CASE HISTORIES

Premature Coating Disbonding on Ships and Offshore Structures

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Delamination is the loss of interfacial adhesion between coating layers and is a common type of coating failure. 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. There are, however, 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 surfaces contaminated with amine blush and moisture.

In the ship and offshore structure industries, the following three elements are very desirable: 1) reduce dry times before subsequent coating and seawater exposure, 2) increase the maximum recoating interval, and 3) maintain good adhesion.

In particular, to have better workability and productivity regardless of the season, coatings should have a short curing time. Consequently, amine-cured epoxy coatings have been selected to meet the fast curing requirement. Recently, however, premature coating failures occurred on Korean vessels and structures. Epoxy/epoxy coating systems or epoxy/urethane coating systems experienced intercoat adhesion failure (Figure 1), especially during the winter and spring seasons. Failures led to an overall delay in the coating program and subsequent delay in the construction schedule.

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 pH indicator paper and Fourier transform infrared (FTIR) spectroscopy. We now use improved epoxy paints for marine/offshore structures.

Epoxy/urethane coating systems are widely used for ships and offshore structures because of their excellent resistance to ultraviolet radiation and protection against corrosion. Recently, some of these coating systems used in Korea experienced premature failure. This work investigated the root cause of the failures using pH tests and Fourier transform infrared spectroscopy.
Analytical Test Methods for Intercoat Delamination

**Amine Blush Check Using pH Indicator Paper**

Amine curing agents mixed in the epoxy coatings react with moisture and atmospheric carbon dioxide (CO$_2$) to form amine salts such as ammonium bicarbonate (NH$_4$HCO$_3$) and/or ammonium carbamate (NH$_4$NH$_2$CO$_3$). Generally, pH of the amine salt is of a high alkalinity (pH >9), because it contains the ammonium ion (NH$_4^+$). 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.

**FTIR Spectra Analysis**

FTIR 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. Because chemical functional groups are known to absorb infrared radiation at specific frequencies, FTIR is the typical chemical analysis technique used in the laboratory for coating failures. Attenuated total reflection (ATR) FTIR spectroscopy is also widely employed for analysis of a cured coating surface. It allows minimum sample preparation without grinding or pressing compared to conventional FTIR analysis.$^{4-5}$

In this study, ATR FTIR spectroscopy was used to identify the absorbance peaks of surface contaminants such as ammonium carbonate, ammonium carbamate, isocyanate group, etc.

**Case Studies and Discussion**

There are several types of coating failures, notably intercoat adhesion failure, sagging, and longer drying time. In particular, the coating delaminations occur most frequently in the winter and spring seasons in Korea. Therefore, the delay of coating projects and construction

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardener Type</th>
<th>Mixing Ratio (Vol)</th>
<th>Pot Life (h)</th>
<th>5 °C</th>
<th>15 °C</th>
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<td>EA</td>
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<td>4:1</td>
<td>3 (20 °C)</td>
<td>8 (touch)</td>
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<td>Case I</td>
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<td>16 (through)</td>
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<tr>
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<td>6 (touch)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>3 (10 °C)</td>
<td>20 (through)</td>
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<tr>
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<td>6 (touch)</td>
<td>3 (touch)</td>
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<td>1 (touch)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7 (15 °C)</td>
<td>25 (through)</td>
<td>10 (through)</td>
<td></td>
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</tbody>
</table>
Delamination of epoxy (EB)/epoxy (EB) coating system.

FTIR Spectra Analysis
To determine the cause of coating delamination, the peeled epoxy film and standard cured epoxy film were examined using the attenuated reflectance (ATR FTIR) technique. Both spectra appeared to be of similar paint resin chemistry, and were amine-based epoxy resin. We observed in the spectrum of the failed film an additional intense carbon-oxygen absorption band at ~1,650 cm⁻¹ and a weak absorption band at ~1,716 cm⁻¹, which might indicate that it was bicarbonate or carbamate.

To identify the cause of coating delamination, pH indicator paper and ATR FTIR were used to determine the pH level and identify the absorbance peak of peeled film, respectively. As a result, we concluded 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

For epoxy/epoxy and epoxy/urethane coating systems, the pH values of both coating systems were pH >9. The results indicate a presence of ammonium carbonate 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 conditions (Figure 4[c]) show that the humidity was very high and the outdoor temperature fluctuation was very large during the urethane painting. Also, the steel structure was near wet ground. The urethane coating might have been applied on a damp or icy surface. The isocyanate might react with water on the epoxy instead of reacting with the polyol group to form urea. According to the relative reactivity of isocyanates with...
active hydrogen compounds, the reaction with water will lead to reduction in adhesion strength at the interface of the epoxy and urethane coating, and lead to intercoat adhesion failure.\(^5\)

**FTIR 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 properly cured film.\(^7\) So the proper urethane coating film has an excess of reactive isocyanate.

In this case of coating failure, the ATR FTIR technique was performed on the peeled urethane film and the cured standard urethane film. Two similar spectra were obtained. In general, urethane coating film has the absorption bands at 1,730, 1,690 (a weak shoulder), and 1,530 cm\(^{-1}\), and the band of the isocyanate group is near 2,270 cm\(^{-1}\).\(^8\) The two spectra were for urethane coating films. The good film has an intense isocyanate absorption band at around 2,270 cm\(^{-1}\), while the failed film doesn’t have any peak in the same band. In the case of the failed film, it can be determined that the isocyanate reacted with moisture on the epoxy-coated film to form the incompletely cured urethane film. As a result, insufficient intercoat adhesion was formed between the urethane coating and the epoxy coating because some isocyanate reacted with water instead of the polyl.\(^9\)

**Case Study III—Amine Blush-Resistant Epoxy Coating System**

To reduce the amine blush, carbamate formation should be minimized by proper formulation with a small free amine such as the primary amine because the primary amine reacts with moisture and CO\(_2\) 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 FTIR spectra of 1,640 cm\(^{-1}\) and 3,200 cm\(^{-1}\) generally indicate the carbon-oxygen absorption band, which can be assigned as the amide peak of epoxy hardener. By adducting a portion of epoxy binder and hardener in advance, the absorption bands at the same peak become weak. This phenomenon means that the amine blush can be reduced by adducting the epoxy resin and the amine or amide curing agent in advance.

Figure 5 shows the results of adhesion and amine blush resistance for epoxy/urethane coating systems before and after addition of epoxy coating. Based on adhesion test results after water immersion for three days, the adhesion of the adducted epoxy was superior to one of nonadducted epoxy. The pH test results indicated that the adducted epoxy coating surface appeared to be neutral, while the nonadducted epoxy coating surface revealed it to be alkali.

Based on these results, it was determined that all 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 the investigation of three case studies on the failed epoxy/epoxy and epoxy/urethane coating systems, the following conclusions can be made:

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

- 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.
- Application of the urethane coating system on the epoxy coating surface requires more strict control of moisture condensation to prevent intercoat disbonding.

References

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