Studying Antioxidants in Lubricants with EPR

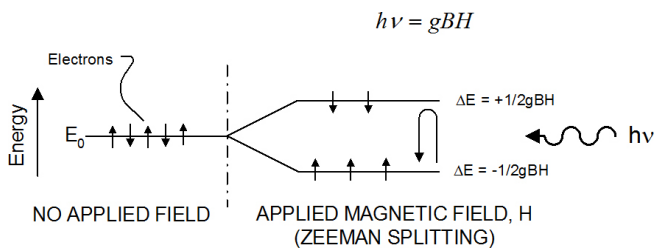
Electron Paramagnetic Resonance (EPR) measures the concentration and composition of free radicals in a sample. Samples can be either liquid, solid or gas. Free radicals are atomic or molecular species with unpaired electrons that can be highly reactive. There are also many stable free radicals, such as melanin in hair and ultramarine blue pigment. Many transition and rare earth metals have unpaired electrons, and are EPR active. Some minerals (eg amethyst, smoky quartz and fluorite) receive their color from unpaired electrons, and are also EPR active.

EPR, also known as Electron Spin Resonance (ESR), is a form of magnetic resonance spectroscopy, along with NMR and MRI. In NMR and MRI, the atomic nucleus interacts with electromagnetic radiation (EMR); with EPR, the reaction is with one or more unpaired electrons.

Even though not all nuclei are NMR active, most compounds have an NMR signal. This is not true of EPR. It is the magnetic component of EMR that interacts with the atomic nucleus or electron's magnetic moment in all forms of magnetic resonance. Spin-paired electrons have a net magnetic moment of zero, and are therefore EPR silent.

In an EPR spectrometer, the sample is loaded into a high frequency resonant cavity in a slowly varying, uniform magnetic field. When irradiated with microwave radiation at a fixed frequency, the unpaired electrons undergo resonant transitions between spin 'up' and spin 'down' state in a particular magnetic field, governed by the equation in Figure 1. The magnetic field at resonance is a function of the g-factor, and the amplitude of the resonant peak is determined by the concentration of the radical in the sample.

Figure 1



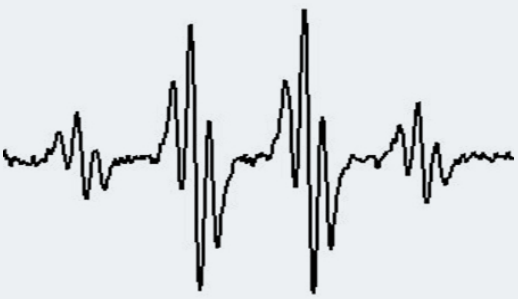
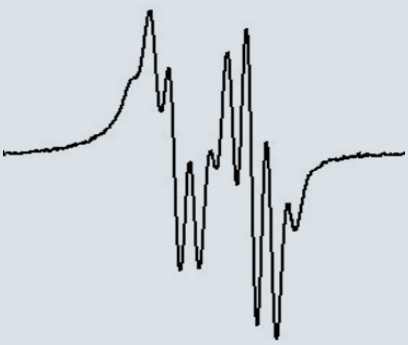
Electron transitions stimulated by incident microwave energy.
h = Planck's constant; B = Bohr Magneton; ν = resonant frequency; H = applied magnetic field; g = a characteristic of the radical (the "g-factor," an empirically determined number, typically around 2 for organic radicals)

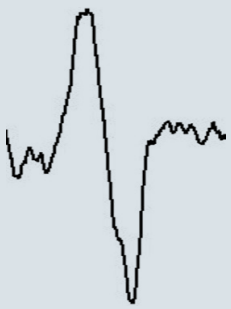
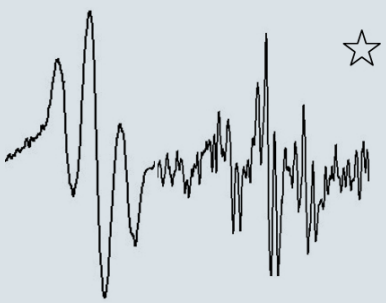
The EPR effect was first measured in 1945. Historically, EPR spectrometers consist of large water-cooled electromagnets that generate a variable magnetic field. They often have a similar design to older NMR spectrometers. This causes significant portability issues; the electromagnet assembly weighs upwards of 200 kg and requires several kW of power. Bruker microESR spectrometers overcome this problem with a small, strong rare-earth magnet and a low power electromagnetic coil. The sample is placed in a high-Q resonant cavity, which has a large 'fill factor' compared to a conventional system. This reduces the size of the instrument by a factor of 100, without compromising high sensitivity and excellent resolution.

There have also been fundamental innovations in the design of the microwave bridge and receiver. These now use modern, low-cost integrated components similar to those in wireless communication devices, which are smaller and cost less than those in conventional EPR spectrometers. These innovations have resulted in a shift away from large centralized EPR systems, towards small, portable, versatile instruments that can even be used in the field.

Studying Antioxidants in Lubricants

Modern lubricants contain antioxidant additives to prolong their lifetime. These additives are often phenols, amines or a combination of both. The thermal oxidative degradation of lubricants involves free radicals, making EPR an ideal tool for understanding the reaction mechanisms involved, and developing better lubricant formulations. Many common additives produce identifiable, stable radicals that are easily observed by EPR. Table 1 shows examples of common lubricant antioxidants that can be studied with EPR.

Radical	g-factor	Hyperfine Splitting (Gauss)	EPR Spectrum
Butylated hydroxyl toluene (BHT)	2.0048	aCH3 = 11.8 aH = 1.9	
Gavinoxyl radical	2.0040	aH = 5.99 aHmeta = 1.54	
Ethanox 4703/ IONOL 1031	2.0056	aCH2=11.06	

PANA Phenyl-α-naphthyl amine	2.0043	aN=10.1	
APANA Alkylated phenyl-α-naphthylamine	2.0036	aN=10.4	
Poly (dicyclopentadiene-co-p-cresol)	2.0054		
Ethanox 4702[2]	2.0045	$\mathbf{a}_{CH2}$=9.9 $\mathbf{a}_{CH2}$=12.7 (Not all hyperfine splitting is visible)	
Irganox 1706[3]	2.0033	$\mathbf{a}_{CH2}$=8.7 $\mathbf{a}_{H}$=1.9	

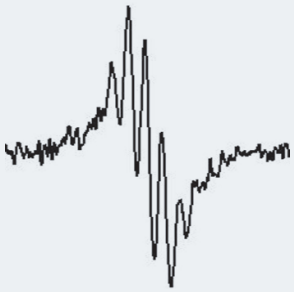
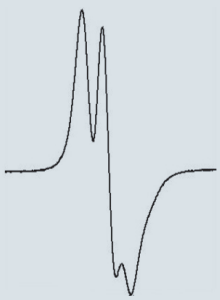
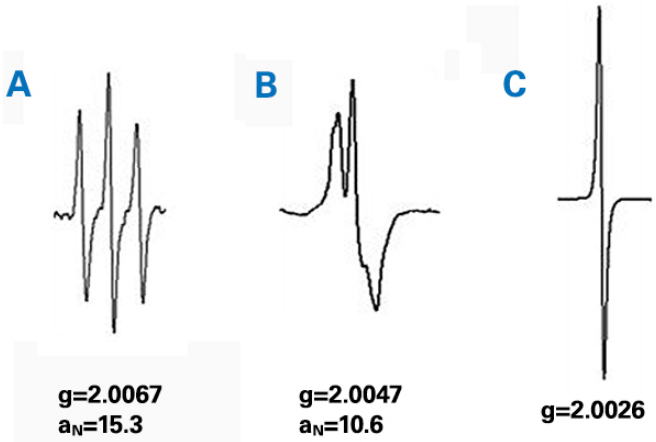
Butylated Hydroxy Analine (BHA)	2.0042		
Vanlube 961[4]	2.0060	$\mathbf{a}_N$=10.6	
Ethanox 4716[5]	2.0051	**a**=7.9	
Nonylated Diphenylamine	2.0051	$\mathbf{a}_N$=10.5	

Table 1:EPR signatures of common antioxidants. ☆ = Sample run with lowered modulation coil amplitude to illustrate the fine structure.

1. 2,6-Di-*tert*-butyl-4-(dimethylaminomethyl)phenol
2. 4,4-methylenebis (2,6-Di-*tert*-butylphenol)
3. Octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate
4. Benzeneamine-N-phenyl- reaction with 2,4,4-trimethyl pentane and 2-methylpropene
5. Hindered phenolic ester

EPR is particularly effective for directly monitoring antioxidant radicals in lubricants as they age. The solution can be monitored over a long periods of time, to see if the radical signature evolves as in Figure 2.

Figure 2

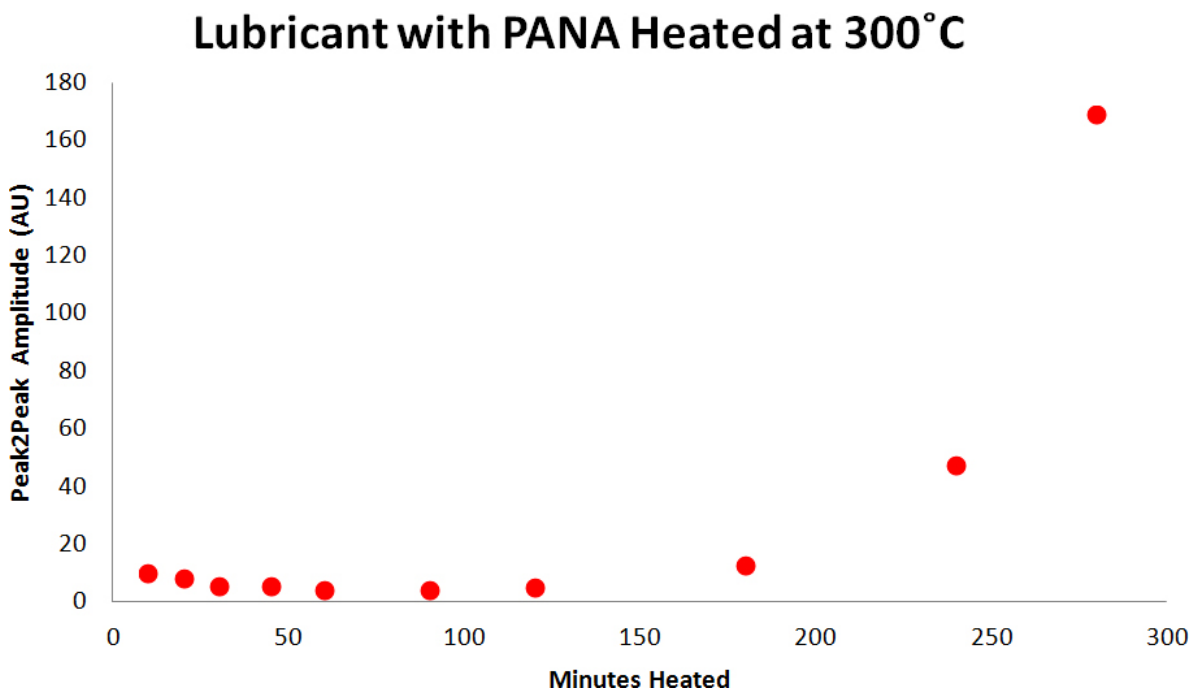


A = Nitroxide signal initially present in the lubricant; B = EPR signal from an amine radical (PANA); C = Products of oxidative thermal degradation. The amplitude of signal C is 34 times the amplitude of signal B after 5 hours at 300°C.

The EPR signals in Figure 2 show the behavior of antioxidant additives in a hindered polyolester lubricant. This lubricant has an initial EPR signal from a stable radical, nitroxide (A), before heating. Once the lubricant is heated above 100°C, the nitroxide radical signal disappears and an amine radical signal (B) appears. The antioxidant reacts with radicals produced by oxidative thermal degradation, and keeps the radical level at a low, steady state. Once the amine additive is depleted, the signal from oxidative thermal degradation products (C) rapidly increases in intensity. Figure 3 depicts the EPR signal over the time the lubricant is being heated. Thermal degradation products build up quickly once antioxidant additives are depleted. The amplitude of signal C is 34 times the amplitude of signal B after 5 hours at 300°C.

The additive galvinoxyl is a stable radical, which is EPR active without heating. The magnitude of the galvinoxyl radical can be quantified easily with EPR, to determine antioxidant consumption over time. Spin traps could be used to detect other free radicals with half-lives too short to be observed directly, and identify other species present in the mixture, for insights into radical reaction mechanisms. This information is useful in antioxidant development .

Figure 3



Behavior of the antioxidant additive in a hindered polyolester lubricant during heating. Once the additive is depleted, the signal from thermal degradation products increases rapidly.

References

[1] Kagan,V., Serbinova, E,. and Packer, L., *Archives of Biochemistry and Biophysics*, 280(1), 33-39 (1990).

[2] Van den Hoek, W.J., *"Electron Spin Resonance Studies on Dynamic Processes in Some Phenoxy Radicals"*, Ph.D. Thesis, 1972.

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