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Case Study

Vibrational spectroscopy: an effective technique for characterization and failure analysis of automotive materials

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Abstract

Fourier transform infrared spectroscopy (FTIR) is used to identify compounds very rapidly and conclusively. Plastics, rubbers, fillers, paints, coatings, resins, adhesives and blends are some examples of compounds which can be identified by using FTIR. The sensitivity of FTIR enables detection of contamination present in very small quantity which makes it a vital tool for quality control and quality assurance applications. Thus, FTIR plays an important role to compare batch-to-batch products for meeting quality standards. This paper presents application of FTIR as an effective tool for evaluation of materials. A few case studies of analysis of variety of automotive materials including contaminate analysis of brake fluid, fabric sample used in roof lining of passenger car, painted panel of fuel tank and compatibility of material with alternate fuel using FTIR are presented. The evaluation using FTIR for the above cases provided objective evidences for confirmation of probable causes for material failure.

Keywords: Fourier transform infrared spectroscopy; automotive materials; vibrational spectroscopy, failure analysis; polymers.

Introduction

FTIR spectroscopy is used to identify compounds very rapidly and conclusively. Plastics, rubbers, fillers, paints, coatings, resins, adhesives and blends are some examples of compounds which can be identified by using FTIR[1-4]. Organic and Inorganic compounds can also be determined by using FTIR. Sample in any state i.e. solids, liquids and gaseous can be analysed with minimal sample preparation[5]. It can be applied across all stages of the components lifecycle which includes design, manufacture, and failure analysis. Functional group and molecular structure are identified with the infrared absorption bands[6]. This technique depends on measurement of the absorption of infrared radiation by the sample component versus wavelength[7].Infrared region is subdivided into three regions, near, mid and far region. Most of the infrared region used for identification of molecule is originated from the mid infrared region. Wave numbers, 4000-400 cm^{-1}[8,9].

When a sample is irradiated with infrared radiation it absorbs some infrared radiation which excites the molecules into a higher vibrational state causing molecular vibrations. Light absorbed by any chemical bond will vibrate at a specific frequency now if this infrared frequency matches with the vibration frequency of an atoms bonded together, the light will be absorbed. Energy difference between the ground state and excited vibrational states is a function of the wavelength of light absorbed by a particular molecule. A plot of absorbance (or transmittance) of the radiation by the molecule versus wavelength (or frequency) where frequency is represented by reciprocal of centimetre is called infrared Spectrum. Every sample has a unique infrared spectrum and infrared spectrum is considered as compound's fingerprint. The wavelengths that are absorbed by the sample are characteristic of its molecular structure[10]. Strength of the bond corresponds to the absorbance of the frequency i.e. stronger bonds absorbs at higher frequencies and vice-versa. Every functional group absorbs at its own frequency[11-14].

For quantitative analysis Attenuated total reflectance (ATR)-FTIR is successfully used. Non-destructive analysis can be performed using ATR-FTIR;. It is a precise measurement technique and does not require any other external calibration. The ATR accessory is made of polished surface of diamond, germanium and zinc selenide (ZnSe). Infrared reflection is attenuated when the beam of rays penetrates a few micrometres deep into the sample. ATR accessory requires good contact with source, but that is easy for most polymers, and the benefit is that no sample preparation is required[15,16]. Therefore, powders, films, gels and even polymer solutions can be characterized very effortlessly. FTIR is also used in environmental studies. It gives significant amount of compositional and structural information. The nature of pollutant can also be determined by FTIR analysis. Continuous air pollutants analyser (SO_2, NO_2, O_3, NH_3), on-line gas chromatography (GC) are the simple real-time instruments which are used to measure gas pollutants. Several sensors are also used to analyze multiple gas pollutants simultaneously[17,18].

The possibility of quality control in the polymer industry have been enhanced by introduction of FTIR. Even the contaminants present in trace amount can be identified because of its sensitivity making it an appropriate tool for quality control and quality assurance applications. A pyrolysis technique followed by Infrared spectroscopy has been a method of choice for characterizing plastics, rubbers and their derivatives for batch-to-batch comparisons to meet quality standards i.e. purity assessment[19]. Examples of application of infrared spectroscopy in failure analysis have recorded in many studies. Spectra for the identification of some additive in automotive industries are available. A recent atlas of plastic additives contains more than 700 spectra with description. In nutshell, apart from polymer identification, FTIR has numerous applications for trace level analysis involving samples in various forms like, resins, composite materials, extracted solvents for leached-out contaminants, unknown solvents and additives[20].

Present paper describes some case studies which signifies the versatile application of FTIR technique. The case studies presented include simple case such as identification of contaminant by matching of spectra of sample with inbuilt library, to the objective evaluation of suspected material in the sample matrix using spectral matching with library and evaluation of spectra for signals at specific wavelength. A case study involving complex failure analysis case including preparation of samples simulating probable scenario and then identifying the cause of failure through detailed analysis is also presented.

Case 1: Contamination of Brake fluid

Case study Background: Brake fluid is a safety critical component of the automobile braking system. Any contamination in the brake fluid can lead to compromised performance during its application. The brake fluid sample under test has shown some degradation in terms of its physico-chemical properties indicating contamination of the same (Figure-1).

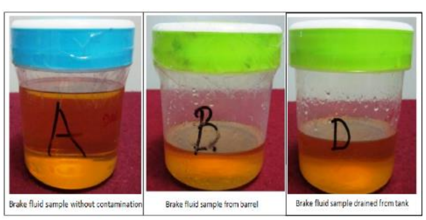

Figure-1: A-Brake fluid sample without contamination, B-brake fluid sample from barrel and D-brake fluid sample drained from tank.

Objective: To identify the contaminants present in brake fluid sample from barrel and drained from tank.

Methodology: Brake fluid sample without contamination, brake fluid sample from barrel and brake fluid sample drained from tank were analysed using Miracle ATR accessory in spectral range 4000- 400cm^{-1}. The FTIR spectrum in %Transmittance (%T) was interpreted. The obtained FTIR Spectra were compared with the inbuilt Lubricant Library software and then searched for the best spectral match.

Results and Interpretation: FTIR spectrum of Brake fluid sample without contamination was compared with inbuilt lubricant library and the best match was found with the spectra of Brayco 791 Hydraulic fluid. Likewise, FTIR spectrum of Brake fluid sample from barrel was compared with inbuilt lubricant library and the best match was found with the spectra of Brayco 746 as a Hydraulic Fluid and Cosmoline 1049 as Lubricating oil which is used as internal combustion Engine preservative. Similar pattern of FTIR Spectra was observed for Brake fluid sample drained from tank and Brake fluid stored in polyethylene bag. FTIR Spectra of Cosmoline 1049 from Library is presented in Figure-2. Overlay of spectra of brake fluid sample without contamination, Brake fluid sample from barrel and Brake fluid sample drained from tank is presented in Figure-3 and Figure-3 is the zoom version representing the peak which is specific to cosmoline oil.

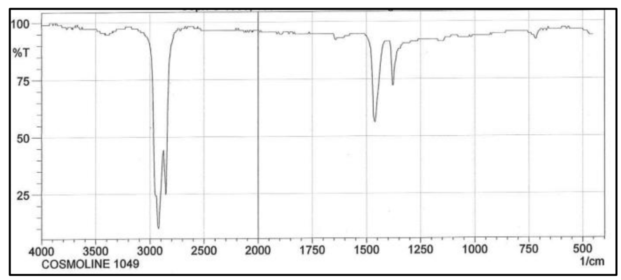

Figure-2: FTIR Spectra of Cosmoline 1049 from Library.

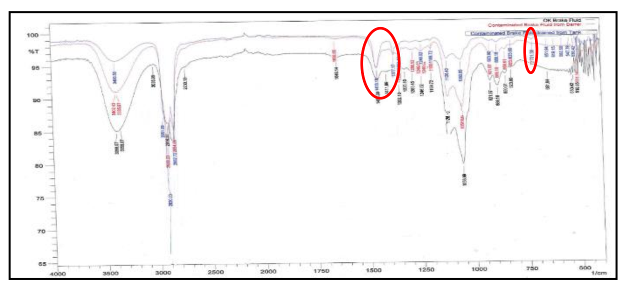

Figure-3: Overlay of all spectra.

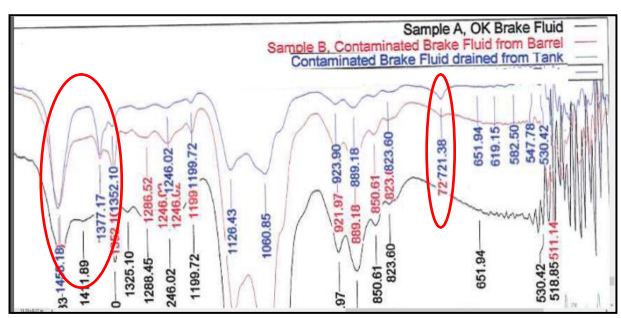

Figure-3: Zoom View of Overlay of all spectra.

Conclusion: Cosmoline 1049 (Lubricating oil used as Internal Combustion Engine preservative) was identified as the contaminant in brake fluid sample from barrel andbrake fluid sample drained from tank.

Case 2: Identification of cause of colour dots on fabric sample

Case study Background: Appearance of vehicle interior's ceiling has a finished look. It is covered with a various types of fabrics material which serves a purpose of insulating the car from the cold, muffling noise and any other vibrations from the outside. It gives a finished look to the vehicle.Brown colour spots were observed on sample of roof lining interior material of the car, received for analysis (Figure-5). Contamination on the fabric of roof lining has negative impact on appearance of the vehicle interior.

Objective: To identify the source of contaminants present on the fabric of roof lining material.

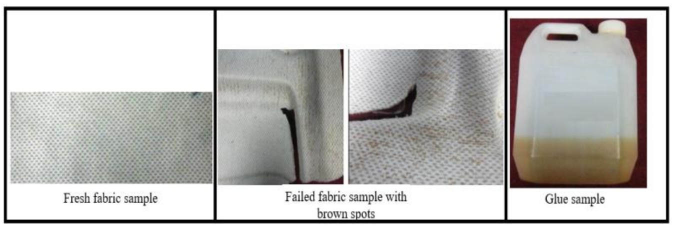

Figure-4: Fresh sample, failed fabric sample with brown spots and Glue sample.

Methodology: Fabric sample without brown spots (Figure-5), Fabric sample with brown spots (Figure-7) and glue sample used for pasting Fabric (Figure-8) were analysed using Miracle ATR accessory in spectral range 4000 – 400cm^{-1}.

Results and Interpretation: FTIR spectrum of fabric sample was compared with Sadtler spectral Library and the best match was found with the spectra of polyester (Figure-9). Similarly, FTIR spectrum of glue sample was compared with Sadtler spectral Library and the best match was found with the spectra of polyurethane (Figure-10). The FTIR spectrum of Fabric sample without brown spots was subtracted from Fabric sample with brown spots and the obtained spectra was compared by overlaying with the spectra of glue sample (Figure-11).

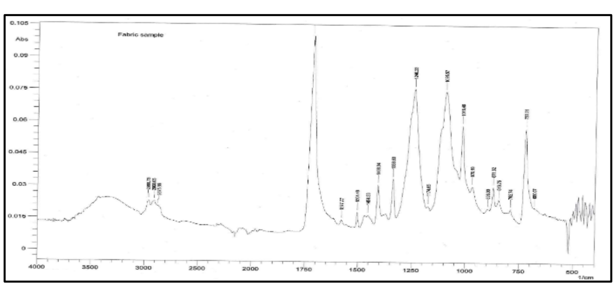

Figure-5: Fabric sample.

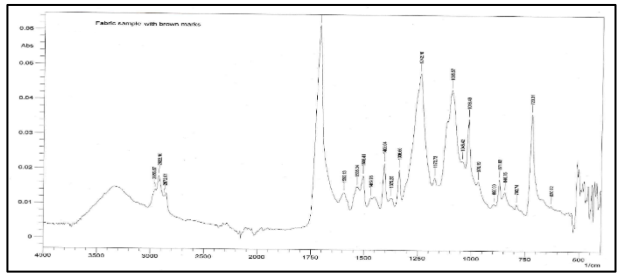

Figure-6: Fabric sample with brown spots.

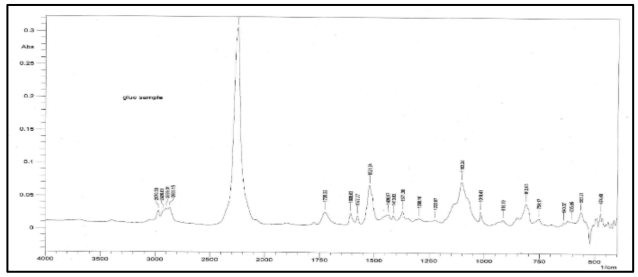

Figure-7: Glue sample.

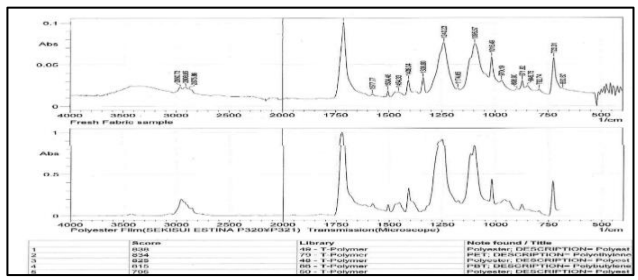

Figure-8: Library comparison: fabric sample matching with Polyester spectra.

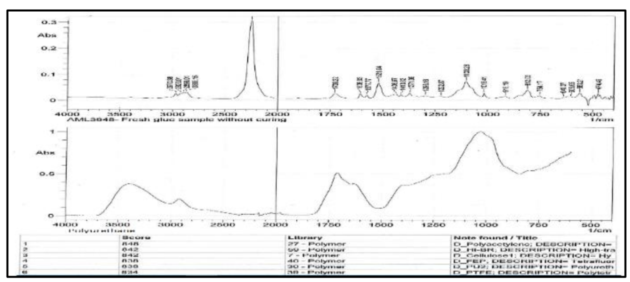

Figure-9: Library comparison: glue sample matching with Polyurethane.

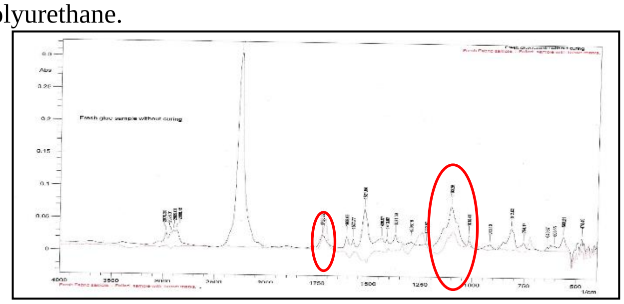

Figure10: Subtraction of Fabric sample with brown spots from Fabric .

Conclusion: Brown spots on the fabric sample showed the presence of glue material i.e. polyurethane.

Case 3: Identification of traces of elastomers leached into fuel

Case Background: Alternative fuel such as alcohol blended with gasoline is considered as a potential alternate fuel to gasoline due to its reduced exhaust emissions from vehicle. Present vehicular fuel system is designed with gasoline as fuel for combustion. It is, therefore, necessary to understand impact of alcohol blended gasoline on polymeric materials used in fuel system components. A study on impact of M15 fuel (15% ethanol in gasoline) was conducted to evaluate impact on polymeric material like Fluoroelastomers (FKM).

Objective: The objective of present work was to ascertain presence, if any, of the leached out material in M15 Blend (82% Reference Gasoline + 15% Methanol + 3% Coupler) after ageing.

Methodology: FKM sample was immersed in M15 Blend for a specific time period. FKM polymer, M15 Blend and Residual M15 blend after immersion of FKM were analysed using Miracle ATR accessory in spectral range 4000- 400cm^{-1}.

Results and interpretation: FTIR spectra of FKM (Figure-12) was recorded before immersion in M15 blend. Likewise FTIR spectra of M15 blend (Figure-13), Residual fuel after FKM immersion in M15 Blend (Figure-14) and Residual fuel after FKM immersion in M15 Blend (Figure-15) were recorded.

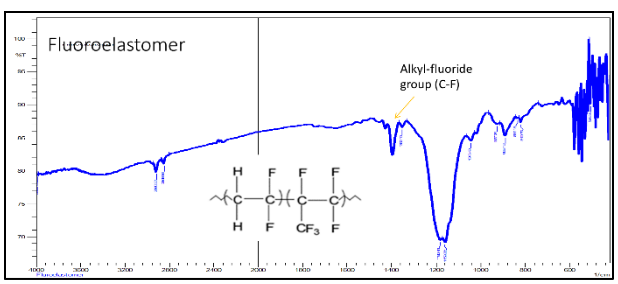

Figure-11: FKM before immersion in M15.

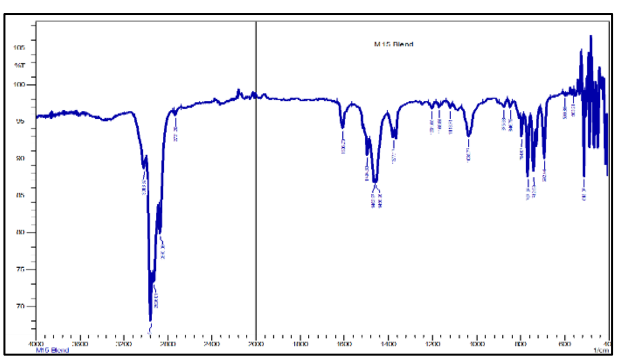

Figure-12: Methanol blended gasoline-M15.

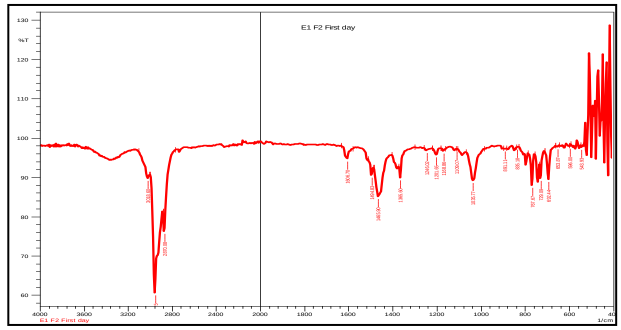

Figure-13: Residual fuel after FKM immersion.

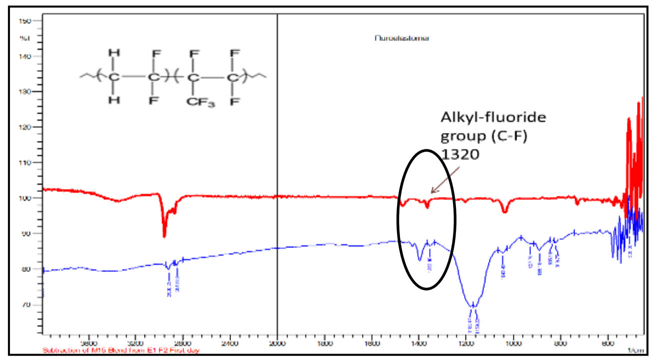

Figure-15: Subtraction of M15 Blend from Residual fuel after PA FKM immersion.

Conclusion: It was observed that some traces of FKM polymers is present in M15 blend. Above exercise explains and confirms leaching of polymer material in M15 blend.

Case 4: Route cause analysis of impressions found on painted panel

Case Background: The fuel tank of a two wheeler vehicle has a finished appearance but it was found to have some impressions. This is undesirable from appearance point of view. Impressions were observed on the painted panel of two wheeler vehicle, which were presumed that they were because of rexine of seat cover. Seat cover is a sandwich of Rexine, resin and fabric material (Figure-16). Adhesive (resin) was used for pasting Rexine and fabric. The probable source of impression is objectively evaluated in this case study.

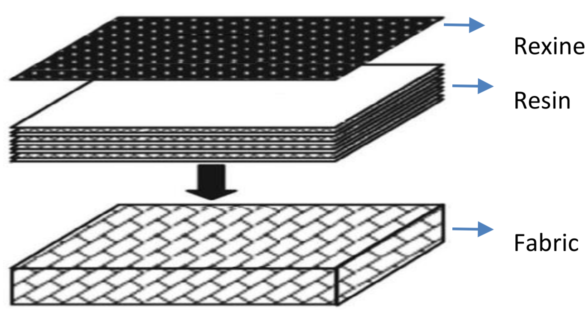

Figure-16: Schematic diagram of seat cover.

Before After

Figure-17: painted panel before and after simulation.

Objective: To evaluate the source of impressions on painted panels.

Methodology: Painted panel (Figure-17) and components of seat cover i.e. Rexine sample (Figure-18), Fabric sample (Figure-19) and PVC resin Geon 124 (Figure-20) were analysed using Miracle ATR accessory in spectral range 4000- 400cm^{-1}. Simulated samples were prepared in laboratory to obtain the impressions of rexine and fabric sample on painted panel. Painted panel sample after simulation with rexine and fabric were also subjected to FTIR using Miracle ATR accessory in spectral range 4000-400 cm^{-1}. Evaluation of subtraction of spectra of simulated samples of painted panels with components of seat cover and painted panel without impression was carried out.

Results and interpretation: The spectra obtained for the materials above are compared with Sadtler spectral Library. Acryloid K-175 and Scopacron 10SB - Acrylic based polymer are present in Painted panel before simulation (Figure-21-22). Polyvinyl chloride (PVC) polymer and plasticizer were confirmed in Rexine sample (Figure-23). In fabric sample the presence of Poly (ethylene terephthalate), Polyester fibre, Melinex SUN/92 were confirmed (Figure-24). Polyvinyl chloride (PVC) homopolymers, Geon Resin was identified in PVC Resin Geon 124, GRN (Figure-25). Similarly, KodaFlex DOP Mixture of Bis (2-ethyl hexyl) phthalate and Adhesion promoting plasticiser for PVC resins and copolymers were confirmed after subtraction of Painted panel before simulation from painted panel after simulation with impressions of Rexine (Figure-26).

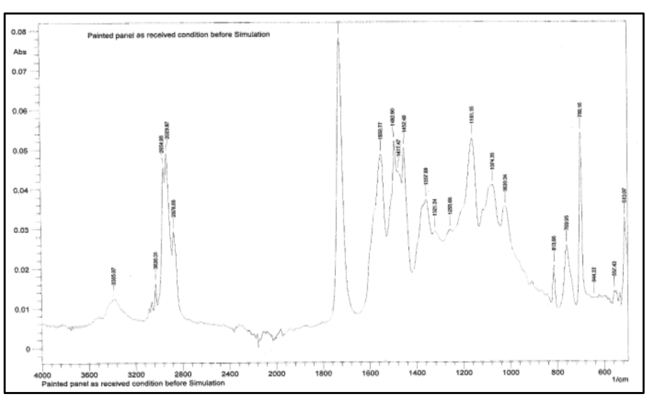

Figure-17: Painted panel before simulation.

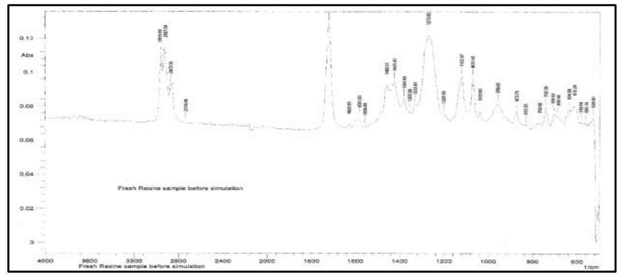

Figure-18: Rexine sample before simulation.

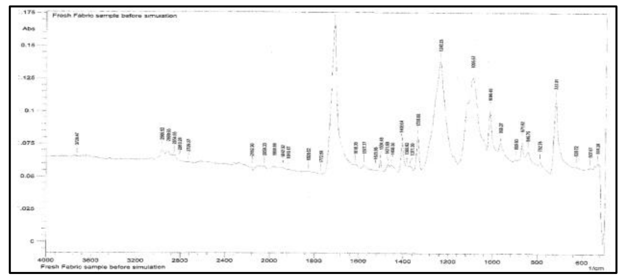

Figure-19: Fabric sample before simulation.

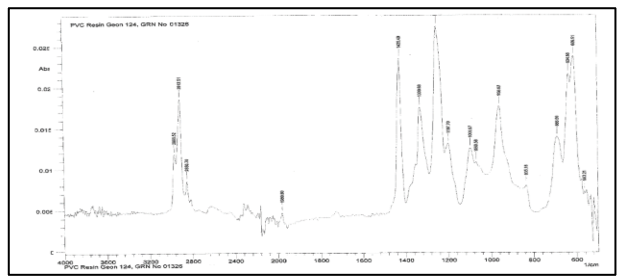

Figure-20: PVC resin Geon 124.

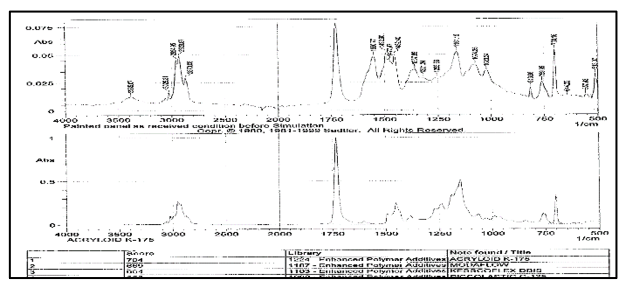

Figure-21: Library: Spectra of Painted panel.

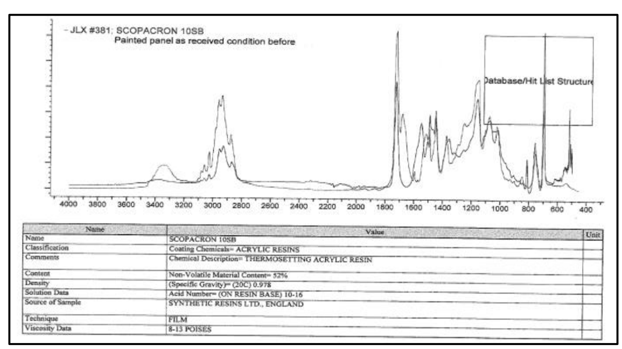

Figure-22: Library: Spectra of painted panel.

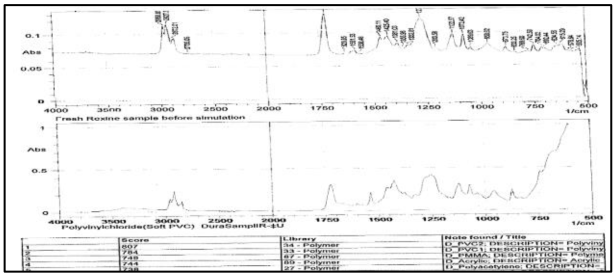

Figure-23: Library: Spectra of rexine sample.

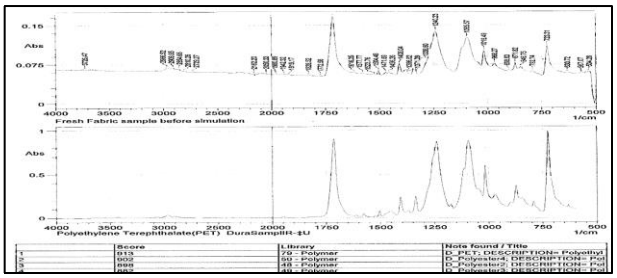

Figure-24: Library: Spectra of fabric sample.

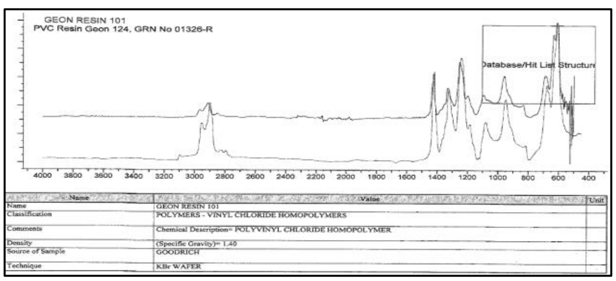

Figure-25: Library: Spectra of PVC Geon Resin.

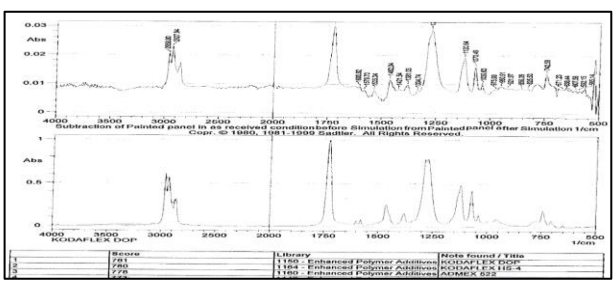

Figure-26: Library: Spectra of Subtraction of Painted panel before simulation from painted panel after simulation with impressions of Rexine.

Conclusion: It is confirmed that the impressions on the painted panel are of rexine.

Conclusion

Vibrational Spectroscopy (FTIR) can be utilized for simple analysis for presence of certain material using in-built library search to a complex failure analysis.A few case studies of analysis of variety of automotive materials including contaminate analysis of brake fluid, fabric sample used in roof lining of passenger car, painted panel of fuel tank and compatibility of material with alternate fuel using FTIR are discussed using Vibrational Spectroscopy (FTIR).The evaluation using FTIR for the above case studies provided objective evidences for confirmation of presence of certain materials leading to identification of-Source of contamination, Presence of a material in a matrix and Probable sources of material leading to failure of a process.

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