

Mechanisms of mineral oil-based lubricant degradation and aggregation: towards an understanding of varnish formation

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To develop a more detailed understanding of the underlying mechanisms of varnish formation in oil-based lubricants, we have studied the degradation of two commercial lubricant formulations under varying simulated operating conditions. Electron paramagnetic resonance (EPR) spectroscopy allows for the determination of radical intermediates in early stages of lubricant degradation. The observed radical species derive primarily from C-C and C-H homolytic bond cleavage of base oil components. Radical recombination is rapid under anaerobic conditions, minimizing detrimental degradation pathways and leading to limited long-term degradation. In the presence of dioxygen (O₂), however, radical trapping to form oxygenated species leads to the formation of oxidatively degraded oil byproducts. These studies indicate that O₂ is a critical component in the degradation of lubricants albeit not via direct oxidation but through radical trapping.

Key Words: EPR, radical intermediate, varnish, lubricant

1. Introduction

Lubricants are generally used to minimize friction, wear, and operating temperatures between surfaces under mechanical stress.[1, 2] In most applications, lubricants are exposed to a thermo-oxidative environment[2, 3] that leads to the formation of various oxygen-containing compounds such as aldehydes, esters, ketones, peroxides and acids. Ultimately, aggregation and precipitation of these primary oxidation products from the non-polar base oil matrix leads to the formation of sludge and insoluble surface deposits known as *varnish*. [4–9] The presence of varnish on equipment inner surfaces decreases machinery performance by increasing friction, elevating operating temperatures, increasing wear and finally resulting in failure of expensive components and lost production hours.[4, 5, 9–11] Nowhere is this problem more acute than in turbine applications where varnish is frequently associated with servo valve sticking and subsequent, costly unit trips. However, additives have extended the lifetime of lubricants by orders of magnitude. Different lubricant formulations are typically complex due to the specific needs of particular applications. Antioxidants are one of the most important classes of lubricant additives, as they assist in the prevention of oxidative degradation of lubricants and depletion of other additives.[2] Aromatic amines and sterically hindered phenols are amongst the most commonly used antioxidants in oil-based lubricant

formulations.[12, 13] However, such additives are consumed over time and result in the formation of additional degradation products.[14]

To date, a number of studies have sought to elucidate the nature of varnish and determine the mechanism by which it forms. In all cases, dioxygen is assumed to initiate varnish formation via radical processes.[9, 15] Primary free radicals are believed to be formed via cleavage of hydrocarbon C-C and C-H bonds that react with dioxygen leading to the formation of oxygen-containing radicals. Insoluble surface deposits subsequently form through oligomerization of these radical species.[6, 7, 16, 17] A number of techniques have been used to study the final oxidation products resulting from oxidative degradation including: tribological tests,[8] color changes,[18] Fourier transform infrared (FTIR) spectroscopy,[15, 19] gas chromatography-mass spectroscopy (GC-MS),[9, 15, 19] and high performance liquid chromatography-mass spectroscopy (HPLC-MS).[2]

Notably, most studies have focused on the determination and analysis of *final oxidation products* and lack direct probing of the radical intermediates; studies involving the direct measurement of radical products and their kinetics within the context of varnish formation have not been performed. Herein, we describe the use of electron paramagnetic resonance (EPR) spectroscopy to probe the formation of radical intermediates[20, 21] in the early stages of lubricant thermo-oxidative degradation. EPR, in combination with appropriate spin trapping methods, can be used to detect and identify even short-lived free radicals. Spin trapping methods typically utilize additives (spin traps) that rapidly react with primary free radicals to form more long-lived radical species (spin adducts).[22–24] This study, therefore, aims to directly measure the amount of radical intermediates produced by thermo-oxidative lubricant degradation and to explore their correlation to varnish formation by EPR spectroscopy, using spin-trapping methods.

2. Experimental

Two commercial group II mineral oil-based lubricant formulations, with and without additives, were studied under varying simulated operating conditions including aerobic and anaerobic atmospheres. N-tert-Butyl- α -phenylnitron (PBN) was used as a spin trap in certain experiments.[23, 25]

All reagents and solvents were purchased commercially and were reagent grade. N-tert-Butyl- α -phenylnitron (PBN) ($\geq 98\%$), 2,2-Diphenyl-1-picrylhydrazyl (DPPH) ($>95\%$) and Hexane ($\geq 98.5\%$) were purchased from Sigma Aldrich and used without further purification. Petro-Canada Turboflo™ 32 (R&O) and Flushing Fluid (FL) were purchased from Petro-Canada.

Four lubricant samples of commercially available ISO 32 Group II rust and oxidation turbine oil (R&O) and its analogous non-additized Flushing fluid (FL) (2 x R&O and 2 x FL) with PBN in a 2.5% weight-to-weight ratio (w/w) were heated at 95°C under controlled-atmosphere in round bottom flasks. Two of these samples were heated under argon atmosphere and the remaining two samples were heated under air atmosphere.

For EPR data acquisition, a 500.00 μL aliquot of each lubricant sample was diluted by hexane in a 1:1 volume-to-volume ratio in a 1.00 mL volumetric flask to decrease the viscosity of the lubricant samples. 550.00 μL of each sample then was transferred into a 4.2 mm (internal diameter) quartz EPR tube with the sample height of maximum 40 mm in order not to exceed the vertical height of the microwave cavity. Each sample was then degased by blowing argon inside the tube for 5 minutes. A calibration curve was obtained using DPPH by dissolving 0.0108 g of DPPH in hexane in a 100.00 mL volumetric flask followed by successive dilution to obtain variety of concentrations.

A Bruker Elexsys E500 series continuous wave EPR spectrometer was used to acquire EPR spectra. All samples were analyzed under the same instrumental settings. The spectrometer was operated at a frequency of 9.83 GHz (X-band), 50 KHz field modulation, 2 G modulation amplitude, 0.63 mW microwave power and 60 dB receiver gain. Each spectrum was acquired with the highest resolution possible (8192 data points). A DPPH ($g = 2.0036$) standard was used for spectral frequency calibration,[26] as well as an external spin concentration calibrant. OriginPro 9 was used to integrate the derivative spectra, perform baseline corrections and calculate the area under the peak for each spectrum. A radical concentration calibration curve was determined under the conditions of the experiments, allowing for the determination of radical concentrations using the following equation:

$$\text{Peak area} = 1.3185 \times 10^7 \times \text{concentration}(M) - 3.6621$$

3. Results and Discussion

To probe radical formation under thermal and thermo-oxidative stress, EPR data during degradation studies were obtained under various conditions. EPR spectra were acquired at different time spans over a period of seventeen weeks (120 days). **Figure 1** shows typical EPR spectra for spin-trapped PBN-adducts as both the raw derivative form (Figure 1b) and as integrated (Figure 1a) for quantitation of total spins. Spin-trapped PBN adducts have a characteristic three peak pattern due to ^{15}N hyperfine coupling with the electron spin. Using DPPH as an external spin calibrant, the concentration of radicals was obtained for each time point, allowing for the construction of a time profile for radical concentration in the lubricant over 120 days. Details of the obtained data for R&O and FL lubricant samples both under aerobic and anaerobic atmospheres are discussed below.

3.1. Degradation study of lubricant sample without additives (Flushing Fluid (FL))

Figure 2 shows integrated EPR signal observed for base oil FL heated at 95°C for a period of 120 days. The observed signal results from PBN-trapping of radical species formed under *aerobic* (**Figure 2b**) and *anaerobic* (**Figure 2a**) conditions. Under aerobic conditions, the observed radical signal increases during the first week, reaches a steady plateau for the next three weeks, followed by a decrease to lower concentrations at longer times (day 40+). The decrease in radical concentration between 25-40 days correlates with the formation of visible varnish deposits at the start of week four (indicated by a vertical

dashed line in **Figure 2**). Under anaerobic conditions, the profile is more complex, with two observed maxima during the time of the experiment. An initial maximum is similar to that observed under aerobic conditions, although the maximum is somewhat delayed and its intensity is significantly greater. A second maximum (~70 days) also occurs in these data, which correlates with a significantly slower formation of varnish under these conditions. While the slower formation of varnish under anaerobic conditions was anticipated, the observation of increased radical levels in the absence of O₂ (generally believed to initiate mineral oil oxidation) was, at first glance, surprising; we attribute this observation to the significantly greater lifetime of the free radicals in the absence of dioxygen. Similar experiments with FL *in the absence of a spin trapping agent* (data not shown) show no signs of varnish formation under anaerobic conditions, which suggests that radical trapping by PBN provides secondary pathways for oxidation/aggregation processes.

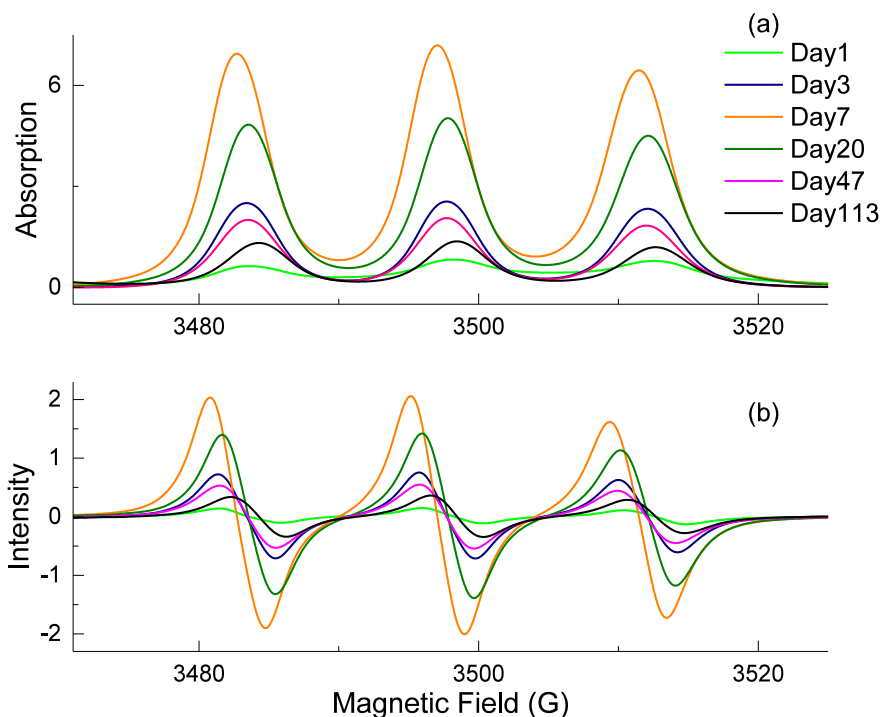


Figure 1. (a) Integrated EPR spectra of Figure 1(b). (b) Overplot of EPR spectra at different time spans for R&O lubricant sample with spin trapping agent, PBN in a 2.5% weight-to-weight ratio under air.

These results provide strong evidence for the importance of dioxygen as a primary factor in base oil varnish formation. Importantly, rigorous exclusion of dioxygen does not prevent radical formation; thermal homolysis of C-C and C-H bonds will necessarily occur under thermal stress. Radical trapping by O₂ to form longer-lived polar radical products, however, leads to significantly faster varnish formation. These results are consistent with the idea that the polarity of oil degradation products is a determining factor in

early nucleation and aggregation processes that lead to varnish formation. Importantly, even the use of a radical trapping agent to form stable adducts is sufficient for increased aggregation at early times. This reveals that aggregation is not limited to formal oxidative processes and that any polar functionality may lead to increased aggregation and varnish formation.

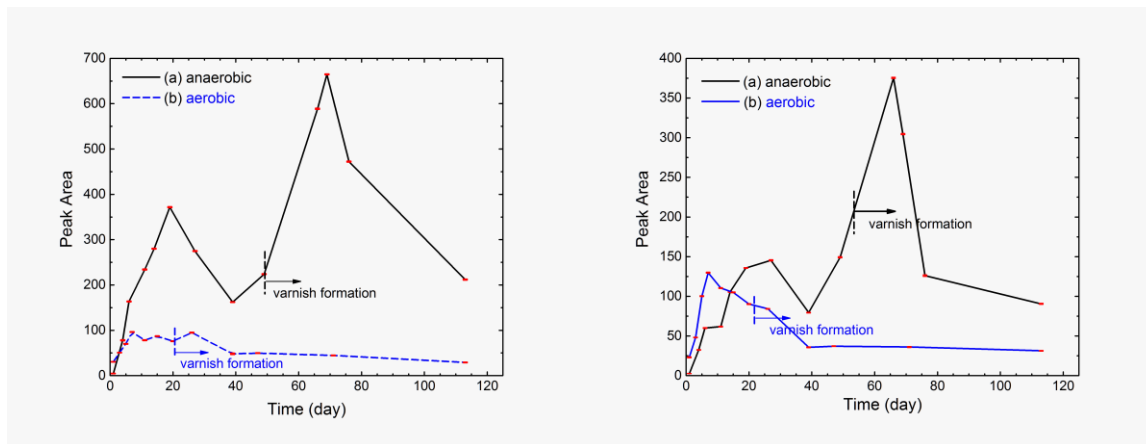


Figure 2. (a) Peak area of EPR spectra for FL lubricant sample with 2.5% weight-to-weight ratio under Ar. (b) Peak area of EPR spectra for FL lubricant sample with 2.5% weight-to-weight ratio under air.

Figure 3 (right). (a) Peak area of EPR spectra for R&O lubricant sample with 2.5% weight-to-weight ratio under Ar. (b) Peak area of EPR spectra for R&O lubricant sample with 2.5% weight-to-weight ratio under air.

3.2. Degradation study of lubricant sample with additives (Turboflo 32 (R&O))

Figure 3 shows the changes in radical intermediate concentrations for PBN-adducts of R&O samples under controlled atmosphere of air (**b**) and argon (**a**) over a period of 120 days. Under *aerobic* conditions, free radical concentration increased until reaching a maximum on day seven, followed by a gradual decrease until day forty at which point radical concentrations level off. Varnish deposits were observed (visual inspection) at the start of week four (day 22). Overall, the behavior under aerobic conditions is extremely similar to that observed for FL under similar conditions. As with FL, decreases in radical concentrations correlate with increased aggregation and the formation of insoluble varnish after three weeks.

Under anaerobic conditions (see **Figure 3(a)**), we again observe a similar profile with R&O as was observed with FL. Two maxima are observed at four weeks and ten, respectively. Varnish was also observed following the observed minimum at week eight. Similar experiments with R&O *in the absence of a spin trapping agent* (data not shown) show no signs of varnish formation under anaerobic conditions, which suggests that radical trapping by PBN accelerates the aggregation processes. This also suggests that well-selected antioxidant additives, although polar, do not contribute to varnish formation under the conditions examined. The comparison of aerobic versus anaerobic data for R&O is also very similar to that

observed in FL, where greater radical concentrations and slower varnish formation were observed under anaerobic conditions.

We note that the presence of additives in R&O provided only small delays (approximately 4 days) in the observation of visible varnish deposits in our experiments using the PBN spin trap. However, the concentration of radicals was greater in FL samples under anaerobic atmosphere compared to R&O under the same conditions. This suggests that the additives greatly decrease the amount of radical intermediates in the R&O sample through competition between PBN and additives for the trapping of reactive carbon-centered radicals. It should be noted that the presence of PBN in R&O under anaerobic conditions accelerated the varnish formation compared to R&O sample with no PBN (no varnish was observed under anaerobic condition in the absence of PBN in R&O sample during a 120-day period). This can be attributed to the higher reactivity of PBN towards the free radicals compared to the additives that ultimately led to the aggregation of polar PBN-adducts compared to the sample with no PBN.

In summary, comparison of aerobic and anaerobic degradation studies of lubricant samples (see **Figure 2 and 3**) indicate that radical intermediates are generated by homolytic cleavage of hydrocarbon bonds in lubricant samples regardless of dioxygen availability. These results call into question the role of dioxygen as a mineral oil oxidation initiator. In the presence of O₂, however, radical intermediates formed by thermal homolysis generate polar species whose recombination and aggregation result in insoluble varnish. Comparison of the amount of PBN adducts in both R&O and FL samples (**Figure 2(a) and 3(a)**) showed that the presence of antioxidant additives in lubricant samples decreased the total amount of free radicals as intended.

4. Conclusion

The thermal and oxidative degradation of two commercial Petro-Canada lubricant samples was explored by EPR spectroscopy. A systematic study of early radical processes that lead to varnish formation was performed by EPR detection of spin-trapped species. The results suggest that homolytic bond cleavage of hydrocarbons initiates the formation of radical intermediates regardless of the presence of O₂. The recombination of these radical intermediates is very fast under anaerobic atmosphere.; Such radical aggregation generates soluble nonpolar products which do not contribute to lubricant varnishing. However, in presence of O₂, the rate of varnish formation increases dramatically as a result of accelerated aggregation of polar byproducts through nucleation processes in nonpolar base oil. These results also support the fact that the presence of additives increases lubricant lifetime. These studies suggest that strategies for controlling and/or removing both dissolved O₂ and soluble lubricant degradation products are likely to mitigate the risk of insoluble varnish formation. Using such strategies to reduce lubricant degradation could allow industries to avoid the negative environmental and economic impacts of varnish formation.

5. References

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