Technical Article 1

Application of FTIR Structural Analysis for Dried Coating Failure Investigation in Oil & Gas Industry

ZAINAL Nurul Fatahah Asyqin[1], **ABDUL HALIM** Suhaila Idayu[2], **KAMARDIN** Muhammad Zaid[3], **MANSOR** Muhammad Afiq[3], **CHAN** Chin Han*[2]

[1]Centre of Foundation Studies, Universiti Teknologi MARA, Cawangan Selangor Kampus Dengkil, 43800 Dengkil, Selangor, Malaysia
Email: nurulfatahah@gmail.com
[2]Universiti Teknologi MARA, Faculty of Applied Sciences, 40450 Shah Alam, Selangor, Malaysia
E-mail: cchan_25@yahoo.com.sg (*corresponding author), suhailaidayu@gmail.com
[3]PETRONAS Group Technical Solutions, 50050 Kuala Lumpur, Malaysia
E-mail: zaid_kamardin@petronas.com, muhammadafiq.mansor@petronas.com

Introduction

Coatings are extensively used in the oil and gas industry for corrosion protection or passive fire protection on steel structures. Most coating failures occurred in the industry are believed to be caused by poor surface preparation and application. However, some premature coating damage or failure experienced may be contributed by other factors such as substandard materials supplied, incompatible coating systems and/or unwanted chemical reaction of the paint components with the external environment. For premature coating failure analyses, robust, accurate, quick and economical analytical methods are necessary to identify the possible cause(s) of the coating failure. The results of the test(s) will provide guides on corrective actions needed for the repair of the prematurely failed coating systems.

This paper discusses, based on an actual case study, the application of Fourier-transform infrared (FTIR) structural analysis in reference to IMM FP03 standard in suggesting the possible cause(s) of premature coating failure at one of the oil and gas processing facilities in Malaysia. Development of tackiness of the topcoat of a three-coat system on four refinery tanks is observed after 2 to 8 months of application on the structures. The tackiness of the polyurethane (PU) topcoat may be originated from the accumulation of low molar mass components on the surface of the topcoat. After carried out the "controlled" experiments, possibilities of (1) improper blasting and painting work, (2) reformulation of paints and (3) improper product specification of primer were ruled out. What could be the cause of the tackiness of the topcoat, which develops over time? If the repair work has to be done, should (1) topcoat or (2) top and middle coats have to be removed and reapplied?

Method

The failed three-coat system consists of PU and amine-based paints which serve as the top coat and middle coat, respectively, of the refinery tanks located in a hot and high humidity environment. The schematic diagram of the coating system is shown in **Figure 1**. The middle coat is the dried and cured amine-based 2-pack paints used as passive fire protection (PFP) of the tanks. From the materials safety data sheet (MSDS), part A and part B of these 2-pack paints mainly comprise a mixture of organic-inorganic components (isocyanate-based components) for part A as the base; and amine-based components for part B (moisture sensitive amine as the hardener). Meanwhile, PU coating is dried and cured 2-pack paints that consist of polyol-based components (part A) and isocyanate-based components (part B as the hardener).

Roughly 2 to 4-cm diameter of topcoat and middle coat were removed from different spots of different tanks after 8 months of application. The topcoat after 1 week of application was used as the Reference of the topcoat. The FTIR analysis was done on the as-received condition. At least 6 spots with 3 FTIR scans per spot were carried on each sample. FTIR analysis was performed using Bruker Alpha I (Billerica, Massachusetts, USA) equipped with an ATR sampling accessory with a diamond crystal. The spectra were recorded in absorbance mode ranging from 4000–700 cm^{-1} by averaging 32 scans at a resolution of 4 cm^{-1} (with reference to IMM FP03:2020) [1]. A *compare* function was performed using OPUS software (Bruker, Billerica, Massachusetts, USA). The samples' coding and description are tabulated in **Table 1**.

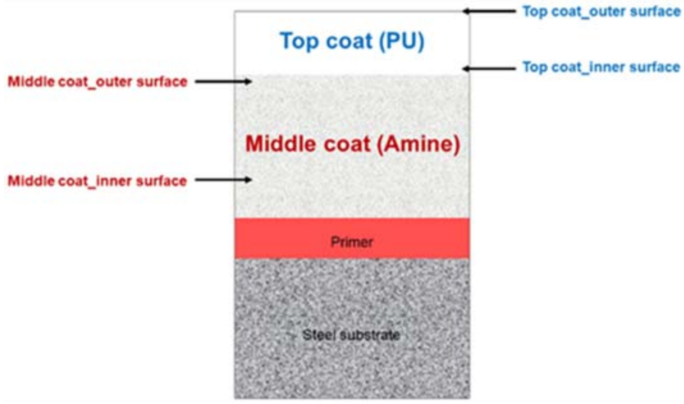

Figure 1: Schematic diagram of the dried coating system applied on a refinery tank.

Results and discussion

Coating failure analysis 1 – FTIR spectral inspection and band assignments

Based on the literature, amine blooming [2] may be the attributing factor for the tackiness behavior developed on the topcoat. It is caused by water-soluble compounds migrating from the middle coat to the top surface drawn up by surface moisture. When the moisture evaporates, the migrated (leached) components will appear on the top surface as sticky deposits. Therefore, the interpretation of the absorbance bands is focused on the functional groups of **free NH** stretching (3700 – 3600 cm^{-1}) [3] and **bonded NH** stretching (3400 – 3250 cm^{-1}) [3-5]. These absorbance bands show notable differences between the fresh (*i.e.* Reference) and old (8 months) samples.

Topcoat_Fresh_outer surface (PU coating) displays a typical FTIR spectrum (*c.f.* **Figure 2**) and all absorbance bands are consistent with references [6, 7]. The disappearance of the isocyanate absorbance band around 2250 cm^{-1} in the spectrum indicates that all isocyanates have been reacted with the polyol-based component in the curing reaction. The **bonded NH** band observed at ~3300 cm^{-1} is assigned to the N-H stretching in PU as illustrated in a chemical equation in **Figure 3**.

Table 1. Details of the dried coating samples

Sample coding	Sample description
Topcoat_Fresh_outer surface	1. PU dried coating (one week after application). 2. The outer surface was exposed to the atmospheric environment.
Topcoat_Fresh_inner surface	1. PU dried coating (one week after application). 2. The inner surface was in contact with Amine dried coating.
Middle coat_Old_outer surface	1. Amine dried coating (eight months after application) 2. The outer surface was in contact with PU dried coating.
Middle coat_Old_inner surface	1. Amine dried coating (eight months after application) 2. The inner layer of the middle coat.
Topcoat_Old_outer surface	1. PU dried coating (eight months after application). 2. The outer surface was exposed to the atmospheric environment.
Topcoat_Old_inner surface	1. PU dried coating (eight months after application). 2. The inner surface was in contact with Amine dried coating.

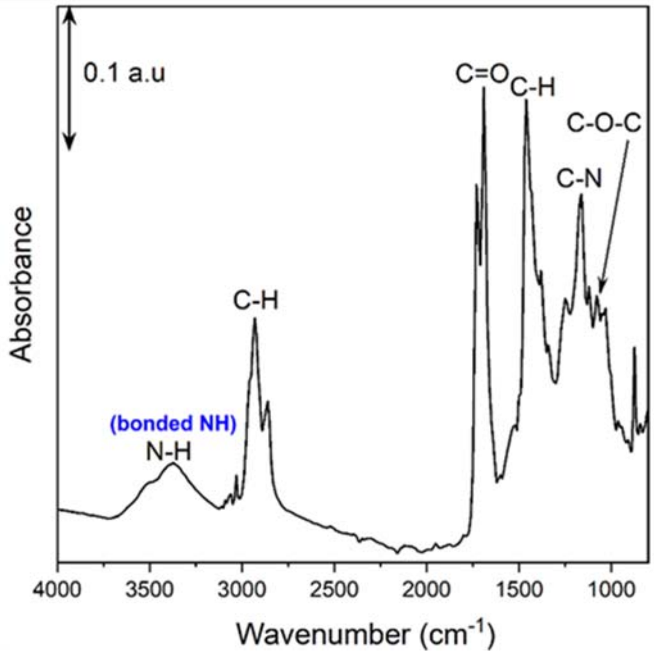

***Figure 2:** FTIR spectrum of **Top coat_Fresh_outer surface** (PU coating).*

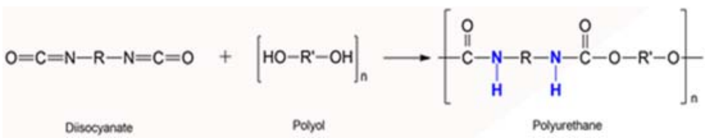

***Figure 3:** The chemical reaction of diisocyanate and polyol-based component to form PU.*

The FTIR spectrum for the **Middle coat_Old_outer surface** is shown in **Figure 4**. It presents the typical functional groups in polyurea [8], except for the free NH functional group observed at ~3600 cm^{-1}. The presence of free NH implies the excess amount of amine-based components in Part B which are not fully reacted during the curing process. The ‘complete’ and ‘incomplete’ reaction in the 2-pack coating of the middle coat is suggested in **Figure 5**. The **bonded NH** displayed in the spectra is assigned to the amide functional group present in polyurea.

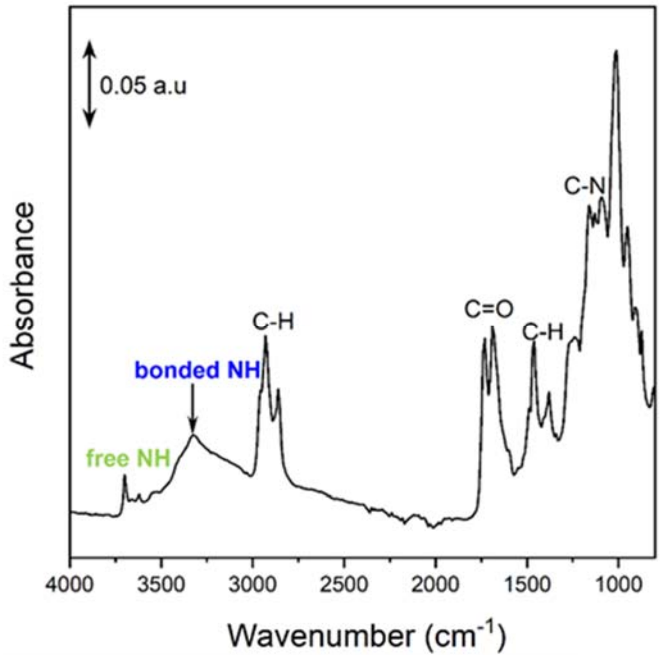

***Figure 4:** FTIR spectrum of **Middle coat_Old_outer surface**.*

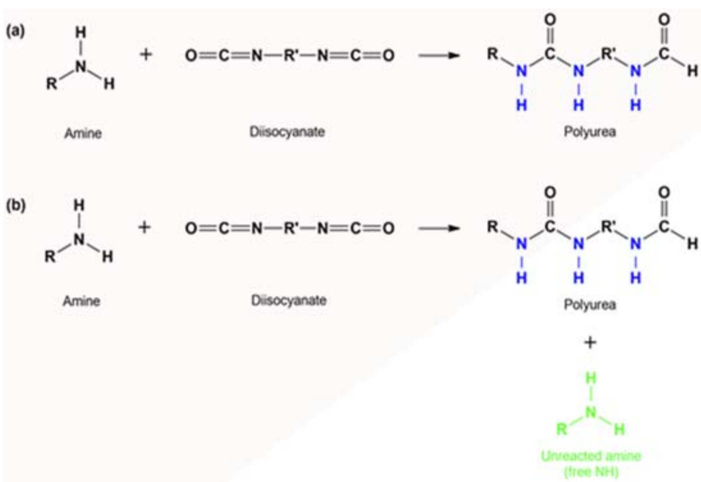

***Figure 5:** The schematic chemical reaction of (a) complete reaction and (b) incomplete reaction of amine and isocyanate to form polyurea. Note: the chemical equations are not balanced and for illustration purposes.*

The FTIR spectra for all samples are shown in **Figure 6**. Comparison between the fresh and old samples through visual inspection is highlighted here. As shown, the **Top coat_Old** sample displays the free NH absorbance band which indicates the presence of a free NH functional group on the top coat after eight months of application. It is suggested that the free NH observed in **the Top coat_Old_outer surface** is very likely originated from the middle coat. The excess amount of amine-based components described earlier may have migrated to the topcoat after some time. The hot and high humidity environment has drawn up these amine-based components from the middle coat to the topcoat and causes the top surface to be sticky.

In general, both FTIR spectra of the topcoat and middle coat exhibit similar functional groups at the same wavenumber regions *i.e.*, N-H, C-H, C=O and C-N. Thus, the comparison between the two spectra through visual inspection is difficult, unless performed by expert personnel. Hence, degree of similarity (*r*) of the two spectra using a numerical approach is performed as a quick yet reliable technique to distinguish any two spectra from one another.

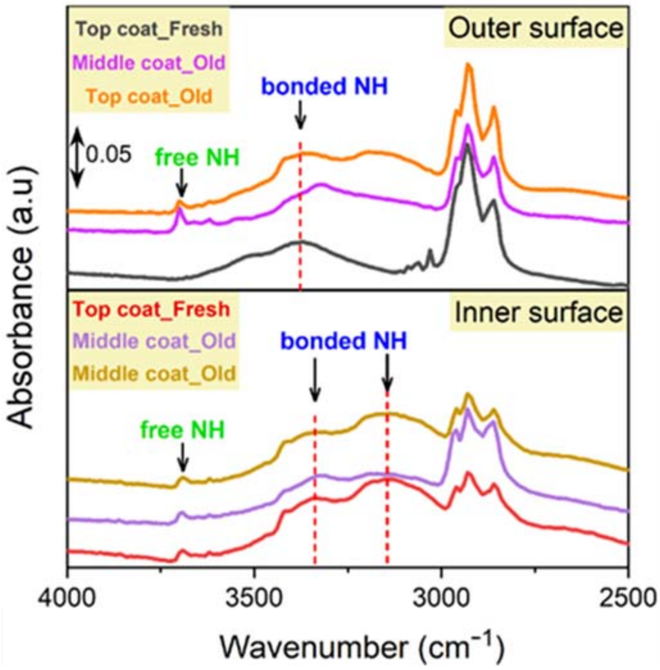

***Figure 6:** FTIR spectra of the topcoat and middle coat.*

Failure analysis 2 – Estimation of the degree of similarity (*r*) of FTIR spectra in reference to IMM FP03:2020

The estimation of the degree of similarity (*r*) values of two spectra (sample in comparison to Reference spectra) is following the FTIR structural tests of IMM FP03:2020 [1]. Several main aspects of FTIR structural tests in IMM FP03:2020 [1] are listed below:

- Estimation of *r* of the sample to that of the Reference shall be performed with *high sensitivity compare* function.
- *High sensitivity compare* function depends on *x*-(wavenumber) and *y*- (absorbance) vectors.
- However, *r* shall not be correlated to the performance of the dried coating. It is only an indication of the resemblance to the Reference.
- *r* shall be within $0 \leq r \leq 1$, with an acceptance threshold of *r* greater than or equal to 0.898
- When $r \geq 0.898$ (or $r \geq 0.900 \pm 0.002$), it indicates the sample has high degree of similarity to the Reference.
- When $r \ll 0.898$, indicates the sample has low degree of similarity to the Reference.

The criteria mentioned above were followed for the following coating failure analysis. The **Topcoat_Old** and **Middle coat_Old** were referred as sample and the **Topcoat_Fresh** was referred as reference. Here, we compare the samples to the Reference using *high sensitivity compare* function as it can distinguish minute changes of *x*-[wavenumber (structural)] and *y*-[absorbance (compositional)] vectors. The simplified interpretation of *r* values of 8-month samples to the fresh sample as in **Table 2** are listed below:

1. Topcoat_Fresh_inner surface ≠ Topcoat_Fresh_outer surface
2. Middle coat_Old_outer surface ≠ Topcoat_Fresh_outer surface
3. Middle coat_Old_inner surface ≠ Topcoat_Fresh_outer surface
4. Topcoat_Old_outer surface ≠ Topcoat_Fresh_outer surface
5. Topcoat_Old_inner surface ≠ Topcoat_Fresh_outer surface

A lower degree of similarity between **Middle coat_Old** and **Topcoat_Fresh** is expected because both coats have different chemical components as indicated in their materials safety data sheets. However, the difference of **Topcoat_Old** from **Topcoat_Fresh** might be owing to the appearance of **free NH** group and significant shifting of the **bonded NH** group to lower wavenumber as can be observed in the FTIR spectra of **Topcoat_Old** after 8-month of application (see **Figure 6** for the differences). These occurrences may indicate the chemical structure of the topcoat as well as its composition changes after a certain time.

***Table 2:** Degree of similarity (r) of 8-month samples in reference to **Topcoat_Fresh_Outer Surface** using high sensitivity compare algorithm*

Sample	*High sensitivity* (IMM FP03) [1]		Reference
	r 4000 – 700 cm^{-1}	*r* 2000 – 900 cm^{-1}	
Topcoat_Fresh_ outer surface	0.999	0.999	Topcoat Fresh outer surface
Topcoat_Fresh_ inner surface	0.368	0.286	
Middle coat_Old_ outer surface	0.631	0.564	
Middle coat_Old_ inner surface	0.326	0.278	
Topcoat_Old_ outer surface	0.636	0.659	
Topcoat_Old_ inner surface	0.354	0.318	

*black font indicates $r > 0.898$ (high degree of similarity)
*red font indicates $r < 0.898$ (low degree of similarity)

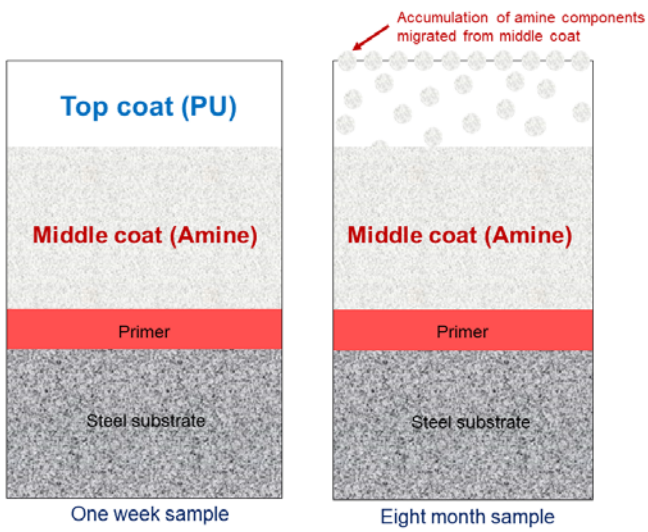

***Figure 7:** Comparison of the fresh (one week) and the old (eight months) samples.*

Conclusions

Failure analyses 1 and 2 demonstrate that the **Topcoat_Old** sample has different components and compositions as compared to the **Topcoat_Fresh** sample. This is due to the amine component that is present on the surface of the **Topcoat_Old** after eight months of application. This amine component is very likely originated from the middle coat, which is in agreement with the *r* value as listed in Table 2. The free NH may have migrated from the middle coat to the surface of the topcoat after eight months of application as illustrated in **Figure 7**. Hence, the repair works is suggested to be targeted not only to the topcoat but also to the middle coat of the coating system. Furthermore, this analysis has shown that the FTIR technique is practical as it provides a quick evaluation test, reliable results, economical and does not need any sample preparation. The utilization of IMMFP03 in this work has demonstrated its practicability and feasibility to be used in coating failure analysis.

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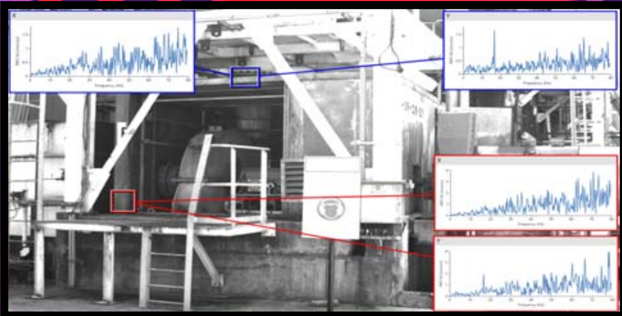
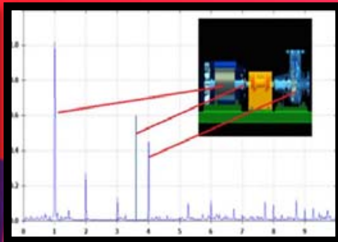
HIGHLIGHTS

- Advanced Vibration Troubleshooting on A Rotating Equipment.
- Application of FTIR Structural Analysis for Dried Coating Failure Investigation in Oil & Gas Industry.
- Utilization of Natural Fiber Towards Structural Applications Under Dynamic Loading Through MWCNT Enhanced Polymer Nanocomposite.





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INSTITUTE OF MATERIALS, MALAYSIA

Suite 515, Level 5, Block A, Kelana Centre Point (Lobby B), No. 3 Jalan SS 7/19, Kelana Jaya, 47301 Petaling Jaya, Selangor.
Tel: +603-76611591

secretariat@iomm.org.my
www.iomm.org.my
+60 18-911 3480
Institute of Materials, Malaysia

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