

ON-SITE ADDITIVE DEPLETION MONITORING IN TURBINE OILS BY FT-IR SPECTROSCOPY



PAL SERIES™

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INTRODUCTION

The availability of the Portable Analyzer for Lube (PAL™) Series FTIR (Fourier Transform Infrared) spectrometers, which are compact, easy-to-use and affordable systems, provides new capabilities for real-time, on-site analysis of high value assets such as turbines. With PAL spectrometers, the lubrication specialist now has the ability to simultaneously monitor key parameters such as oxidation, additive depletion and levels of water in lubricants. This application brief will demonstrate the ability to monitor the depletion of key additives using the PAL FTIR spectrometer.

ANTIOXIDANTS IN TURBINE OIL

The phenolic and aminic antioxidants in turbine oils function as preservatives which prevent the oil from oxidizing. Oxidation causes turbine oils to quickly lose viscosity and wetting characteristics which protect metal contact surfaces and prevent wear. Oxidation arises from a combination of sources including elevated temperatures, extreme pressures, high shear conditions, the presence of water and metal particles, and is accelerated by electrostatic sparking, particularly in certain gas turbine systems. Antioxidants inhibit the formation of these decomposition products, however once the antioxidants are consumed the process accelerates exponentially and at a certain critical point corrective action has negligible benefit. The PAL FTIR system measures both the antioxidant levels and the amount of oxidation present to ensure that corrective action is taken before this critical point is reached.

MEASURING ANTIOXIDANTS IN TURBINE OIL BY PAL INFRARED SPECTROSCOPY

The primary and most abundant antioxidant is the phenolic antioxidant, which works synergistically with the aminic antioxidant. It is postulated that the phenolic antioxidant protects the workhorse aminic antioxidant, which has the ability to recharge itself over and over during the cycles of oxidation. This is consistent with data we have obtained, as we will demonstrate later in this application note.

The phenolic and aminic antioxidants in turbine oil have prominent absorbance bands in select regions of the infrared spectrum, thus enabling FTIR spectroscopy to be an ASTM preferred means of measurement. Figure 1 shows one of the major infrared bands of the phenolic antioxidant in turbine oil and the change in the band, as a function of time, as the antioxidant is depleted. Similarly, figure 2 illustrates the incremental diminishment of the aminic antioxidant as the turbine oil ages. These bands are so characteristic of these two species that they are often called “fingerprint bands” and they are the functional groups that are automatically tracked by the PAL Series Spectrometer software.

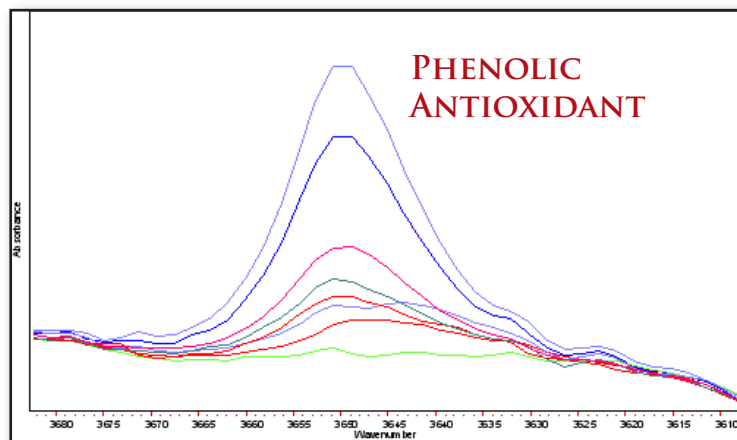


Figure 1: FTIR spectral overlay of the phenolic antioxidant functional group bands depleting as a function of time. The strongest band (Light Blue) is that of new ISO 32 turbine oil and the weakest absorbance (Light Green) is from turbine oil that has started to show some oxidation.

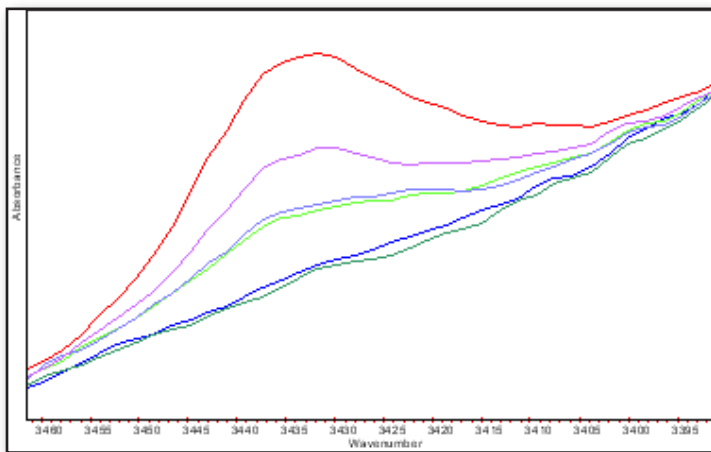


Figure 2: FTIR spectral overlay of the aminic antioxidant functional group depleting as a function of time. The strongest absorbance (Red) is aminic antioxidant in new ISO 32 turbine oil and the weakest bands (Blue and Green) are from turbine oil with spent antioxidant.

PAL software (Figure 3) stores the FTIR spectrum of the initial new or reference oil. When in service used oil is measured, it's compared to the reference oil and the user is provided a percentage of depletion value for each additive as well as a visual overlay of the spectral regions associated with each additive. The PAL software is also programmed to inform the user via a yellow "Monitor Frequently" warning

when each additive is nearing the critical depletion points. Likewise, a red "Change Immediately" warning is displayed for any additive, or other component such as water or oxidation, which has reached a critical threshold. Therefore, if both the phenolic and aminic antioxidants are in the red zone oxidation is imminent. The regions of the infrared spectrum used to measure oxidation and water are also shown in comparisons to the reference oil.

THE RELATIONSHIP BETWEEN ANTIOXIDANT DEPLETION AND OXIDATION

We will demonstrate the relationship of antioxidants and oxidation formation as well as the ability of the PAL system to both predict and detect oxidation formation before the critical point is reached. Metallic iron and copper, known oxidation catalysts, were added to used Chevron ISO 32 turbine oil that was in service 4 months in a steam turbine system. The iron and copper catalysts accelerate the inherent thermal oxidation mechanism, and are used in most oxidation potential tests such as RPVOT (D2272), Universal Oxidation Test (D6514 and D5846), and TOST (D943).

This mixture was heated at 135°C for 26 days at atmospheric pressure in air, and small samples of the oil were removed every 2-3 days. The samples were analyzed using a PAL FTIR spectrometer. The peak area measurements for phenolic antioxidant, aminic antioxidant, and oxidation products were recorded and plotted as a function of time as shown in Figure 4. As shown, the phenolic antioxidant diminishes to about 40% of the original amount in a relatively short time; however, the aminic antioxidant is observed to stay above 80% for almost the whole life span of the oil. Some of the initial drop in the phenolic antioxidant is due to evaporation which is a known problem with certain more simple phenolic antioxidants. The aminic antioxidant is observed to have three stages:

- **STAGE 1:** The aminic antioxidant level is fairly constant and remains at this level approximately halfway thru the useful life of the oil. The initial slight increase in aminic may be due to volatiles in the oil, which can evaporate from the new oil during high temperature operation, thus slightly increasing the concentration of the aminic antioxidant.
- **STAGE 2:** The aminic antioxidant depletes rapidly by about 25% at the mid-way point in the useful life of the oil.
- **STAGE 3:** After the phenolic drops below 30% of the original concentration (70% depletion) the aminic begins a rapid descent from 80% to 40%. At this critical point, the oxidation process accelerates exponentially. Corrective action would need to be taken prior to this stage in order to extend the useful lifespan of the oil.

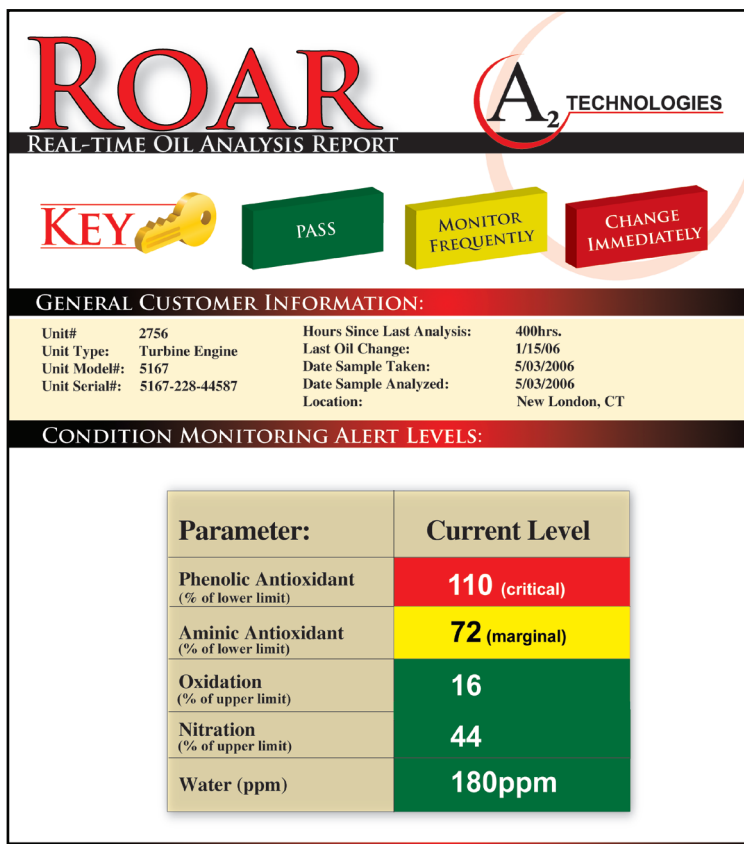


Figure 3: PAL series software presents the user with specific information about the level of phenolic and aminic antioxidants as well as crucial information about oxidation by-products and level of water contamination.

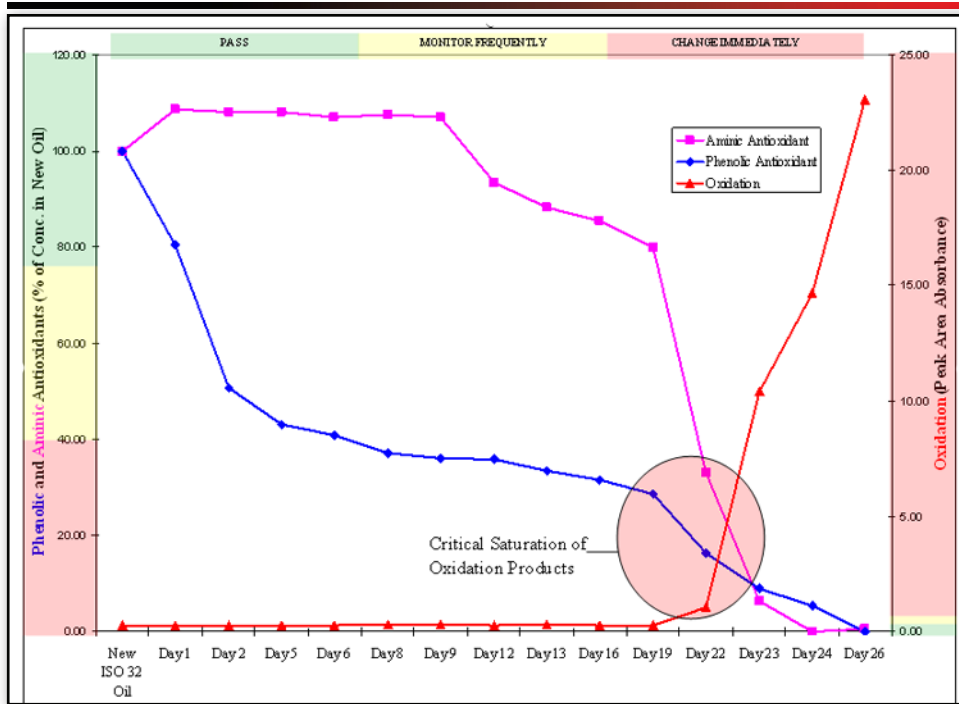


Figure 4: The additive depletion % relative to new oil concentrations, (left scale) and oxidation formation (right scale) trend analysis in thermally stressed ISO 32 turbine oil generated using the PAL Series FT-IR Spectrometers.

LUBE “USEFUL LIFE” MEASUREMENTS - PAL FTIR VS. VOLTAMMETRIC METHODS

As we have demonstrated in this application note, the PAL FTIR system measures each antioxidant species individually, as well as providing a direct measurement of the degree of oxidation in the oil.

Cyclic voltammetric methods rely on a measurement of the total antioxidant level (do not provide specific information on the independent species, but rather rely on an inference method to predict lube life) and cannot directly measure oxidation, water or nitration. In fact, the presence of these by-products may negatively influence the validity of the voltammetric measurement. Moreover, The PAL Series FTIR Spectrometers can also detect the presence of contaminants such as EHC hydraulic fluid in turbine oils or gear oil in turbine oil.

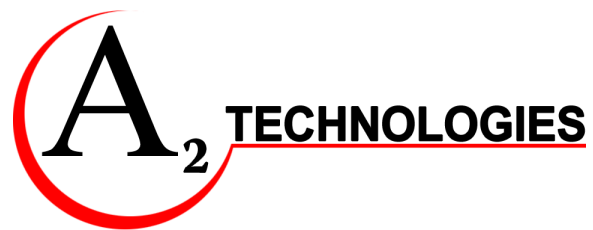
The PAL FTIR system requires only a drop of neat oil for its measurements and no sample preparation. Voltammetric systems, on the other hand, require careful pipetting techniques and an extraction step using an electrolyte solution. The extraction step used in voltammetric systems assumes that all of the antioxidants are extracted from the oil into the electrolyte solution (i.e. 100% efficiency), however, this is never the case. Extraction efficiencies are variable for additives in oils and can range from 50-90%, meaning that 10-50% of the additives remain in the oil after extraction and are not measured. Voltammetric electrodes require inconvenient maintenance, such as conditioning in buffer solutions. Metal particles, water, or organic salts (i.e. ionized carboxyls such as copper carboxylates) will not interfere with the antioxidant measurements using the PAL system. The PAL

system has virtually no learning curve, requires no maintenance nor special chemicals or reagents. Since the antioxidants can be monitored independently using the PAL, re-additization can be carefully controlled and monitored. The effectiveness of top-offs, bleed and feed, filtration, and dehydration can be monitored as well.

CONCLUSIONS

A2 technologies’ PAL Series Spectrometers are capable of independently measuring phenolic and aminic antioxidants in turbine oil and provide the time sensitive results necessary to assist personnel in preventing a non-scheduled shutdown by ensuring reliable operation of the turbine equipment. The PAL system is designed to alert, at pre-set warning levels, when the phenolic and aminic antioxidants are at or approaching depletion milestones, and thus help prevent turbine oils from reaching the critical point in the oxidation cycle of oil.

The capability of measuring additives in turbine oil by FTIR spectroscopy eliminates the issues associated with other measurements including the need for calibrating, maintaining, and conditioning electrodes based on voltammetric systems. The measurements are more rapid than electrode based antioxidant monitoring equipment, and minimize the dependency on the skill of the operator and the operating condition of the equipment. As importantly, the ability to measure antioxidant levels at-site via FTIR means that the results will be more convenient, more frequent, and obtained far more rapidly than samples that are sent for off-site analysis to a traditional oil analysis lab.



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