ELECTROCHEMICAL IMPEDANCE AIDING THE SELECTION OF ORGANIC COATINGS FOR VERY AGGRESSIVE CONDITIONS

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LNDC – Laboratory of Nondestructive Testing, Corrosion and Welding
Who are we?

- Inaugurated on April 2009
- LNDC construction was sponsored by Petrobras
- To act in an interdisciplinary fashion to propose solutions for the main issues faced by the oil industry.
- LNDC is equipped with on point technology on corrosion, welding and non-destructive evaluation.
The problem ...

• The primary processing of petroleum involves very aggressive conditions, such as: high salinity with H₂S and CO₂, high temperatures (120-150°C), thermal cycling, electric field.

• To withstand such aggressive conditions, equipments have been constructed with super duplex steels.

• Despite being famous by excellent anticorrosion properties, inadequate working conditions may impair its performance.

• Coatings have been applied to extend the life of the equipment.

• LITTLE INFORMATION EXISTS ABOUT THE PERFORMANCE OF COATINGS APPLIED ON SUPER DUPLEX.
The problem ...

- IF A COATING EXISTS TO WITHSTAND SUCH AGGRESSIVE CONDITIONS, ONE CAN RE-USE COATED CARBON STEEL IN PLACE OF SUPER DUPLEX.
One Purpose ...

- Compare the performance of commercial organic coatings applied on carbon and super duplex steels, subject to conditions present in the primary processing of oil.

**Chloride: 70,000 ppm**

Sodium acetate: 21 g / L
Initial pH: 5 (adjust with HCl 37%)
Deaerated: N₂ injection/24h

**Continuous bubbling: 96%CO₂ +4% H₂S**

**Temperatures: 150 and 180 °C**

Pressure: 70 and 130 psi (vapor pressure of water in the respective test temperatures).
Another Purpose ...

- Access the state of the art for commercial coatings with proposed performance under such aggressive conditions.

Six composite coatings:

A – 750-1000 µm
B – 650-850 µm
C – 1000 µm
D – 500-800 µm
E – 800 µm
F – 1000-1500 µm
Methodology...

Immersion tests at room temperature, 150 and 180°C with performance monitoring by electrochemical impedance, visual inspection and adhesion measurements after 4, 8 and 12 months.
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Main Conclusions:

✓ R&D of coatings are required for this area.

✓ The main problem with super duplex is adhesion.

✓ “Bierwagen method” can aid on development and rating coatings for long-term exposition at high temperatures.
Results...

Adhesion Measurements – ASTM D4541
Room Temp. – NaCl 3.5%

POTS (MPa)
Pull Off Tensile Strength

10MPa

A/B 100%
A/B 60%
NaCl 3,5%
Adhesion Measurements – ASTM D4541
Room Temp. – NaCl 3.5%

A

B

C

D

E

F
Problems with super duplex surface treatment:

Hardness: 220HV (SD) vs. 120HV(CS)
Abrasive incrustation: higher
Surface energy: lower
Adhesion Measurements – ASTM D4541 – 150°C

A

C

POTS (MPa)

10MPa

D

E

F

A/B 100%

A/B 90%
Adhesion Measurements – ASTM D4541 – 180°C

B

C

D

E

F

5MPa

POTS (MPa)
The effect of autoclave testing – Coating A

150°C - Carbon Steel

150°C – Super Duplex

Phase shift (degree)

|Z| (Ω.cm²)

Frequency (Hz)
Adhesion Measurements – ASTM D4541 – 150°C
The effect of autoclave testing – Coating F

150°C - Carbon Steel

150°C – Super Duplex

Phase shift (degree)
Increasing temperature – Coating F

180°C - Carbon Steel

180°C – Super Duplex
A, B and C with better performance
Harmful effect of temperature

Autoclave at 150°C

Autoclave at 180°C
Immersion test at room temperature-3.5% NaCl

|Z| (Ω.cm-2)

Initial Impedance

10^{13}

After 8 months

10^{13}

Phase shift (degree)
### THERMAL ANALYSIS:

**TGA**

<table>
<thead>
<tr>
<th>Coating</th>
<th>$T_i (^\circ C)$</th>
<th>%RS*</th>
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<tbody>
<tr>
<td>A</td>
<td>333.33</td>
<td>66.44</td>
</tr>
<tr>
<td>B</td>
<td>329.74</td>
<td>75.44</td>
</tr>
<tr>
<td>C</td>
<td>322.26</td>
<td>71.38</td>
</tr>
<tr>
<td>D</td>
<td>333.36</td>
<td>42.11</td>
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<td>E</td>
<td>330.63</td>
<td>33.09</td>
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<tr>
<td>F</td>
<td>335.80</td>
<td>47.18</td>
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### DMA

<table>
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<tr>
<th>Coating</th>
<th>Tg</th>
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<tbody>
<tr>
<td>A</td>
<td>63.29</td>
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<tr>
<td>B</td>
<td>64.43</td>
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<tr>
<td>C</td>
<td>57.30</td>
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<tr>
<td>D</td>
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<td>E</td>
<td>63.70</td>
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<tr>
<td>F</td>
<td>65.05</td>
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</table>

- Impedances measured at room temperature do not reflect the actual properties of the coatings during autoclave testings, but the consequences of irreversible injury after long-term exposition.
FREE FILMS IMPEDANCE WITH THERMAL CYCLE

$|Z| (\Omega \cdot \text{cm}^{-2})$ vs. $f$(Hz)
$|Z|_{0.1\text{ Hz}} (\Omega \cdot \text{cm}^{-2})$ vs $1/T$ (K$^{-1}$)
Final Remarks

✓ All coatings presented some kind of deterioration, pointing to the need for research and development in this area.

✓ There have been cases in which the super duplex adhesion losses were more significant than in carbon steel, suggesting that special attention in surface treatment of super duplex is important.

✓ With free films of coatings impedance was measured during temperature cycling. The results show the importance of the characterization of the thermal behavior of coatings for exposure conditions involving temperatures above Tg.

✓ The inclusion of this methodology for testing protocols of organic coatings can provide relevant information to the development of more efficient formulations, and also to rate performance predicting long-term testings.
ACKNOWLEDGEMENTS