PREVENTION OF COT BOTTOM PITTING CORROSION BY ZINC-PRIMER

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Corrosion Problem in COT

- A form of corrosion on inner bottom: Pitting of bowl shape
- On every dry docking (every 2.5 years)
  ⇒ Pitting corrosion, 4 mm and more depth, are repaired.
  ⇒ A lot of pitting corrosion = A lot in repair cost!

Max. Pitting Rate: 4mm/y (10mm/2.5y)
Environment on Inner Bottom of COT

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**Mechanism of Pitting**

- Defect of oil-coat
- Salt-water
- Sludge, S (Cathode)

Pitting Growth

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**Full Load Condition**

- Oil-coat
- Salt-water about 8% NaCl, Salt-water
- Sludge
- Solids in Oil
- Drops from ceiling (Sulfur, Rust) → Cause of Pitting

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**Mcro-cell corrosion**

***Initiation and growth of pitting corrosion***
## Field Examination of Crude Oil Tankers

**Tanker Type:** Double Hull Tanker (VLCC, Suez-Max)  
**Number:** 6  
**Age:** 2.5 - 12.5 years

### Table: Examination items.

<table>
<thead>
<tr>
<th>Inner Bottom</th>
<th>Tanker</th>
<th>2.5Y-dock</th>
<th>5Y-dock</th>
<th>7.5Y-dock</th>
<th>10Y-dock</th>
<th>12.5Y-dock</th>
</tr>
</thead>
<tbody>
<tr>
<td>No paint applied</td>
<td>VLCC A</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VLCC B</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>Shop-primer applied</td>
<td>VLCC C</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VLCC D</td>
<td>○, ★</td>
<td></td>
<td>○, ★</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VLCC E</td>
<td>○</td>
<td>○, ★</td>
<td></td>
<td>○</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Suez/M F</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>○</td>
<td>○, ★</td>
</tr>
</tbody>
</table>

〇: Investigation of the Amount of Pitting Corrosion  
★: Analyzing the Rust on the Inner Bottom Plate
## Results of Field Examination

Table: The Amount of Pitting Corrosion Need to Repair
   (per vessel, VLCC : 4 mm and more depth, Suez Max. : 3 mm and more depth)

<table>
<thead>
<tr>
<th>Inner Bottom</th>
<th>Tanker</th>
<th>2.5Y-dock</th>
<th>5Y-dock</th>
<th>7.5Y-dock</th>
<th>10Y-dock</th>
<th>12.5Y-dock</th>
</tr>
</thead>
<tbody>
<tr>
<td>No paint applied</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VLCC A</td>
<td>1323</td>
<td>2356</td>
<td>1082</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VLCC B</td>
<td>1246</td>
<td>2919</td>
<td>1756</td>
<td>1138</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shop-primer applied</td>
<td>VLCC C</td>
<td>49</td>
<td>213</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VLCC D</td>
<td>44</td>
<td>61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VLCC E</td>
<td>88</td>
<td>39</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suez/M F</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>47</td>
<td>684</td>
<td></td>
</tr>
</tbody>
</table>

*Better result for when a shop-primer was applied!*
No-paint Applied : Always 1000 or More
Shop-primer Applied : Keep Low Level (at 10 Years after Delivery)
Pitting Corrosion on Inner Bottom of COT

A lot of pitting corrosion!

Photo. VLCC B applied No-paint
(10 years after delivery,
Total 1138 Pits, Max. 412 Pits/tank)

Very little pitting corrosion!

Photo. VLCC D applied Shop-primer
(5 years after delivery,
Total 61 Pits, Max. 9 Pits/tank)
Cutting out the COT Bottom Plate

Photo. Cutting out the Inner Bottom Plate of COT (VLCC D applied shop-primer, 5 years after delivery)
Quantitative Analysis of Zn in the Rust

Table Content of Fe and Zn in the Rust.

<table>
<thead>
<tr>
<th>Tanker</th>
<th>VLCC D (2.5y)</th>
<th>VLCC D (5y)</th>
<th>VLCC E (5y)</th>
<th>Suez/M F (12.5y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample No.</td>
<td>A0</td>
<td>B0</td>
<td>C4</td>
<td>D3</td>
</tr>
<tr>
<td>Elements</td>
<td>Fe</td>
<td>Zn</td>
<td>Fe</td>
<td>Zn</td>
</tr>
<tr>
<td>(g/m²)</td>
<td>205</td>
<td>8.9</td>
<td>235</td>
<td>1.7</td>
</tr>
</tbody>
</table>

ICP Analysis Method
1. Specimen: About 30 x 30 mm
2. Dissolved all rust by HCl
3. ICP analysis

After 12.5 years, Zn is existing in the rust.
**Distribution of Zn in the Rust Layer (1)**

**VLCC D**  
(applied shop-primer, 2.5 years)

Thickness of rust layer:  
$100 \sim 200 \mu m$

EPMA Method  
(1) Cutting out the *cross section* of sample with the rust layer  
(2) Polish  
(3) EPMA Mapping

(a) SEM Image (cross section)  
(b) Zn  
Zn coexists with S  
Zn coexists with O

(c) S  
(d) Fe  
(e) O

Fig. Results of EPMA Analysis.
Distribution of Zn in the Rust Layer (2)

VLCC E
(applied shop-primer, 5 years)

Thickness of rust layer:
200～400 μm

Zn coexists with S
Zn coexists with O

Zn : Sulfide or Oxide

(a) COMP Image (cross section)
(b) Zn
(c) S
(d) Fe
(e) O

Fig. Results of EPMA Analysis.
Identify the Chemical Composition in the Rust

**XRD Analysis Method**
- Scraping and collecting the rust
- Grinding
- Deciding the existing elements by EDX: Fe, Zn, Si, S, Cl, C, O, (Ca, Na)
- XRD analysis

**Fig.** Results of XRD Analysis (VLCC D applied shop-primer, 5 years)
Chemical Composition in Rust

Table Results of XRD Analysis

<table>
<thead>
<tr>
<th>Tanker</th>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>VLCC D (applied shop-primer, 5 years)</td>
<td>(Certainty) $\alpha$-FeOOH, $\beta$-FeOOH, $\gamma$-FeOOH, Fe$_3$O$<em>4$, (Uncertainty) Fe$</em>{0.85-x}$Zn$_x$O, ZnS, ZnSO$_4$</td>
</tr>
</tbody>
</table>

(1) Metal Zinc
Not exist.

(2) Chemical Composition of Zinc
ZnS, ZnSO$_4$, Fe$_{0.85-x}$Zn$_x$O, etc.
Influence of Zn (1)

(1) Zn-oxide, Zn-rust:
Keep Fe-rust the amorphous state, and lift the ability to protect of steel.

By Zn-oxide (ZnO, ZnCl₂·4Zn(OH)₂) → Decrease of Corrosion of Steel

By Zn-rust (ZnO, ZnCl₂·4Zn(OH)₂) → Fe-rust Keeps the Amorphous State

Rust, S (Cathode)

Influence of Zn (2)

(2) Zn$^{2+}$ : Decreasing the dissolution of Fe under acidity

In the acidity chloride solution (pH=3.5), the anodic dissolution of Fe is decreasing with the increasing of the concentration of Zn$^{2+}$ in the solution.

Conclusions

After the field examinations and analysis of pitting corrosion on the inner bottoms of COT, the following results were obtained.

(1) Zinc-primer is effective to the decrease of the number of pitting corrosion in need of repair.

(2) Zinc in the zinc-primer stays in the iron oxide on the inner bottom plate of COT after oxidation, and keeps giving the effect to corrosion resistance. This effect continues for several years at least.