Premature Coating Disbonding on Ships and Offshore Structures

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ABSTRACT

Epoxy/urethane coating systems are widely used for weather parts of ships and offshore structures due to its excellent resistance to UV radiation as well as corrosion protection. Recently, epoxy/epoxy coating systems or epoxy/urethane coating systems have experienced lots of premature coating failure such as intercoat adhesion failure during winter and spring seasons in Korea. In this work, the root causes of premature coating failure were investigated using pH test and Fourier transform infrared spectroscopy (FT-IR) for several failed epoxy/urethane coating systems. We found that coating failure was attributed to the amine blush and urea formation by the reaction of isocyanate(-NCO) with moisture and free amine. The premature coating failure have been successfully controlled by the use of amine adduct or amide adduct hardener and the proper control of atmosphere for coating application in the winter and spring seasons.

Keywords: Intercoat adhesion failure, amine blush, FT-IR, epoxy/urethane coating system.
INTRODUCTION

Delamination is the loss of interfacial adhesion between coating layers and is a common type of coating failures. In general, these coating failures occur most often where repair or maintenance coatings are being applied over existing coatings that have been in service for some period of time [1]. However, there are many causes for intercoat delamination such as incompatibility of adjacent coatings, improper mixing of base resin with hardener, application of the subsequent coating on the fully cured coating surface and contaminated coating surfaces with amine blush and moisture, etc..

In the ship and offshore building industries, the following three elements are very desirable: (1) reduce dry times before subsequent coating and seawater immersion, (2) increase the maximum recoating interval, and (3) maintain good adhesion. In particular, in order to have better workability and productivity regardless of season, coatings should have a short curing time. Consequently, amine cured epoxy coatings have been selected to meet the fast curing requirement. However, we have experienced premature coating failures recently. Epoxy/epoxy coating systems or epoxy/urethane coating systems have intercoat adhesion failure as shown in Figure 1, especially during the winter and spring seasons in Korea. For that reason, overall delay of coating program and subsequent delay in building schedule was consequential.

Therefore, in this study, the analyses of the root cause of the intercoat delamination failure for epoxy/epoxy and epoxy/urethane coating systems were carried out using the pH indicator paper and Fourier Transformed Infrared Spectroscopy (FT-IR). The improved epoxy paints are now used for marine/offshore structure in our ship yard.
ANALYTICAL TEST METHODS FOR INTERCOAT DELAMINATION

In this study, intercoat delamination, which is related to surface contaminations by amine blush and moisture were evaluated using pH indicator paper and Fourier transform infrared (FT-IR) spectroscopy.

Amine Blush Check using pH Indicator Paper

Amine curing agents mixed in the epoxy coatings react with moisture and atmospheric carbon dioxide to form amine salts such as ammonium bicarbonate and/or ammonium carbamate as shown in Figure 2. Generally, pH of the amine salt is of a high alkalinity (> pH 9), because it contains the ammonium ion (NH₄⁺) [2] [3]. Therefore, there is a strong correlation between pH of the delaminated coating film and the amine blush. The presence of the amine blush can be confirmed by comparing the color of the saturated pH paper to the standard color chart provided in the container.

In this study, the alkalinity of the delaminated coating films were measured using pH indicator paper (pH 0.0~14.0).

FT-IR Spectra Analysis

FT-IR can measure the frequencies, in which the sample absorbs the radiation and the intensities of the absorptions, to allow identification of the sample’s chemical makeup. It is because chemical functional groups are known to absorb infrared radiation at specific frequencies. FT-IR is the typical chemical analysis technique used in the laboratory for coating failure analysis. Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy is also widely employed for analysis of cured coating surface. It allows minimum sample preparation without grinding or pressing compared to conventional FT-IR analysis [4] [5].

In this study, ATR FT-IR spectroscopy was used to identify the absorbance peaks of surface contaminants such as ammonium carbonate, ammonium carbamate and isocyanate group etc.
CASE STUDIES AND DISCUSSION

There are several types of coating failures such as intercoat adhesion failure, sagging, longer drying time, etc. In particular, the coating delaminations in the winter and spring seasons in Korea are the common failure mode. Therefore, delay of coating project and building schedule was inevitable. Physical properties of delaminated coating materials employed in the actual project are summarized in the Table 1.

Case Study I. Coating Failures by Amine Blush

Amine Blush Check by pH Indicator Paper

It was well known that pH of the amine salts such as ammonium bicarbonate and/or ammonium carbamate is of high alkalinity because of containing the ammonium ion (NH$_4^+$). The presence of amine blush can be easily detected by the measurement of pH value on the epoxy coating surface.

Figure 3 and Figure 4 shows a coating delamination and amine blush test results for epoxy/epoxy and epoxy/urethane coating systems. The pH values of both coating systems appeared in the basicity (> pH 9). The results indicate a presence of ammonium carbamate and/or ammonium bicarbonate between the delaminated film surfaces. It also confirms that these coating failures are resulted from amine blush by reaction between the free amine with moisture and carbon dioxide as shown in Figure 2.

FT-IR Spectra Analysis

In this study, in order to determine the cause of coating delamination, the peeled epoxy film and standard cured epoxy film were examined using the attenuated reflectance (ATR FT-IR) technique. Both spectra appeared to be of similar paint resin chemistry, and were amine-based epoxy resin, as shown in the FT-IR given in Figure 5. We have observed, in the spectrum of failure film an additional intense
carbon-oxygen absorption band at around 1650cm⁻¹ and a weak absorption band at around 1716cm⁻¹, which might indicate that it was bicarbonate and/or carbamate.

To sum up, in order to identify the cause of coating delamination, pH indicator paper and ATR FT-IR were used to determine the pH level and identify the absorbance peak of peeled film, respectively. As a result, we conclude that the main cause of coating failure was amine blush.

**Case Study II. Isocyanate’s Reactivity with Moisture**

**Amine Blush Check by pH Indicator Paper**

Figure 6(a) & (b) shows coating delaminations and amine blush test results for the failed epoxy/urethane coating system. The pH appears to be neutral and it indicates that there aren’t an ammonium carbamate and/or ammonium bicarbonate between delaminated coating layers. Therefore, it can be clarified that the main reason of coating failure is not amine blush.

The outdoor weather condition as shown in Figure 6(c), shows that the humidity was very high and the outdoor temperature fluctuation was very large for the urethane painting. Also, the steel block was near a wet ground. The urethane coating might be applied on the damp or icy surface. The isocyanate might react with water on the epoxy instead of reaction with the polyol group to form the urea as shown in Figure 7. According to the relative reactivity of isocyanates with active hydrogen compounds in Table 2 [6], the reaction with water will lead to reduction in adhesion strength at the interface of epoxy and urethane coating, and result in the intercoat adhesion failure.

**FT-IR Spectra Analysis**

Typically, the ratio of the reactive groups of the polyol to isocyanate in a liquid polyurethane is maintained at just over 1.0 or slightly isocyanate rich to form the proper cured film [7]. So the proper urethane coating film has an excess of reactive isocyanate left.
In this case of coating failure, ATR FT-IR technique was performed on the peeled urethane film and the cured standard urethane film. Two similar spectra were obtained, as shown in Figure 8. In general, urethane coating film has the absorption bands at 1730, 1690 (a weak shoulder), and 1530 cm\(^{-1}\), and the band of the isocyanate group is near 2270 cm\(^{-1}\) [8]. The two spectra, shown in Figure 8, were for urethane coating films. The sound film, has an intense isocyanate absorption band at around 2270 cm\(^{-1}\), while the failed film doesn’t have any peak in the same band. In case of the failed film as shown Figure 8, it can be determined that the isocyanate reacted with moisture on the epoxy coated film to form the incomplete cured urethane film. As the result, the insufficient intercoat adhesion was formed between the urethane coating and the epoxy coating because some isocyanate reacted with water instead of the polyol [9].

**Case Study III. Amine Blush Resistant Epoxy Coating System**

In order to reduce the amine blush, the carbamate formation should be minimized by proper formulation with a small free-amine such as the primary amine because the primary amine hydrogen react with moisture molecule and carbon dioxide to form amine blush. A method to minimize carbamate is to prereact primary amines with epoxy resin [10]. So, in this study, the amine blush resistance coating of the amide cured epoxy coating system was improved and applied by adducting a part of epoxy binder and amide-hardener in advance.

The FR-IR spectra of epoxy paint before and after improvement are shown in the Figure 9. Spectra of 1640 cm\(^{-1}\) and 3200cm\(^{-1}\) generally indicate the carbon-oxygen absorption band, which can be assigned as the amide peak of epoxy hardener. As adducting a portion of epoxy binder and hardener in advance, the absorption bands at same peak becomes weak. This phenomenon means that the amine blush can be reduced by adducting the epoxy resin and the amine or amide curing agent.
Figure 10 shows the results of adhesion and amine blush resistance for epoxy/urethane coating systems before and after adduction of epoxy coating. Based on adhesion test results after water immersion for 3 days, the adhesion of the adducted epoxy was superior to one of non-adducted epoxy. pH test results indicated that adducted epoxy coating surface appeared to be neutral, while non-adducted epoxy coating surface revealed to be alkali as shown in the Figure 10(a) & (b).

Based on the above results, it was clarified that all of amine- and amide cured epoxy paint can produce amine blush at the weather conditions of low temperature and high humidity. The amine blush can be minimized by adducting the amine or amide curing agents and the proper coating material should be selected.

CONCLUSIONS

Based on investigation of three case studies on the failed epoxy/epoxy and epoxy/polyurethane coating systems, following conclusions can be made;

1. In case of the adhesion failure between epoxy and epoxy or urethane coat, the pH indicator paper test and ATR-FT-IR spectroscopy can be used to analyze the main cause of coating failures.

2. Not only amine cured epoxy paint but also amide cured epoxy paint can produce amine blush at the weather conditions of low temperature and high humidity. The amine blush can be minimized by adducting the amine or amide curing agents.

3. Application of urethane coating system on the epoxy coating surface require more strict control of moisture condensation in order to prevent intercoat disbonding.

REFERENCES


Table 1 Physical properties of delaminated coating materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardener Type</th>
<th>Mixing Ratio (Vol)</th>
<th>Pot Life (hrs)</th>
<th>Drying time (hrs)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5°C</td>
<td>15°C</td>
</tr>
<tr>
<td>EA</td>
<td>Amine</td>
<td>4:1</td>
<td>3 (20°C)</td>
<td>8 (touch)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>16 (through)</td>
</tr>
<tr>
<td>EB</td>
<td>Amine</td>
<td>4:1</td>
<td>2 (23°C)</td>
<td>6 (touch)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3 (10°C)</td>
<td>20 (through)</td>
</tr>
<tr>
<td>EC(a)</td>
<td>Amide</td>
<td>1:1</td>
<td>6 (23°C)</td>
<td>6 (touch)</td>
<td>3 (touch)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7 (15°C)</td>
<td>38 (through)</td>
</tr>
<tr>
<td>EC(b)</td>
<td>Amide adduct</td>
<td>1:1</td>
<td>7 (23°C)</td>
<td>3 (touch)</td>
<td>1 (touch)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7 (15°C)</td>
<td>25 (through)</td>
</tr>
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</table>

Table 2 Relative reactivity of isocyanates with active hydrogen compounds [7]

<table>
<thead>
<tr>
<th>Active hydrogen compound</th>
<th>Typical compound</th>
<th>Relative reaction rate*</th>
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<tbody>
<tr>
<td>Primary aliphatic amine</td>
<td>R-NH2</td>
<td>100,000</td>
</tr>
<tr>
<td>Secondary aliphatic amine</td>
<td>RR’NH</td>
<td>20,000 – 50,000</td>
</tr>
<tr>
<td>Primary aromatic amine</td>
<td>Ar-NH2</td>
<td>200 – 300</td>
</tr>
<tr>
<td>Primary hydroxyl</td>
<td>RCH2-OH</td>
<td>100</td>
</tr>
<tr>
<td>Water</td>
<td>HOH</td>
<td>100</td>
</tr>
<tr>
<td>Carboxilic acid</td>
<td>RCOOH</td>
<td>40</td>
</tr>
<tr>
<td>Secondary hydroxyl</td>
<td>RR’CH-OH</td>
<td>30</td>
</tr>
<tr>
<td>Ureas</td>
<td>R-NH-CO-NH-R</td>
<td>15</td>
</tr>
<tr>
<td>Tertiary hydroxyl</td>
<td>RR’R”C-OH</td>
<td>0.5</td>
</tr>
<tr>
<td>Urethane</td>
<td>R-NH-CO-O-R</td>
<td>0.3</td>
</tr>
<tr>
<td>Amide</td>
<td>RCO-NH2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

* uncatalyzed at 25°C
Figure 1 Premature adhesion failures in the shipyard and offshore structure

$$R_1R_2NH + CO_2 \rightleftharpoons R_1R_2NH^+COO^-$$

Primary or secondary amines

$$R_1R_2NH^+COO^- + R_1R_2NH \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+$$

Zwitterion

$$R_1R_2R_3N + CO_2 + H_2O \rightleftharpoons R_1R_2R_3NH^+ + HCO_3^-$$

Tertiary amine

Carbamate acid zwitterion

an ammonium carbamate

an ammonium bicarbonate

Figure 2 Mechanism of amine blush formation

Figure 3 Delamination of Epoxy (EA) / urethane coating system
Figure 4 Delamination of Epoxy (EB) / Epoxy (EB) coating system

Figure 5 FT-IR spectrum of standard & failure paint film (EA)
(a) Delaminated coating failure  
(b) Amine blush check

\[
\begin{array}{c|c|c|c|c}
\text{Epoxy (2/23)} & 24 & 25 & \text{UT(2/26)} & 27 \\
\includegraphics[width=0.5\textwidth]{temperature_24_25_27.png} & \text{-4.0°C} & \text{3.0°C} & \text{-0.2°C} & \text{-1.1°C} \\
\text{5.2°C} & \text{8.3°C} & \text{4.7°C} & \text{9.9°C} \\
\end{array}
\]

(c) Outdoor weather condition

Figure 6 Coating failure (EA) and Outdoor weather condition

Figure 7 Formation of urea from the reaction between isocyanate groups and water molecules
Figure 8 FT-IR Spectra of regular (a) and delaminated (b) urethane film

Figure 9 FT-IR spectra before and after improvement of epoxy hardener
Figure 10 Evaluation results before and after improvement

(a) Before improvement, EC(a)

(b) After improvement, EC(b)

Figure 10 Evaluation results before and after improvement