FAILURE ANALYSIS OF RESIN OF DIFFERENT COATING MATERIALS BY INFRARED SPECTROSCOPY

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Abstract: Different organic and inorganic coating material like Coal Tar Epoxy, Glass Flake Epoxy, Polyurethane, High Build Epoxy, Concrete and Cold Galvanizing are considered. Films / sheets of above coating materials are prepared and are subjected to FTIR and spectrum are recorded. Further, film / sheets of above coating are undergone salt spray test as per ASTM B117 for 2000 hours and FTIR are carried out and spectra are also recorded. IR spectrum of original coating and after salt spray are compared for each coating and assessment about degradation of resin of each coating are made. Finally based on assessment of degradation of resin of each coating, inference are drawn and ranking of coating are established.

Keywords – FTIR, IR Spectrum, Salt Spray, Degradation of resin.

1. INTRODUCTION

Many analytical techniques available to study coating failures, infrared spectroscopy is the most versatile and recent one. The basis of infrared spectroscopy is the interaction of light in the infrared region of the electromagnetic spectrum with matter. The infrared region of the spectrum ranges approximately 0.75 µm to about 500 µm, which puts approximately in the middle of the electromagnetic spectrum. Thus, infrared light is energetic enough to interact with molecular vibrations and infrared spectroscopy is considered a form of vibrational spectroscopy.

The infrared region of the spectrum is further subdivided in to the near infrared, mid infrared, and far infrared regions. Most analytical work is performed in the mid infrared (mid IR) region, which extends from about 2.5 to 25 µm. Rather than expressing the features of an infrared spectrum in the terms of wavelength units (such as micrometers, or microns), it is more common to identify a peak in the spectrum by wavenumber units, or reciprocal centimeters (cm\(^{-1}\)). This is a unit of frequency, and is related to wavelength as follows:

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\text{Frequency (cm}^{-1}\text{)} = \frac{104}{\text{wavelength (micrometers)}}
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An infrared spectrum, then, is really just a plot of the frequency of infrared light versus how much of that light is either transmitted through or absorbed by the sample. Because different groupings of atoms vibrate at different frequencies, and because these frequencies are characteristic of their vibration, it is possible to extract chemical information from an infrared spectrum. Infrared spectroscopy has several uses in failure analysis, which include the followings:

Identification of coating type

- Identification of certain pigments
- Determination of degree of cure for certain coating types
- Determination of mix ratio for certain types of two component coatings
- Detection of contamination
- Detection of coating degradation
- Identifying batch to batch variations

Coatings can degrade under a variety of situations. Some are sensitive to various chemicals, some have upper limits of temperature, and others are sensitive to environmental factors such as heat and sunlight. If the mechanism of degradation is such that chemical bonds are being broken and the structure of the coating is being changed, this might be reflected in changing in the infrared spectrum.

Our current studies are made on different organic and inorganic coating / paint material used to mitigate corrosion of steel structure / pipeline and TMT bars. Film / sheet are made from different organic and inorganic coating material. After proper curing of the film / sheets a portion are cut and reflectance of IR spectrum are recorded. Simultaneously, same film / sheet are subjected to salt spray as per ASTM B117 for 2000 hours. The IR spectra are also recorded for each coating film / sheet after this test is over. The comparative studies are done of IR specters data for each film before and after salt spray and assessments are made about the degradation pattern of different resin system.
In presence of saline water as is the case of a salt spray test the resins degrade and mainly the functional groups like ester, amides, urethanes, ethers etc. are cleaved and new functional groups are created. All the functional groups are not hydrolyzed or cleaved to same extent. For example the ester groups are most susceptible to hydrolysis producing carboxylic and hydroxyl functional groups. On the contrary the ether linkages are very strong and do not cleave easily. Another factor also to consider that the breakage of a functional group does not depend only on its chemical structure but also depends on the nature and packing of the polymer chains to which these functional groups belong. For example the urethane linkage (NHC(O)O) in a polyurethane film are hydrogen bonded to each other and can absorb a high level of physical and chemical stresses before an irreversible bond breakage.

2. MATERIALS & METHODS

2.1 SAMPLE PREPARATION

For glass flake epoxy, high build epoxy, coal tar epoxy and polyurethane films are drawn using airless spray technique by mixing the base and the hardener in the desired ratio. For cement sheet, cement, sand and aggregate are mixed. For cold galvanizing films are made by using brush / rollers. In each case, two numbers of samples (films / sheets) are prepared for FTIR before and after 2000 hrs salt spray.

2.2 DETAILS OF THE APPARATUS

In a conventional IR spectrophotometer, an IR beam is directed through the sample chamber and measured against a reference beam at each wavelength of the spectrum.

IR Spectroscopy has been dramatically improved by the development of the Fourier Transform method.

The heart of an FTIR spectrophotometer is an Michelson Interferometer built around the sample chamber. Radiation from an IR source was directed through the sample cell to a beam splitter. Half of the radiation was reflected from a fixed mirror while the other was reflected from a mirror moved continuously over a distance of about 2.5 micrometers. When the two beams were recombined at the detector, an interference pattern was produced. A single scan of the entire distance took about 2 seconds and was stored in the computer.

3. RESULTS AND DISCUSSIONS

FTIR spectra are given below. There is comparison between Original and after Salt Spray. After salt spray the resin gets degraded and mainly functional groups like ester, amides, urethane are cleaved and new functional groups are created.

For Coal Tar Epoxy

Coal tar epoxy is a three component system comprising of coal tar, epoxy resin and polyamide resin. The cross linked ether linkages peak of epoxy resin is found at 1000 cm\(^{-1}\). The peaks in the region of 1200 to 1500 cm\(^{-1}\) are due to -C = C- stretching of coal tar and N-H bending vibrations of the polyamide cross linker. From the FTIR spectrum, it is clear that the relative transmittances of samples before and after the salt spray test are very close to each other. So it leads to conclude that in this case the resin system is not degraded in the presence of salt spray.
Polyurethanes

Polyurethane coating consists of resin made from the reaction between isocyanates and hydroxyl containing compounds like polyethers, polyesters, castor oils, polyhydric alcohol etc. The polymerization of polyurethane occurs from di- or poly-functional isocyanates and hydroxyl terminated compounds. Fig. shows the FTIR spectra of the as prepared polyurethane coating. Two vibrational bonds, observed at 1219 cm\(^{-1}\) and 772 cm\(^{-1}\), may be assigned to the = CH symmetric vibration and C-H bending mode in aromatic compounds respectively. The weak additional vibrational bond at 719 cm\(^{-1}\) in the salt sprayed polyurethane corresponds to C-H vibrational bond of alkynes. The appearance of such peak signifies the interaction between polyurethane and salt spray and indicates slow corrosion against salt spray.

Concrete

Concrete has proven itself as a principal building material of recent time and consists of hydrated calcium aluminium silicate. Concrete is strongly alkaline in nature and most widely used as a protective material for steel against acid media. Acid media may readily react with calcium in the complex molecule of concrete. Our FTIR study on concrete coating reveals that there is only single vibrational bond at 772 cm\(^{-1}\) that corresponds to C-H bending mode. The salt spray processed concrete coating exhibits no additional peak, but a sharp decrease in the transmittance spectra at 772 cm\(^{-1}\) has been observed. Such changes in the transmittance spectra can be attributed to the interaction between concrete coating and salt spray that leads to formation of new C-H bonding.

Cold Galvanizing

Galvanization of steel is being carried out in the molten zinc bath and seems to one of the potential method to protect steel from corrosion. FTIR spectra obtained from as prepared cold galvanized steel is found to consist of several vibrational bonds. The weak vibrational bands between 1000 and 1080 cm\(^{-1}\) can be assigned to C-O-C and C-C symmetric stretching mode of vibration. Weak bands at 1288, 1389 and 1566 cm\(^{-1}\) may be assigned to C-O stretching.
C-H vibrational bond and conjugated C=N vibrational bond. After salt spray, transmittance of the galvanized coating changed considerably that leads to conclude that galvanization coating degraded significantly after salt spray.

4. CONCLUSION

The electrochemical reaction occurring at the metal – paint film interface generates hydroxyl ions and the pH of the medium at the interface reaches to about 9-10. Hence the resins which can withstand alkaline conditions without bond cleavage should be very resistant to salt spray, and vis-a–vis the corrosion.

A pure hydrocarbon resin like polyethylene have only C-C and C-H bonds and have no polar acidic functional groups that might be attacked chemically by the generated OH ions and should offer a good resistance to salt spray. However, another factor to be considered here is the necessity of the presence of polar hydroxyl functional groups along a polymer chain for a good level of adhesion to metal. Unless and until a polymer film have a good wetting of the metal surface, the corrosion resistance performance is not developed.

Polymer films having pendant hydroxyl groups in their original structure have the possibilities to offer higher level corrosion resistance since the film adheres so strongly to the metal surface the movement of the ions responsible for corrosion through the metal- polymer film interface are highly hindered.

The glass flake epoxy system is a chemically cross linked structure with much less porosity of the cured film. Also at the same time the epoxy resin does have pendant polar hydroxyl groups. The factors of less porosity and higher metal adhesion synergistically act and a very high level corrosion resistance is offered by such systems. The cross linked structure of epoxy- polyamide contains ether cross links and such chemical links are inert to alkaline conditions and is also another big factor for the extraordinarily good corrosion resistance of epoxy- polyamide systems.

The coal tar- epoxy system is below glass flake and epoxy hi- build & polyurethane system and offers a moderate resistance to corrosion for the reasons as discussed.

Summarizing all the above factors the following order of resistance to corrosion is found to offer by the different systems studied:


REFERENCES