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ANALYSIS OF ACCELERATED ORGANIC COATING MATERIALS USED IN CONJUNCTION WITH BURIED PIPELINE BY FTIR

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Abstract

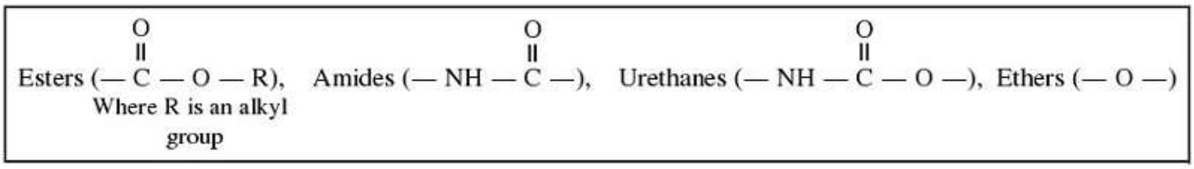
Pipeline coating material such as coal tar enamel, coal tar tape, coal tar epoxy, high build epoxy, polyurethane, cold applied PE tapes and 3 layer polyethylene are prepared as tape / film and FTIR spectrum are recorded. These seven coating material are subjected to accelerated cathodic disbondment test as per ASTM B117 and ASTM G8 Standards. Further, FTIR spectrum are recorded for these disbondment portion of coating. Finally assessment are made about degradation of different resin systems.

Introduction

The current studies are basically "STUDIES OF THE ACCELERATED CORROSION RESISTANCE OF VARIOUS PIPELINE COATINGS BY ASTM B 117 METHOD AND ASSESSMENT OF THE EXTENT OF CHEMICAL DEGRADATION OF THE RESIN STRUCTURES BY FTIR AND ITS CORRELATION TO THE COATING PERFORMANCE IN THE ACCELERATED TESTS" and were made on different types of cured paint films/polymeric tapes. The paint film was applied on abrasive blast cleaned mild steel substrate up to cleanness level of SSPC SP10 and surface anchor profile of 60 to 80 µm and after application and proper curing of the films, a portion was cut out and reflectance FTIR spectrum was recorded. Simultaneously, a set of panels were subjected to Salt spray test as per ASTM B 117 for 2000hrs and cathodic disbondment test as per ASTM G-8. The FTIR spectrum were also recorded for each paint film after this test was over. The comparative studies were done of the FTIR spectra data for each film before and after the salt spray test and assessments were made about the degradation pattern of the different resin systems.

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 (Organic Pictorial Structures given in Figure – 1) etc. are cleaved and new functional groups are created. All the functional groups are not hydrolyzed or cleaved to the 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 it depends on the nature and packing of the polymer chains to which these functional groups belong. For example the urethane linkage (NHCOO) in a polyurethane film are hydrogen bonded (as shown in Figure 1) to each other and can absorb a high level of physical and chemical stresses before an irreversible bond breakage.

During cathodic protection with impressed current, under some conditions, excessive amount of CP current to a coated pipeline structure may damage the coating. This is called as cathodic disbondment. The current flow promotes water and ion migration through the coating and an increase in the electrolyte pH at the pipe surface. If the polarized potential is sufficiently negative, hydrogen can also evolve in the form of gas bubbles on the pipe surface. All of these processes are detrimental to coating and promote degradation and disbondment of coating.



$$\text{Esters }(-\overset{\overset{O}{\|}}{C}-O-R),\ \text{Amides }(-NH-\overset{\overset{O}{\|}}{C}-),\ \text{Urethanes }(-NH-\overset{\overset{O}{\|}}{C}-O-),\ \text{Ethers }(-O-)$$

Where R is an alkyl group

Figure - 1

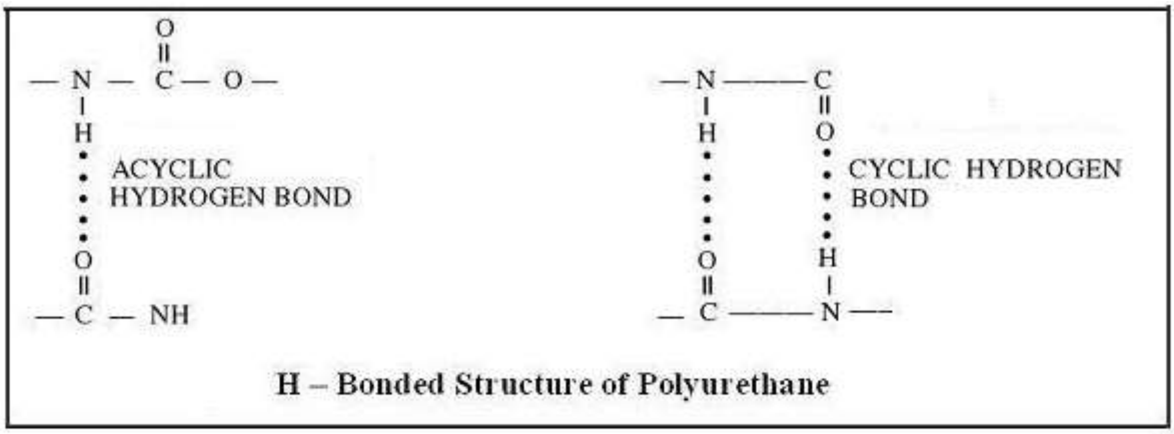


Figure – 2

FTIR Spectroscopy

Of the many analytical techniques available for the study of 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 from approximately 0.75 micrometers to about 500 micrometers, which puts it 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.

An infrared spectrum, 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 well known, it is possible to extract a great deal to 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

Conditioning of Samples before Test

(i) After 2000 hrs. exposure in salt spray (as per ASTM B 117) and followed by cathodic disbondment test (as per ASTM G-8) for 28 days maintained at – 1.5 volt, each coating material is removed from the corroded area and is subjected to Fourier Transform Infrared Spectroscopy analysis which is again compared with the original coating materials.

(ii) This test is carried out to get an idea about the changes in the morphology of the coating material and to find the degradations of the coating materials at the site of corrosion.

Details of Instrument

(i) In a conventional FTIR spectrophotometer, a sample FTIR beam is directed through the sample chamber and measured against a reference beam at each wavelength of the spectrum.

(ii) FTIR Spectroscopy has been dramatically improved by the development of the Fourier Transform method.

(iii) The heart of an FTIR spectrophotometer is a Michelton Interferometer [85] built around the sample chamber. Radiation from an FTIR source was directed through the sample cell to a beam splitter. Half of the reaction 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.

(iv) The performance of an FTIR is dramatically superior to that of conventional instruments. Generally, only a small current of sample will produce an excellent spectrum in a fraction of the time.

Method followed for FTIR Spectroscopy

(i) There are several ways of obtaining an infrared spectrum, but the two most common techniques for studying coatings and coating failures are the potassium bromide pellet method, and the attenuated total reflectance (ATR) method. Here the characteristics of coating failure has been analyzed with ATR method.

(ii) In ATR, the sample was firmly pressed against a special crystal, and the assembly was placed in the optical compartment of the spectrometer in such a way that the infrared beam is focused into the crystal and bounces off of the surface of the sample in contact with the crystal. This can be accomplished with only one reflection (known as a single bounce device), or numerous reflections can occur over the length of the crystal. In either event, a spectrum obtained in this fashion is known as a reflectance spectrum, and is characteristic of the composition not of the bulk sample, but only of the top 2 or 3 microns of the sample surface.

Discussions on Results

3- Layer Polyethylene

The bands at 2900cm, 1400-1700 cm are arising out of the C-H stretching and C-H bending vibrations respectively. The peaks in the region of 700-1000 cm are of = C-H

Bending vibrations originating from the low percentages of olefin end groups of the polymer chains. Since the relative intensities or peak height of all the peaks are found higher in the processed film, than the original one it simply means that a considerable resin degradation has taken place and as a result the concentration of C- H bonds have increased. In each cleavage of a C-C bond along a chain two additional C-H bonds are created.

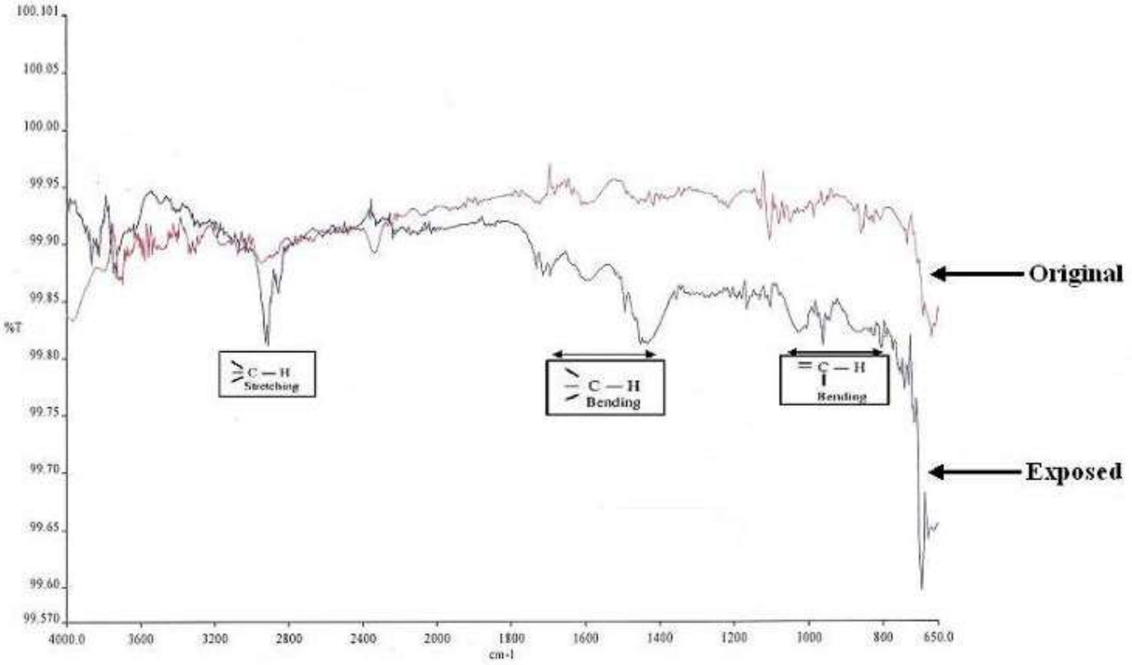


Figure – 3

Coal Tar Enamel

Coal tar enamel contain cyclic aromatic rings and hydroxyl (OH) as functional groups. The FTIR spectra detects the presence of OH groups (3200cm), C-H stretching (3000cm) and C=C stretching (1400-1600 cm). Since the relative intensities of the peaks before and after processing are more or less identical, the degradation of the coal tar enamel if any is very small. Since Coal Tar Enamel having condensed benzene ring type structure required high energy for clearage of bond (ring structure), it should offer a very good resistance to salt spray test.

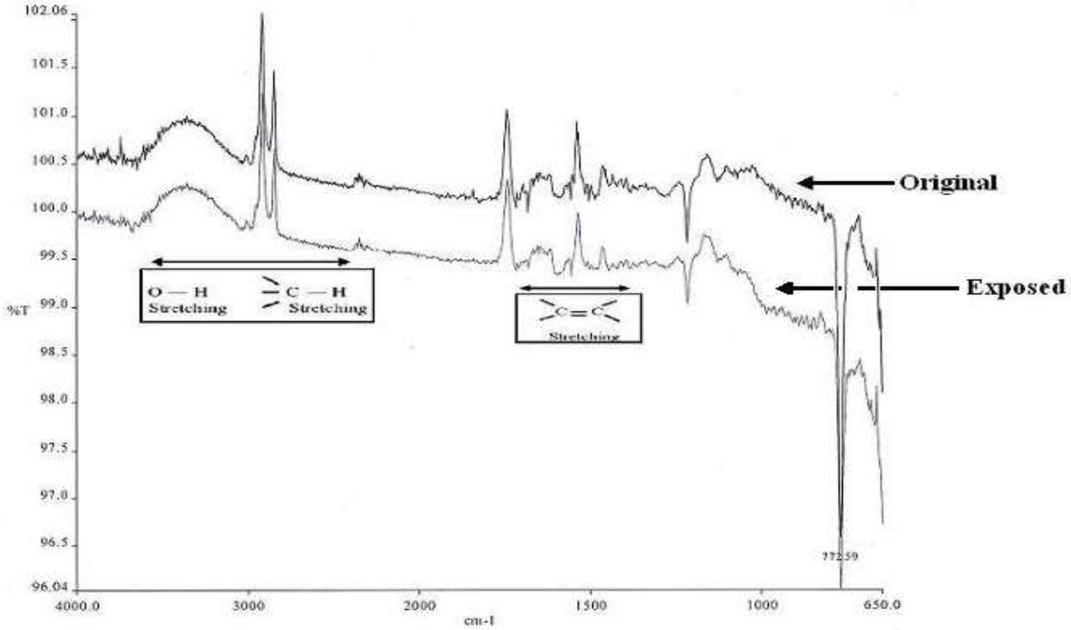


Figure – 4

Coal Tar Epoxy

It is in fact a 3 component system comprising of coal tar, epoxy resin and polyamide resin. At 3200 cm as usual the peak of OH functionality is observed. The cross linked ether linkages peak of epoxy resin is found at 1000cm. The peaks in the region of 1200 1750 cm are due to C=C stretching of coal tar and N-H bending vibrations of the polyamide cross linker.

Here also the relative intensities of the peaks are about the same before and after the salt spray test and again it leads to conclude that in this case also the resin system is not all considerably degraded.

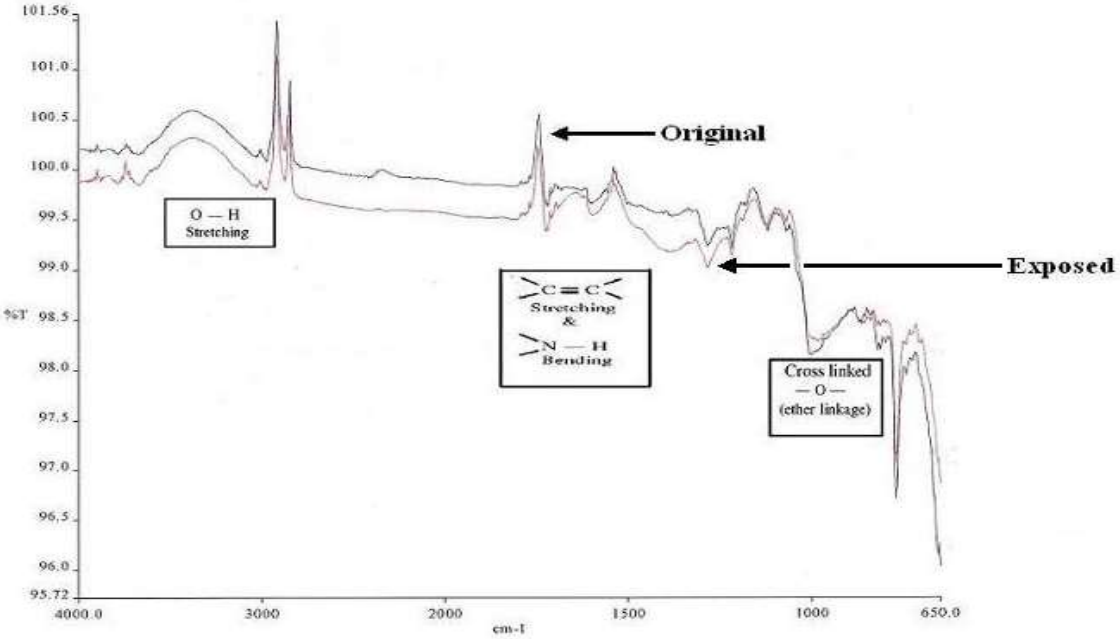


Figure – 5

Coal Tar Tape

The spectra's are very similar to coal tar enamel and the peak heights before and after the experiment are found too close. This indirectly reveals its stability is extremely good and should also offer high level of resistance to corrosion.

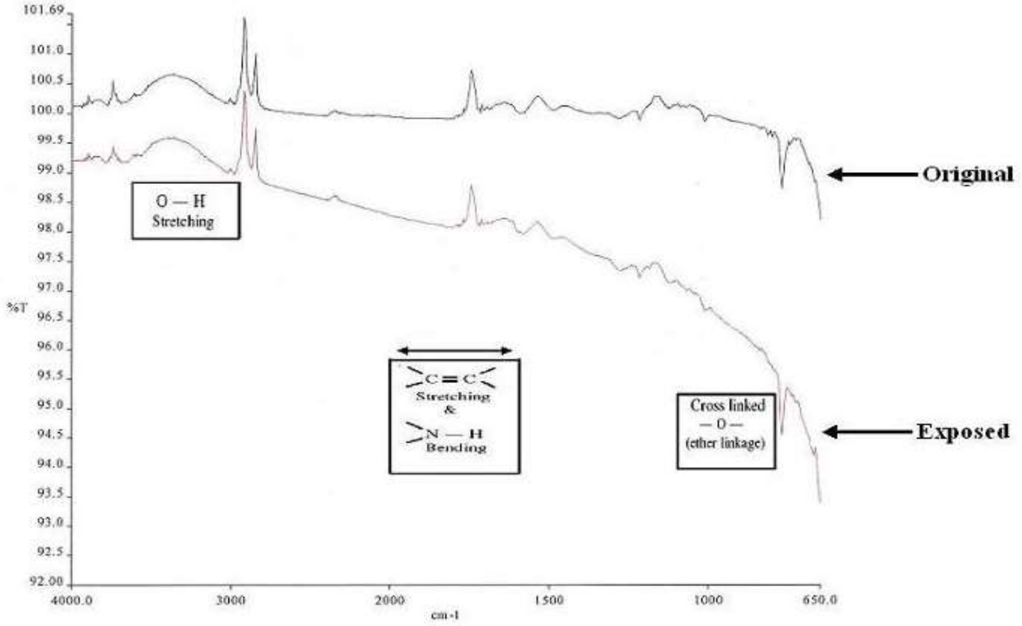


Figure – 6

Cold applied polyethylene

The origin of the peaks is same as that explained for 3 layer polyethylene but in contrast to 3 layer, in this case the resin system is also found degraded to a very little extent as the relative peak intensities are very close here.

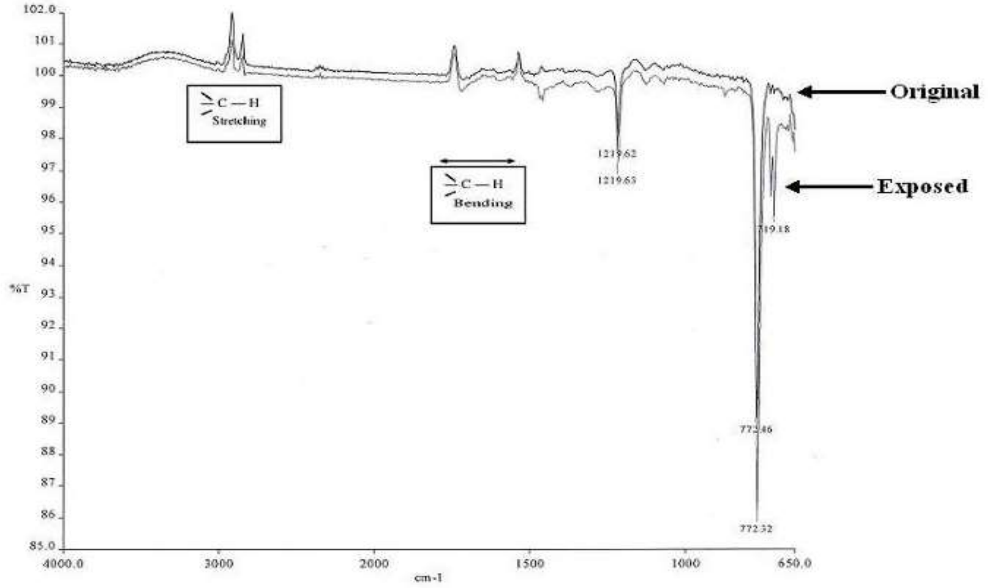


Figure – 7

High – build polyurethane

This system is found to suffer most in the salt spray test. The peak at 3000 cm is for C-H stretching, the peaks between 1500 to 1750 cm are originating from the N-H bending and C=O stretching and the peak at 1050 cm is of the C-O stretching. The urethane NHCOO group contains a N-H linkage, a C=O linkage and a C-O linkage and all the peaks are found in the spectrum. However , the intensities of the peaks of C=O, N-H and C-O all are considerably increased after processing revealing a high level break-down of the polyurethane resin in saline water and as a result its corrosion resistance should not be very good.

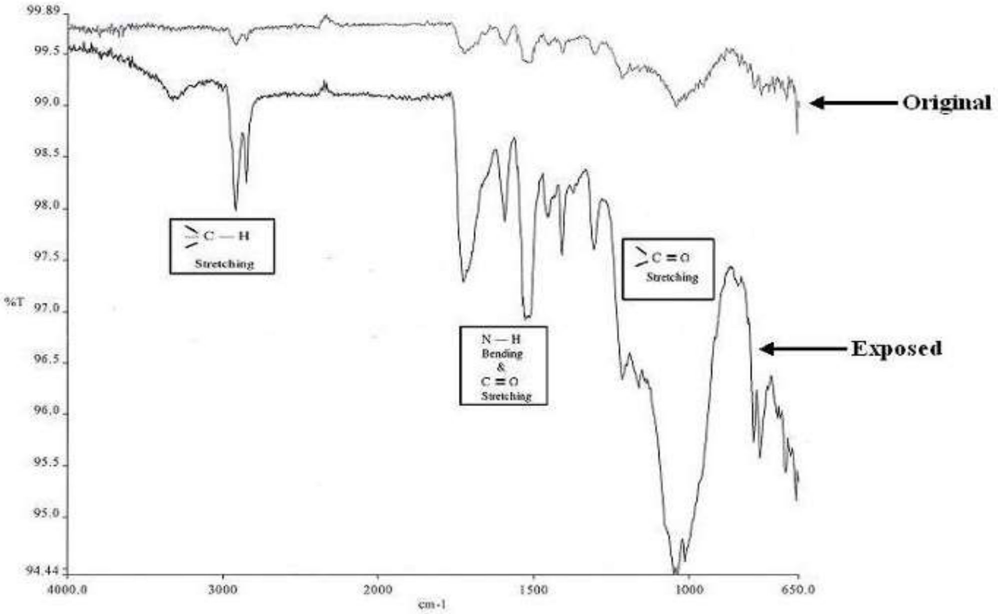


Figure – 8

High Build Epoxy

The high build epoxy system possibly offers a very compact and cohesive resin structure in view of the fact that the intensities of the peaks of the functional groups are very small and which can only result if the functional groups are not exposed to the FTIR beam during its pathway or the structure is so compact that the normal stretching, bending vibrations are very much inhibited. The free volume /porosity of such films are very less also to allow such bond vibrations.

The peak at 3000cm is very weak and the N- H bending and C-O stretching vibrations at 1550 – 1650 and 1070-1100 cm respectively are also weak in their intensities. Since the relative peak intensities are also too close in this case the extent of resin degradation is also too limited and must offer a very high level resistance to corrosion.

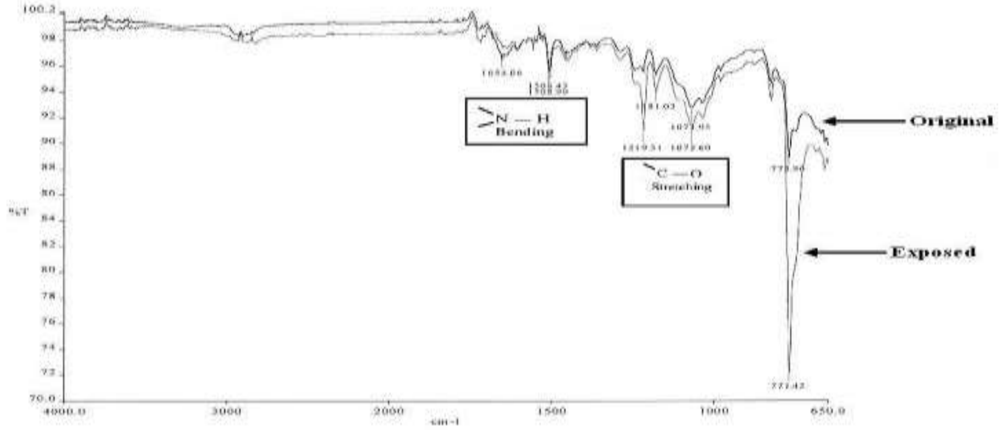


Figure – 9

Inference

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, cathodic disbondment 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 physisorption to metal. Unless and until a polymer film have a good wetting of the metal surface, the corrosion resistance performance is not developed. The cold applied polyethylene possibly lacks the said phenomena of physisorption to metal and as a result its performance is found poor. However 3 LPE application wets the surface to a better extent and have shown better result in regard to corrosion resistance performance.

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. Such is the case for coal – tar enamel/ coal-tar tape and although they are mostly hydrocarbon based (resembling polyethylene) but have got the polar hydroxyl groups which provides an additional higher level anchorage to the base metal compared to polyethylene and hence it stands in better stead than polyethylene in regard to salt spray resistance.

The high build 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 an another big factor for the extraordinarily good corrosion resistance of epoxy- polyamide systems.

The polyurethane system cannot withstand the alkaline condition because the carbonyl groups of the polyurethane functional group (NHCOO) is a potential side of the nucleophillic attack by the OH ions and which leads to alkaline hydrolysis / degradation of the entire resin structure. In view of excessive degradation of resin, the polyurethane system is very much prone to corrosion as the result of FTIR studies already reveal.

The coal tar- epoxy system is in the midway of coal – tar enamel and epoxy hi- build 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:

(a) Hi- Build epoxy (b) Coal tar epoxy (c) Coal tar enamel or tape (d) Three layer polyethylene (e) Cold applied polyethylene (f) Polyurethane

References

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Foot note

ASTM – American Standard and Testing Methods
SSPC – The Society for Protective Coating
NACE – National Association of Corrosion Engineers
ISO – International Organization of Standardization