PREVENTION OF COT BOTTOM PITTING CORROSION BY ZINC-PRIMER

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SUMMARY

On the inner bottom of COT (Cargo Oil Tank) of crude oil tankers, a lot of bowl shaped pitting corrosion of 4 millimeters or more depth occurs, and the time and the cost to repair them in the dock every 2.5 years are the large load to the tanker owners. The relationship between the number of pitting corrosion needed to repair and the zinc-primer application of the inner bottom plate of COT was investigated. As a result, it was discovered that the number of pitting corrosion occurred on the inner bottom painted the zinc-primer was clearly lower than the number of pitting corrosion occurred on the non-painted inner bottom plate. The inner bottom plate samples cut out from COT of the tanker under operation, and analyzed. It was confirmed that zinc or zinc chemical compound remained in the rust on the inner bottom plate surface after 5 years operation.

1. INTRODUCTION

Recently, the corrosion problem of the ship attracts a lot of attention. The corrosion of ship not only loses the safety of operation but also increases an economical load along with the repair. For example, on the inner bottom of COT (Cargo Oil Tank) of crude oil tankers, a lot of bowl shaped pitting corrosion of 4 millimeters or more depth occurs [1], and the time and the cost to repair them in the dock every 2.5 years are the large load to the tanker owners. Figure 1 shows the shape of pitting corrosion in COT.

The relationship between the number of pitting corrosion needed to repair and the zinc-primer application of inner bottom plate of COT was investigated. As a result, it was discovered that the number of pitting corrosion occurred on the inner bottom painted zinc-primer was clearly lower than the number of pitting corrosion occurred on the non-painted inner bottom plate.

The investigation results of the number of pitting corrosion in some oil tankers are shown as follows. And the mechanism of prevention of pitting corrosion supposed from an analytical result of the sample cut out from the inner bottom plate of COT of the tanker under operation was reported.

2. FIELD EXAMINATION

In the dock every 2.5 years, pitting corrosion of 4 millimeters or more depth is inspected, marked and repaired. 6 tankers are chosen (5 VLCC and 1 Suez-max tanker, the inner bottom plate surface of 2 VLCC is no-paint and that of the rest of tankers is painted zinc-primer), and the number of pitting corrosion of 4 millimeters or more depth is counted (as to Suez-max tanker, 3 millimeters or more depth). Table 1 shows the number of pitting corrosion in need of repair.

Table 1: The number of pitting corrosion in need of repair. (Pitting Depth : more than 4mm, Suez-max F : more than 3mm)
3. ANALYSIS OF INNER BOTTOM PLATE

3.1 CUTTING OUT INNER BOTTOM PLATE

Samples of the inner bottom plate were cut out from 2.5 years old VLCC D, 5 years old VLCC D and 5 years old VLCC E. These VLCC were painted zinc-primer on the inner bottom plate of COT. As cutting out location, the areas included no pitting corrosion in need of repair were chosen. Because these areas were thought that the possibility of showing the effect of zinc-primer was high.

3.2 RESULTS OF ANALYSIS

3.2 (a) Chemical analysis by ICP

2 or 3 specimens, about 30 x 30 millimeters area, were cut out from every inner bottom plate samples, and the whole rusts of every specimen were dissolved in hydrochloric acid with inhibitor. Then the quantity of Fe and Zn in the each rust was analyzed by ICP (Inductively Coupled Plasma) atomic emission spectrometer. Figure 2 shows the results of chemical analysis. All of the 8 rust specimens contained Zn. It was confirmed that zinc or zinc chemical compound remained on the inner bottom plate surface after 5 years operation. Table 1 shows that the number of pitting corrosion occurred on the inner bottom painted zinc-primer was still lower than the number of pitting corrosion occurred on the non-painted inner bottom plate in the dock after 5 years operations. After 5 years operations, it is supposed that the existence of zinc or zinc chemical compound decreased the occurrence and growth of pitting corrosion.

3.2 (b) Analysis by EPMA

Specimens for EPMA (Electron Probe Microanalyzer) analysis, also, were cut out from every inner bottom plate samples. Sectional rust layer of every specimen was analyzed by EPMA, and the distributions of elements were mapped. Figure 3 shows the COMP image and the distributions of elements (Zn, Fe, O, S) on the inner bottom plate of COT of 5 years old VLCC D. Zn existed in the rust layer with Fe, O and S.

3.2 (c) Analysis by XRD

The rust specimens for XRD (X-ray Diffraction) analysis were scraped off the surface of every inner bottom plate samples. There is a thickness in the rust layer, so the upper layer rust and the lower layer rust were sorted out and analyzed. All elements contained in the rust specimens were analyzed by EDX (Energy Dispersive X-ray) fluorescence spectrometer first, and then the chemical compounds contained in the rust specimens was analyzed by XRD. By EDX analysis, elements, Fe, Zn, Si, S, Cl, C, O, were detected in all specimens, and elements, Ca and Na, were detected in a part of specimens. Table 2 shows major chemical compounds found by XRD analysis. Main peaks of XRD analysis show some iron oxide and iron carbonate only. The plain peaks of

Figure 2: The quantity of Zn and Fe present in rust.

Figure 3: Results of EPMA analysis. (COMP image, Zn, Fe, O and S distribution)
zinc or the zinc chemical compounds could not be found. This shows the possibility of existence as amorphous that is not crystalline in addition to a little the amount in zinc or zinc chemical compounds.

Table 2: Results of XRD analysis.

<table>
<thead>
<tr>
<th>Tanker</th>
<th>Rust layer</th>
<th>Major chemical compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Upper</td>
<td>alpha-FeOOH, beta-FeOOH, gamma-FeOOH, Fe₃O₄</td>
</tr>
<tr>
<td>VLCC D (5 years)</td>
<td>Lower</td>
<td>alpha -FeOOH, beta -FeOOH, gamma -FeOOH</td>
</tr>
<tr>
<td></td>
<td>Upper</td>
<td>alpha -FeOOH, beta -FeOOH, gamma -FeOOH, Fe₃O₄, FeCO₃</td>
</tr>
<tr>
<td>VLCC E (5 years)</td>
<td>Lower</td>
<td>alpha -FeOOH, beta -FeOOH, gamma -FeOOH, Fe₃O₄, FeCO₃</td>
</tr>
</tbody>
</table>

3.3 EFFECT OF ZINC

It was confirmed that zinc or zinc chemical compound remained in the rust on the inner bottom plate surface after 5 years operation. By XRD analysis, the existence form of zinc could not be identified. However, by EPMA analysis, the distribution of Fe, O, S and Zn was observed at almost the same position. The possibility of existence of ZnSO₄, Fe₀.₈₅₋ₓZnxO and etc. as a chemical compound bonding zinc is presumed. In the zinc coated steel sheet, it is known to have the effect of anti-corrosion even when zinc included in rust as chemical compounds such as zinc oxides, and to stop the form of iron oxide in not the crystalline but the dense amorphous [2]. In this case, the possibility that the rust of inner bottom plate of COT became denser by the existence of zinc, and corrosion resistance improved is presumed.

4. CONCLUSIONS

The field examination and analysis of the inner bottom plate of tankers were carried out, and following results were obtained.

- Painting the zinc-primer on the inner bottom plate of COT is effective to the decrease of the number of pitting corrosion in need of repair, and decreases the number of pitting corrosion from one-fifteenth to one-thirtieth in the first dock inspection.
- 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.

5. REFERENCES


6. AUTHORS’ BIOGRAPHIES

Yasuto Inohara holds the current position of senior researcher at Corrosion Protection Research Department, Steel Research Laboratory, JFE Steel Corporation. He is responsible for development of corrosion resistant steel.