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Spectroscopic analysis of synthetic lubricating oil

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ABSTRACT

Analysis and evaluation of the degradation rate of the synthetic lubricating oil in diesel vehicle engines under the operating effect were carried out by exploiting: Electron Paramagnetic Resonance (EPR) and Infrared Fourier Transform (FTIR).

EPR measurements of the degraded samples reveal that the spectra shape depends on the nature of the used oil and stable free radicals that are produced. Almost a linear correlation between the concentration of these radicals and the degradation rate, expressed in the number of kilometers traveled by vehicle, is observed. The results of FTIR measurements revealed the production of organic compounds from degradation.

Both EPR and FTIR techniques seem to be effective for analyzing the quality of the lubricating oil and the evaluation of its rate of degradation.

1. Introduction

The lubricating oil of engines has various important functions such as cooling engines, reducing abrasion by friction, eliminating corrosive agents [1,2]. It keeps the engine in good operating condition. Lubricants consist mainly of minerals or synthetic base lubricating oil consisting of hydrocarbons paraffin, naphthenic and, to a lesser extent, aromatic hydrocarbons [3], to which is added a quantity of chemical additives which content is between 2% and 25%. The base oil's main function is lubrication, and additives are used to enhance this function or to provide additional properties. Control of the degradation rate of the lubricating oil and its quality enhancement can extend its life, which has both economic advantages by reducing lubricating oil consumption, and ecological advantages by reducing emissions of waste lubricant pollutants. The main causes of the degradation of the lubricating oils are related to oxidation phenomena, degradation of the molecular chains and contamination by insoluble residues and metal impurities, due to thermal phenomena and mechanical abrasions. The degradation of the lubricating oil is accompanied by changes in its viscosity. To analyze the consequences of lubricating oil aging due to thermal deterioration processes or during its use, different methods have been developed. Among these methods there are: chromatography [4,5], infrared spectroscopy [6,7], nuclear magnetic resonance [8], and the atomic absorption spectroscopy. For example, atomic absorption spectroscopy measurements carried out on the lubricating oil of the engine degraded during operation showed an increasing its contamination by metal from the engine or the fuel used [9]. Determining the rate of the insoluble residues from degraded products provides information on the level of degradation of the lubricating oil.

Indeed, these residues can alter the viscosity and seal lubricating oil filters, which can cause wear of the engine parts. The rate of these residues can be identified by thermal gravimetric or optical methods. Analysis by electronic paramagnetic resonance (EPR) showed that the degradation of lubricating oils is accompanied by the production of free radicals [10,11]. Some additives such as zinc dialkyldithiophosphate or sodium stearate or sodium acetylacetonate can improve the quality of the lubricating oil by reducing its rate of oxidation. Infrared spectroscopy has been used for many years to detect the presence of oxidation products in used lubricating oils. This, in most cases, has involved the measurement of carbonyl oxidation products, usually at a single frequency. Consequently, it is possible to study chemical changes in a lubricant during the oxidation process in finer detail than previously reported. This includes the study of additive degradation as well as the examination of the oxidation products.

In this work, EPR and FTIR analysis were performed on synthetic lubricating oil of diesel engine X-5W4, Y-10W40 and X-5W30. EPR aims to highlight the free radicals produced as a result of degradation and monitor their concentration depending on the rate of degradation of the lubricating oil in relation to the number of kilometers traveled by the vehicle. The FTIR method aims to highlight the evolution of absorbing specific molecular fragments of the infrared spectrum, which are produced or disappear as a result of degradation. This allows the identification of additives, contaminants, products of oxidation and

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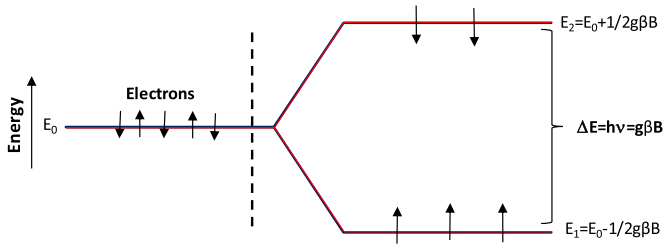

Fig. 1. EPR transitions spin-up and spin-down electron states.

degradation products [12].

2. Experimental study

2.1. EPR technique

Electron Paramagnetic Resonance is a technique used to identify and determine the concentration of chemical species with unpaired electron present in solid or liquid samples. These species are free radicals, transition ions, or even defects in materials [13,14]. The elementary principle of this technique is based on Zeeman effect: Under the effect of precession around itself, the electron acquires a kinetic moment and a magnetic moment of spin. The latter interacts with applied magnetic field and causes the separation of the orbital energy level into two levels of spin energy (see Fig. 1). The excitation of the electron by a radiation

$$h\nu = g\beta B$$

(ν is the excitation frequency, B is the applied magnetic field, β is the Bohr magneton, h is Planck's constant, and g is a factor that depends on the molecule), the electron absorbs this radiation and transits to the excited energy level. The EPR spectrometer analyses absorbed energy by electron. In this work we use EPR in order to identify and follow the evolution of the free radicals produced by degradation of the lubricating oil in diesel vehicle engines.

2.2. Samples preparation and EPR measurements

Samples of the degraded lubricating oil are directly taken from the engine dipstick to about every 1000 km traveled by the vehicle. Thereafter, they are filtered to remove insoluble particles. After filtration, a volume of 1.256 cm^3 of lubricating oil is inserted into a quartz tube, and then analyzed by EPR spectrometer.

Electron Paramagnetic Resonance spectra reflect interactions of the sample with the external magnetic field and magnetic interactions intrinsic to the sample. To what extent these interactions contribute to the spectrum depends on the magnitude of the magnetic field and the microwave frequency. The higher the magnetic field, the larger the Zeeman contribution is. The lower the magnetic field, the more the intrinsic interactions contribute to the spectrum.

The acquisition parameters were optimized to avoid any distortion of the spectral line shape due to saturation, passage, and over-modulation. The X-band spectrum was recorded on a Magnettech MS400 spectrometer equipped with a rectangular TE102 cavity.

Acquisition parameters:

- Magnetic field swept:
  Centered on B_0 =0.3358 T
- Sweeping width: 0.5 T
- Modulation field: 0.0003 T
- Scan time: 30 min
- Measurement resolution: 4096
- Number of scans: 2
- Excitation power: 5.012 mW
- Gain: 50

The power value used was optimized to avoid saturation. While the amplitude modulation of the magnetic field value has been chosen to maintain an acceptable resolution by keeping a measurable signal for the low rates of degradation.

2.3. Fourier transforms infrared spectroscopy

The FTIR instrument used in this work is the Perkin Elmer 1725 spectrometer X. A small amount (2 μL) of the sample was deposited using a Pasteur pipette between two potassium bromide discs (KBr) to obtain a thin film for the acquisition of the sample spectral data. When measuring, a KBr white spectra window was collected and used as reference to calculate the sample absorbance. It was injected in virgin KBr windows to obtain its spectra in the range of 400–4000 cm^{-1}, at 4 cm^{-1} resolution.

3. Results and discussion

3.1. Results of EPR measurements

3.1.1. Analysis of EPR spectra obtained before and after the degradation of the three categories of synthetic lubricating oil

To examine the behavior of lubricating oil according to their brands and categories, we analyzed three different types of lubricants. The results of the EPR measurements on non-degraded samples are shown in (Fig. 2).

Although the observed EPR spectra have different shapes, their amplitudes are low, they are probably due to a low concentration of native free radicals. EPR spectra measured on samples strongly degraded are shown in (Fig. 3). The result shows that the shape and amplitude of the spectrum depends on the nature of the lubricating oil used. Indeed, the observed spectrum of the lubricating oil X-5W40 seems wider than the other spectra measured on X-5W30 and Y-10W40 lubricating oils whose appearance is similar; it is probably due to the contribution of several free radicals. This result shows that the nature of the free radicals produced of the degradation is associated with the initial composition of the used lubricating oil.

3.1.2. Evolution of EPR spectra obtained during X-5W40 degradation of lubricating oil

To analyze the effect of degradation on the form and intensity of EPR spectra measured, in the interval between 0 and 10000 km traveled by the vehicle, we collected about every 1000 km a quantity of lubricating oil of about 20 ml from the engine. Then we performed RPE analysis under the same conditions and using the same measurement parameters. In the case of X-5W40 lubricating oil, results obtained are shown in Fig. 3. We note that for the three oils studied, the shape of the spectra remains relatively invariable, whereas the

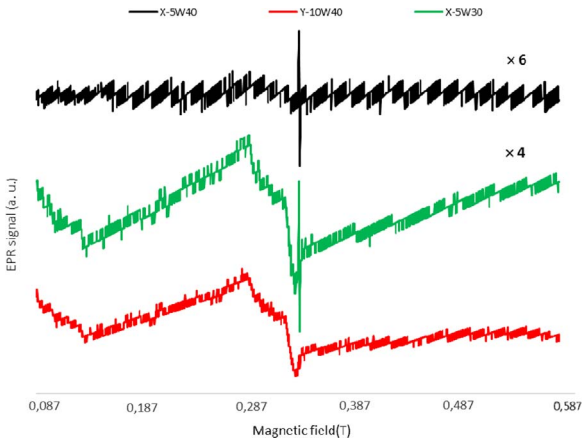

Fig. 2. EPR spectra measured on three categories of new synthetic lubricating oil.