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Investigation of growth of oxides, amines and halogen compounds in engine oil using FT-IR spectroscopy

Pradeep Kewat

Department of Mining Machinery engineering
Indian Institute of technology(Indian School of Mines), Dhanbad, INDIA

pradeep_kewat@mme.ism.ac.in

Abstract. This study focuses on chemical degradation of engine oil chemical degdration causes formation of undesired chemicals which are harmful to the components os the engine. FTIR spectrum indicates the presence of some of the chemicals like oxisdes, Alkanes, Carbonyl Compounds, Amines, Carbodiimides and Halogen Compounds. The growth of the peaks in FTIR spectrum indicate the formation of the undesired compounds.

1. Introduction.

The functions of engine oil are to keep the engine lubricated and to remove heat, wear debris and combustion products. Wear debris are produced due to wear of the engine various components[1]. Wear of piston rings and cylinder liner results in the increased clearance between them thus passage for the combustion products to interact with the oil[2]–[5]. Interaction of engine oil with wear debris and combustion products under high-temperature condition results in the formation of several undesired chemical compounds[1], [4], [6], [7]. Formation and growth of these compounds are the indications of the degradation of the engine oil and frequent replacement of the engine oil is then required [8], [9]. some of the modern engine oil contains antioxidant and other additives which neutralize the chemical changes occurring in the engine oil and reduces friction and wear thus increased service life is achieved. Formation of oxides in a reaction is the primary indication of decomposition of that chemical. Decomposition of the engine oil results in the formation various undesired chemicals including oxides, amines and halogen compounds. To investigate the formation and growth of these compounds Fourier Transform Infrared Spectroscopy is used in this study. Fourier Transformation infrared spectroscopy is based on the absorption of a specific wavenumber of infrared light by a specific compound or chemical bond this detail is given in table 1 [5], [10]–[12]. A chemical compound or bond absorbs a specific wavenumber thus the absorption of a particular wavelength indicates the presence of that chemical or bond and Intensity of the absorption represents quantity [5], [10], [13], [14]. Wavenumber is an inverse of a wavelength so the graphs were plotted between the inverse of the wavenumber and absorbance. In the experiment, infrared light of the wavenumber 400 to 4000 were allowed to pass through each sample and absorption intensity for each wavenumber is recorded. Some chemicals or chemical bonds absorb numerous distinct wavenumbers. The highest peak of absorption is taken into consideration for the study.

Table 1. Characteristics groups their absorption wavenumber.

Characteristics group	**Absorption Wavenumber**	**Characteristics group**	**Absorption Wavenumber**
Alkanes	2850-2960/1350-1470	Carbodiimides	1580-1370
Alkenes	3020-3080/675-1000	Nitro Compound	1590-1570
Alkynes	3300	Thiocarbonyl Group	975
Acetals	1150	Halogen Compound	1380-1220 /760-640
Ethers	1180-970	Silicon Compound	980-910
Carbonyl Compound	3200-2500	Soot	2000
Acid Chlorides	1790	Oxidation (Carbon)	1700
Anhydrides	1800	Nitrarion	1630
Amides	1640-1590	Sulphation	1150
Amines	830-770 / 3180-2000	Diesel	800
Nitriles	2300	Petrol	750
Anti-wear additive	960	Antifreeze glycol	880

This study is conducted on engine oil of a mine excavator having a 13 litre six-cylinder diesel engine which produces max 265 kW and maximum torque 1800 Nm, with 42 litre capacity of engine oil in crank-case, Volvo Drain Specification-3 (VDS-3) recommends the oil to be replaced after every 500 hours of operation is based on the recommendation from American Petroleum Institute for Compression Ignition four stroke diesel engine refer table 2. With the recommended engine oil fuel is also recommended to have sulphur content less than 3000ppm because Higher sulphur content shortens service interval.

Table.2: Specification of oil used

Part no	VOE 11708321
Viscosity Grade	SAE 15W-40
Quality Level	VDS-3, API CI-4
Kinematic viscosity @100^{o}C	14.432
Viscosity index	135
Flash point	220^{o}C

2. Experimental Setup

Fourier Transform Infrared Spectroscopy (FTIR) The FTIR (Perkin Elmer Spectrum100 Series), Schematic diagram shown in figure 1, it consists of light source, interferometer, sample container, detector, interferogram and computer. Infrared energy is emitted from the glowing source detected by detector. The beam enters into interferometer where the spectral encoding is carried out, Signal then come out of the interferometer and enters into the sample where it transmitted through the sample, depending upon the type of analysis being accomplished. Here frequency of energy absorbed which depends on the characteristic of the sample. Then beam reaches the detector for final measurements. The detectors are specially designed to measure the interferogram signal and further this signal sent to the computer where the Fourier transformation takes place in the form of spectral for interpretation and any further manipulation[11].

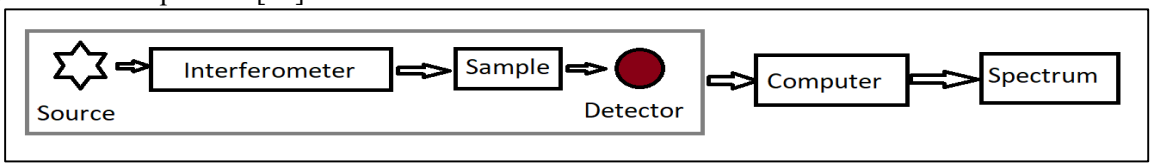
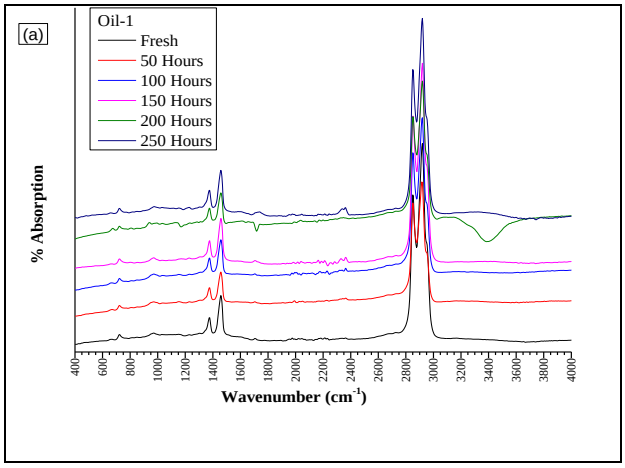
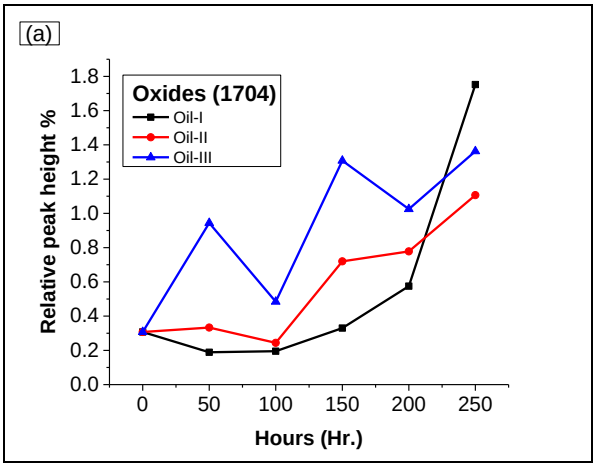


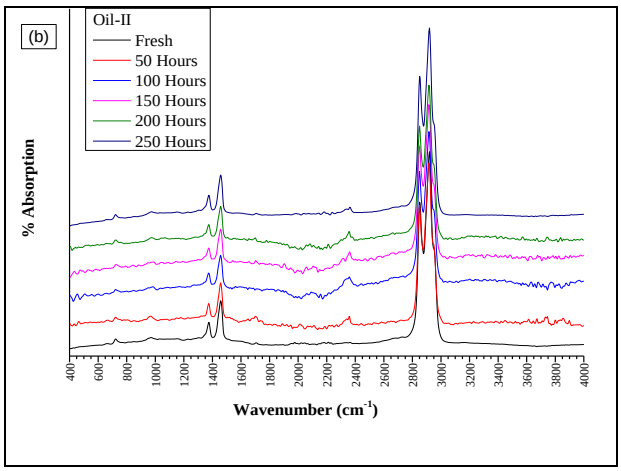
Figure 1. Schematic diagram of FTIR.

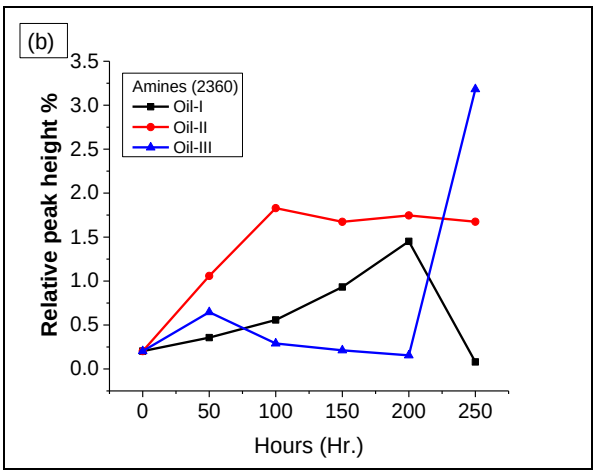
3. Results and discussion

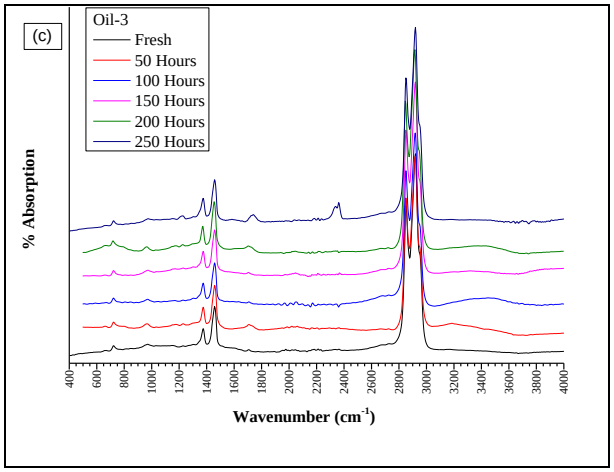
Figures 1 illustrate percentage absorption of infrared light with wavenumbers, in these figures sharp peaks are observed at wavenumbers are 1226, 1376, 1457, 1704, 2360, 2850, 2877 and 2919. Out of which 1376, 1457, 2850,2877 and 2919 are fundamental peaks of the lubricant, fundamental peaks belong to basic constituents of the engine oil.











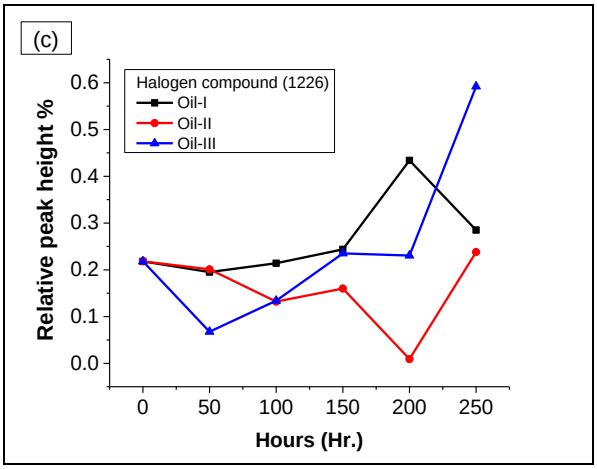


Figure 2. FTIR variation of % Absorbance with wavenumber (a) Oil-I, (b) Oil-II, (c) Oil-III.

Figure 3. growth of relative absorption peaks for (a)oxides, (b) Amines (c) Halogen compound.

Basic constituents of oil are alkanes, carbonyl compounds, amines, carbodiimides, and halogen compounds refer table 1. Wavenumbers 1226, 1704 and 2360 do not belongs to the basic composition their presence indicates the growth of undesired chemicals and degradation of the engine oil.

3.1 Oxides

Oxidation is one of the most important and critical criterion of the evaluation of the engine oil, the oxidation of engine oil refers to formation of acid in the engine oil the amount of oxidation measured by neutralizing the acid formed in the engine oil and measuring the amount of potassium hydroxide to neutralize the acid formed in the engine oil called total acid number. In an engine oil low total acid number implies a better performance of the engine oil and lower corrosion tendency of the engine oil. In Fourier transformation spectroscopy wavenumber 1704 is the indication of the oxidation of the engine oil, higher peak indicates a higher amount of oxidation. Figure 2(a) illustrates oxidation peaks of Oils, I, II and III for 250 running hours. And side by side comparison of three oils is made, Oil-I, II and Oil-III are showing clear chronological growth of the oxidation in the engine oils. However, Oil II and III initial 50 hours oxidation took place followed by activation of anti-oxidants, which is further followed by oxidation and activation of anti-oxidants. Oil I has gone through the activation of anti-oxidants with starting of the evaluation period causing loss of anti-oxidants in the beginning and rapid oxidation is observed after 200 hours. This may be because of different operating conditions such as mining environment temperature, the load on the machine, and antioxidants present in the engine oil and their activation. Oxidation graphs for oil I, II, III agree to the growth of oxidation in the engine oil with time.

3.2 Amines

Amines are the basic constituents of the engine oil the wavenumbers 2850, 2877 and 2919 belongs to amines, the presence of peak at wavenumber at 2360 also belongs to amines (see table-1). However, the peak at wavenumber 2360 does not belong to the fundamental peak of the engine oil it is important to study this wavenumber due to changes occurring in the absorption peak is rapid. Figure 2(b) belongs to wavenumber 2360, growth of amines in Oil I is observed during initial 200 hours after that fall in concentration of amines is noticed, rapid growth of amines took place in Oil II which is stabilized after 100 hours. However, growth of concentration in amines in Oil III has grown for initial 50 hours followed by gradual fall up-to 200 hours then sudden increase in the concentration of amines is observed.

3.3 Halogen compounds

Halogen compounds are excited by wavenumbers 1380-1220 and 760-640 refer table-1. Noticeable changes are observed in Fourier transform spectroscopy in this range of wavenumbers are at wavenumber 1226 and 1376. Wavenumber 1376 belongs to the fundamental peak of the engine oil but peak corresponding to wavenumber 1226 is not a fundamental peak thus peak at wavenumber 1226 is the undesired growth of wavenumber 1226 is focused in this study. Figure 2(c) illustrates side by side comparison of the variation of the wavenumber 1226. Oil-I has stable peak for 150 hours followed by rise at 200 hours and fall at 250 hours the final amount of halogen compound was stable. Oil II has gone through fall in the halogen peak for 150 hours followed by fall at 200 hours and rise at 250 hours the final peak height has less significant changes. Oil III has gone through fall in halogen compounds for initial 50 hours of operation followed by gradual increase for 200 hours and rapid increase after 200 hours.

4. Conclusion

Activation of anti-oxidants in Oil-I has resulted in rapid oxidation of the oil after 200 hours and fall in Amines and Halogen compounds is observer against its's trend after 200 hours. Oxidation of Oil II and III is neutralized periodically resulted in less end oxidation against Oil-I, Oil-I has suffered 28.56 % more oxidation relative to Oil II and 58.30 % more oxidation relative to Oil III. Formation of Amines is

stabilized for Oil II after 150 hours. However, rapid fall is observed in Oil I and rapid increase in observed in Oil III. Rapid formation of halogen compound in Oil II and Oil III after 200 hours is observed unlike Oil I. Oil I and Oil II attended close values those that of beginning but Oil III has a growth of 171.55% in halogen compound relative to initial value.

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