- Currently, their heaters require online spalling every 50 days when wall temperature is 630°C/1166°F → 7 spalls per year
- During spalling operation, 1 of 6 passes needs to be out of service, so overall throughput to the unit is reduced to 85%.
- Spalling time takes approximately 1 day per pass → 6 days per spall

Conclusions

- Due to coke deposition, every year throughput is reduced to 85% for 42 days.
- Estimated potential savings by End user around 3 million USD per year based on large size of their DCU.
Problem description

- Heater tube material: 347H
- Heater requires online spalling every 2-3 months and also mechanical pigging once per year → 4 spalls per year and 1 mechanical pigging
- During spalling, one pass needs to be out of service, so overall throughput to the unit is reduced to 75%. Spalling time takes approximately 1 day per pass → 4 days per spall.
- Pigging requires full unit shutdown for 6 days

Conclusion

→ Due to coke deposition, every year the unit is shutdown for 6 days and throughput is reduced to 75% for 16 days
→ Estimated potential savings by End user around 2.5 million USD per year
Vacuum Distillation Furnace

Problem Description

Furnace outlet line with severe coke fouling causing:

- Outlet line replacement (8”, 10” and 12” OD Tubes) every year
- Frequent decoking operations by mechanical pigging
- Traces of Polythionic acid stress corrosion cracking

Tubacoat Solution

Tubacoat inner coated tubes, bends and reducers installed at the furnace outlet line

Base material: 317L SS @ Dimensions: OD 8” and 10” OD Lines

➢ ROI expected in 1.5 Years
Hydrocracker (RHC)

**PROBLEM DESCRIPTION**

- Each of their 8 Resid Hydrocracker reactors has more than 800 risers that are crucial for proper feed distribution in the reactor.

- Reactors operate at more than 400°C/752°F and more than 130 bar.

- Severe fouling occurs at the bottom section of all Resid Hydrocracker Risers.

- This leads to maldistribution of process stream and reduced conversion rate.

**CONCLUSIONS**

- With coating, fouling will be minimized leading to improved conversion of resid feed to clean fuels.

- High economic benefits under evaluation.
Field references

Vacuum Vistillation Unit (Europe)

*Tubes installed in VDU furnace*

**Tubacoat Solution**

Tubacoat *inner coated* tubes

Base material: 317 SS @ Dimensions: OD 5”, Sch. 40

Trial *in progress*
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Coke Calciner

- **Working Conditions**
  - Oil fumes rich in vanadates at 850°C
  - Metal surface 570°C
  - Low pressure (welded tube)

**Substrate Material**
TP310 (bare)

- Chemical corrosion
- Efficiency loss
Anti-Corrosion solution – Case Study – North America Refinery

Coke calciner

- 9 TP310 (OD63.5; WT2.41) outer coated prototypes were placed in the upper row (the hottest) of the calciner recuperator in May 2015
- Only the 9 coated tubes were remaining in the area, even suffering overheating during last weeks of operation prior to planned plant shutdown
- The rest of tubes were broken and blinded

(Image @ 10 months working)
Coke calciner

≈ 800 tubes (TP310 grade, OD63.5/WT2.41, outer coating), delivered to customer in Jan’2017 and installed in coke calciner in April 2017.

**Status:** facility in full operation (& continuous performance monitoring)
Anti-Corrosion solution – Case Study – North America Refinery

Coke calciner

TUBACOAT SOLUTION:
Operator received 3 times cycle length, savings of US $2 million/yr.

Real pictures of coated tubes in coke calciner recuperator after 15 months running in full operation
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Conclusion – Tubacoat Anti-coking Solutions – Value to customers

Applying inner coating in DCU/ VU/VDU/RHC tubes is:

✓ PROFITABLE
  - Longer run lengths improving overall throughput
  - Easier and much less frequent cleaning operations

✓ SAFE
  - Increased safety by reducing the number of shutdowns and start-up operations and avoidance of hotspots

✓ CLEAN
  - Reduced fuel consumption due to increased heat transfer efficiency and CO2 reduction

✓ RELIABLE
  - Ad-hoc Formula designed for specific applications
  - Ceramic Coating applied to Carbon Steel, Stainless Steel and Nickel Alloy Materials
THANK YOU!

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TUBACOAT PLANT IN CANTABRIA, SPAIN

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