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**ELECTRON SPIN RESONANCE (ESR) SPECTRA
OF BUTYLATED HYDROXYTOLUENE (BHT)
AS EVIDENCE OF FREE RADICAL FORMATION
IN ELECTROSTATIC DISCHARGE (ESD)
DAMAGED LUBRICATING OILS**

**SPEKTRA ELEKTRONOWEGO REZONANSU SPINOWEGO
(ESR) BUTYLOWANEGO HYDROKSYTOLUENU (BHT)
JAKO DOWÓD POWSTAWANIA WOLNYCH RODNIKÓW
W TRAKCIE WYŁADOWAŃ ELEKTROSTATYCZNYCH
(ESD) W TURBINOWYCH OLEJACH SMARNYCH**

Key words:

turbine lubricating oil, antioxidant additives, free radical oxidation, electron spin resonance

Słowa kluczowe:

turbinowe oleje smarne, antyutleniacze, wolnorodnikowe utleniania, elektronowy rezonans spinowy

Abstract

Electrostatic discharges were generated in typical ISO VG 46 cSt turbine lubricating oil by passing the oil through a glass fibre filter element at

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a hydraulic load of $0.06 \text{ L} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$. The oil exhibited electrical conductivity of $8 \text{ pS} \cdot \text{m}^{-1}$ at 25°C . The experiment was performed at room temperature. The maximum amplitude of ESD arcing events recorded was approximately -500 V . The magnitude of these arcing events was sufficient to generate a free radical formation of the BHT antioxidant additive generally employed as an antioxidant in typical turbine lubricating oil formulations. The free radical formation was evidenced by a clearly observable ESR signal corresponding to the BHT radical as recorded on an X-Band MiniScope MS100 spectrometer with a resonant frequency of 9.43 GHz and a maximum field sweep of 400 mT . These results indicate that ESD can well be responsible for initiating the free radical polymerization process postulated to result in varnish formation in turbine lubricating oils.

INTRODUCTION

The lubricating oils typically employed in gas turbine lubricating systems are of the ISO VG 32 or ISO VG 46 type, and it can be generally assumed that they are of the API Group II type or higher. The American Petroleum Institute (API) classifies these as Group I (solvent extracted), II (hydrotreated), and III (hydrocracked), respectively. In this sequence, the more severe processing results in lower sulphur and unsaturates contents, as well as increasing viscosity indices (from 95 to 120) going from Group I to Group III, respectively. Owing to the more severe refining treatment, the more uniform Groups II and III base stocks exhibit improved oxidative stability and better performance characteristics as manifested by the higher viscosity indices (VI). In view of these advantages, there is a general trend to phase out Group I oils and increasingly replace them with Group II or III oils across the board in nearly all industrial hydraulic and lubricating applications. The gradual phase out of Group I oils in industrial applications has been under way since the mid-1990s but gaining momentum, especially in the last decade.

With the wider implementation of the Group II and III stocks, two unforeseen and unexpected side effects associated with higher base stock purity became apparent. These have been the significant decrease in electrical conductivity and a marked decrease in solvency properties, particularly concerning oil oxidation products. In addition, these formulations typically employ only organic (zinc- and metal-free) antioxidant additives (such as phenyl- α -naphthylamine, PANA, and butylated hydroxytoluene, BHT). These seemingly minor changes in chemical makeup have brought about many new phenomena previously not considered in typical applications. The range of these phenomena can be quite broad and includes electrostatic discharge, varnish formation, novel additive interaction, degradation mechanisms, and others. Many of these new behavioural mechanisms have yet to be characterized in greater detail and often require new analytical laboratory techniques as well as

direct, *in-situ* measurements, to evaluate their impact on system performance under normal operating conditions.

One of the possible results of the occurrence of ESD in turbine lubricating systems is the appearance of varnish. Although the exact chemical composition of varnish has not been characterized in detail, it is generally assumed that these sludgy residues consist of oil base stock and/or additive degradation products. Thus, although the term “varnish” itself may suggest a product of some well-defined composition or origin, in practice, many different forms of varnish exist and have been observed. In turbine lubricating systems, the thermal oxidative breakdown is nearly exclusively responsible for both the additive and oil breakdown that leads to varnish formation.

The typical oil formulations employed in turbine lube systems are known to exhibit relatively low electrical conductivities, typically $<10 \text{ pS}\cdot\text{m}^{-1}$ at 25°C . At typical flow rates employed in those systems ($6000 \text{ L}\cdot\text{min}^{-1}$) and the effective hydraulic loads ($0.027 \text{ L}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$), ESD can be expected to occur under normal operating conditions. Because the temperature of arcing events associated with ESD phenomena can easily reach or exceed 5000 K , they provide sufficient energy to break carbon-carbon, carbon-hydrogen, carbon-nitrogen, nitrogen-hydrogen and oxygen-hydrogen bonds present in oil base stock and antioxidant additive molecules employed in these formulations. Breaking these bonds would result in the formation of free radicals that would lend themselves to investigation and identification by ESR spectroscopy. The evidence of the formation of these free radicals in the course of ESD arcing events would then provide a direct confirmation that ESD occurrence in turbine lubricating systems contributes to accelerating oil and additive degradation processes and leads to varnish formation through free radical polymerization.

EXPERIMENTAL

Electrostatic charging of oil leading to arcing events was carried out on a in-house hydraulic test stand constructed at the HYDAC FluidCareCenter[®] Laboratories. The test stand was filled with ChevronTexaco Regal Premium EP turbine lubricating oil conforming to the ISO VG 46 specification. The evaluations were carried at a flow rate of $26 \text{ L}\cdot\text{min}^{-1}$ which yielded a hydraulic load of $0.06 \text{ L}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$. All experiments were carried out at 25°C at which conditions the oil exhibited an electrical conductivity of $5 \text{ pS}\cdot\text{m}^{-1}$. The oil was charged for approximately twenty minutes before the spectra were acquired.

The magnitude of the electrostatic potential building up on the filter element and of the associated ESD events that occurred within the test stand lubricating system were measured with a proprietary, patent-pending, HYDAC-built sensor (Stat-Stick[®]). The signal was acquired with the aid of a Tektronix model P6015A ground-referenced probe, which allows for high voltage measurements when connected to an oscilloscope with input resistance of $1 \text{ M}\Omega$

and input capacitance between 7 pF and 49 pF. The probe carries an internal resistance of 100 M Ω and an internal capacitance of 3.0 pF and attenuates the acquired signal by a factor of 1,000. The probe signals were analysed and stored on the Tektronix model TDS 2014B four-channel 100 MHz (1 GS/s) digitizing oscilloscope.

The ESR spectra were collected using a Magnostech Miniscope 100 equipped with a temperature controller. The spectrometer operates at a resonant frequency of 9.43GHz with the centre field of 333 mT, and the range of the field sweep of 19.90 mT. The experiments were carried out at a modulation amplitude of 0.1 mT, microwave attenuation of 3dB, gain of 900, and field sweep of 30 s. 16 scans were collected to achieve a reasonable S/N ratio.

RESULTS

The oil began to acquire a negative charge immediately after the hydraulic circuit was engaged. The average charge acquired by the oil was approximately -100 V and remained nearly constant throughout the duration of the experiment. This is illustrated in **Figure 1** displayed below:

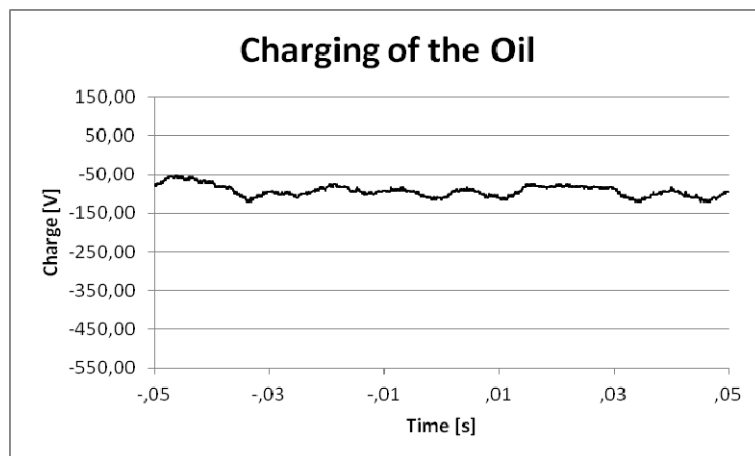


Fig. 1. Charge Acquired by Oil in the Course of the Experiment

Rys. 1. Ładunek nabyty przez olej w trakcie eksperymentu

In addition to the constant charge acquired by the oil, multiple arcing events were observed to occur between the filter element and the housing as well as among the pleats of the filter element mesh pack. Multiple arcing events could be observed on the millisecond time scale, and the individual incidents reached an amplitude as high as -500 V. A sample oscilloscope trace showing the recorded arcing events is displayed in **Figure 2** below:

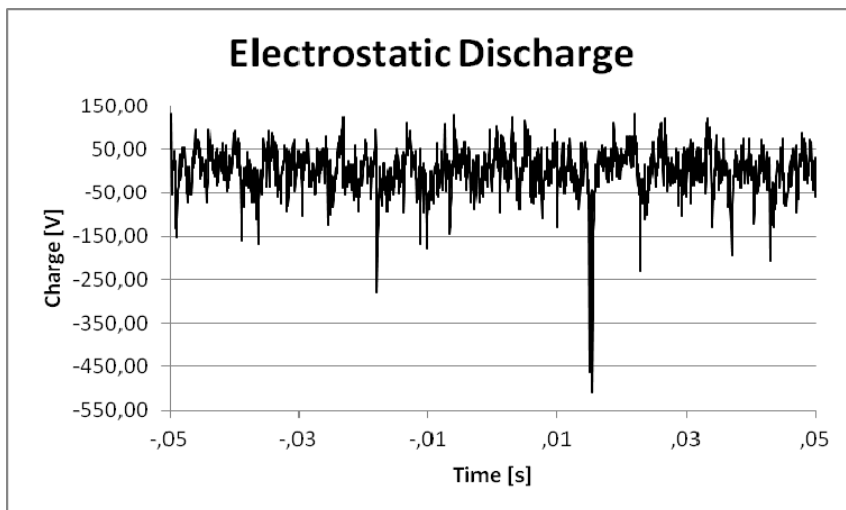


Fig. 2. Oscilloscope Trace Showing Multiple Arcing Events

Rys. 2. Wykres oscyloskopu wykazujący wielokrotne wyładowania elektrostatyczne

After an approximately twenty minute interval of continuous arcing, an attempt was made to collect the first ESR spectrum. An oil sample was withdrawn directly downstream of the filter housing and inserted into the cavity of the ESR spectrometer. Following a brief search with the field sweep, an ESR signal (displayed in **Figure 3** on the following page) was acquired.

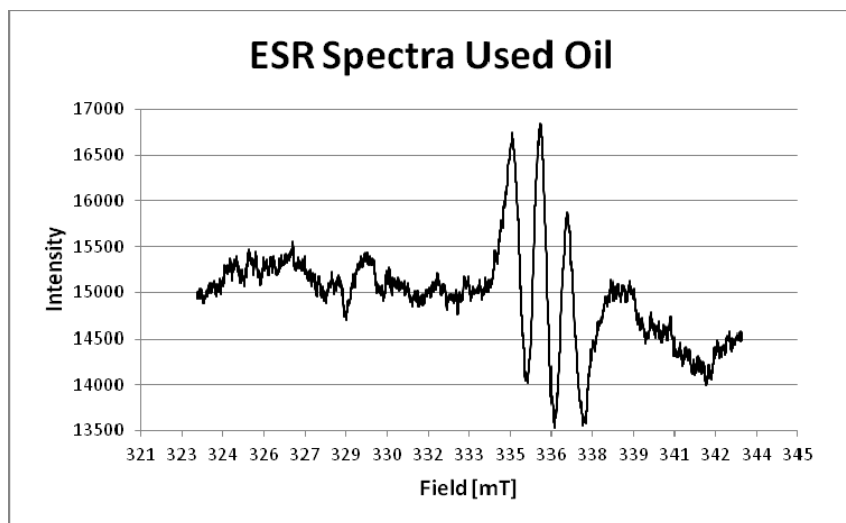


Fig. 3. ESR Signal Obtained of Oil Exposed to Twenty Minutes of Continuous Arcing

Rys. 3. Sygnał ESR otrzymany po dwudziestu minutach ciągłych wyładowań w oleju

In contrast, but as expected, the sample of fresh oil did not exhibit any ESR signals due to the absence of free radicals, as shown in **Figure 4** below:

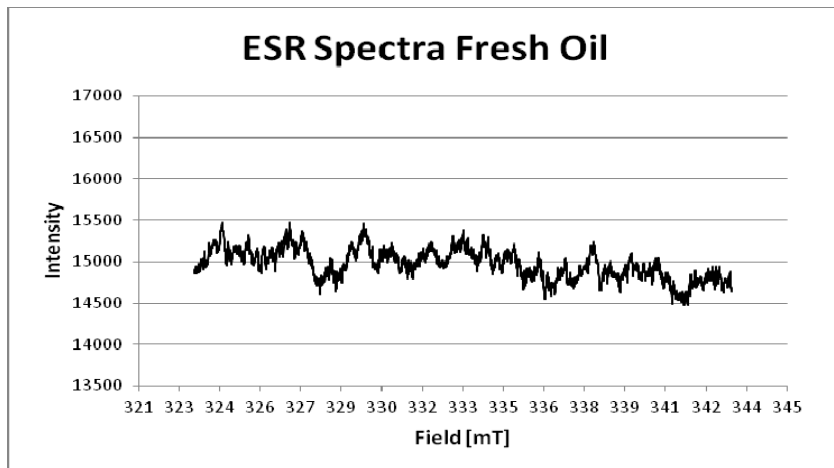


Fig. 4. ESR Signal of Fresh Oil Not Exposed to ESD Arcing

Rys. 4. ESR spektrum świeżego oleju niepoddanego wyładowaniom elektrostatycznym

DISCUSSION

The lubricating oils typically employed in gas turbine lubricating systems are of the ISO VG 32 or ISO VG 46 type, and it can be generally assumed that they are of the API Group II type or higher. The American Petroleum Institute (API) classifies these oil Groups as I (solvent extracted), II (hydrotreated) and III (hydrocracked), respectively [L. 1]. The more severe refining reduces the sulphur and unsaturate contents and increases the viscosity index (from 95 to 120) going from Group I to Group III, respectively. The past ten years have witnessed a gradual but accelerating trend towards replacement of Group I with Group II or III oils across the board in nearly all industrial hydraulic and lubricating applications.

The wider implementation of the Group II and III oils have brought about two unforeseen and unexpected side effects, namely the significant decrease in electrical conductivity and a marked decrease in solvency properties, particularly towards oil oxidation products. Moreover, the elimination of zinc containing antioxidants to create ashless formulations further lowered the conductivity values [L. 2]. These seemingly minor changes in chemical makeup have brought about many new phenomena previously not considered in typical applications. The range of these phenomena is quite broad and includes electrostatic discharge, varnish formation, novel additive interaction and degradation mechanisms and others. Many of these new behavioural

mechanisms have yet to be characterized in greater detail and often require new analytical techniques as well as direct, *in-situ* measurements, to evaluate their impact on system performance under normal operating conditions.

In this regard, field experience based on several years of empirical observations as well as ample experimental evidence strongly suggest that one of the primary contributing factors to accelerated oil and additive degradation is the oxidative breakdown caused by the electrostatic charging of filter elements employed in the turbine lubricating system [L. 3]. However, thus far no direct evidence to that effect has been provided or even found. One possible way of closing this gap and demonstrating the missing link would be to show that ESD arcing could result in the formation of some molecular species known to form and/or play a role in what is accepted as the standard free radical oil and additive oxidative breakdown mechanism [L. 4]. Because the proposed mechanism involves a whole series of organic radicals, finding an ESR signal for any one of them would provide firm evidence that electrostatic charging of filter elements is indeed one of the primary factors contributing to the accelerated aging of oil and additive package components by initiating the oxidative breakdown mechanism.

The ESR spectrum shown **Figure 3** clearly illustrates that, following a twenty-minute period of exposure to arcing, the formation of some free radicals within the oil does take place. As a background check, no ESR spectrum has been observed for a sample of fresh oil, as shown in **Figure 4**. A comparison of these two Figures clearly substantiates the claim that free radicals do form as a result of electrostatic arcing that occurs in turbine lubricating systems under conditions similar to those employed on our test stand. The next point to consider would therefore have to deal with the identity of the free radical species responsible for the signal observed in **Figure 3**.

Considering the whole host of species that form in the course of the free radical driven oxidative breakdown of hydrocarbons, one way of approaching this issue would be to consider the natural lifetime of the individual by-products involved [L. 5]. Even a brief examination of the structures participating either in the initiation, the propagation, or the termination of the free radical polymerization mechanism suggests that most of them would be very short lived, thus making their direct observation extremely difficult or impossible. A notable exception to this regard would be the BHT radical where the free electron is located on the sterically hindered oxygen protected by the tertiary butyl groups and is stabilized by the proximity of the aromatic ring [L. 6]. The formation and structure of the BHT radical are shown in **Figure 5**.

BHT is frequently employed for its antioxidant properties in a wide variety of applications in addition to turbine lubricating oils. For example, it is also a well-known food additive as well as a component in sunscreen lotions. Consequently, abundant data has been published facilitating the comparison of

the collected ESR spectrum “suspect” to its well-known and well-characterized counterpart. This comparison was carried out, and the result is displayed in **Figure 6**.

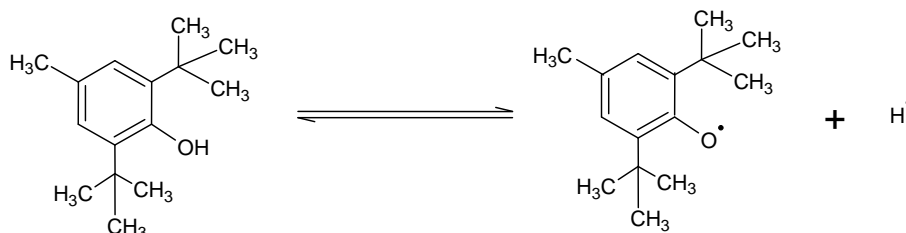


Fig. 5. Formation and structure of the BHT radical

Rys. 5. Powstawanie i struktura wolnego rodnika BHT

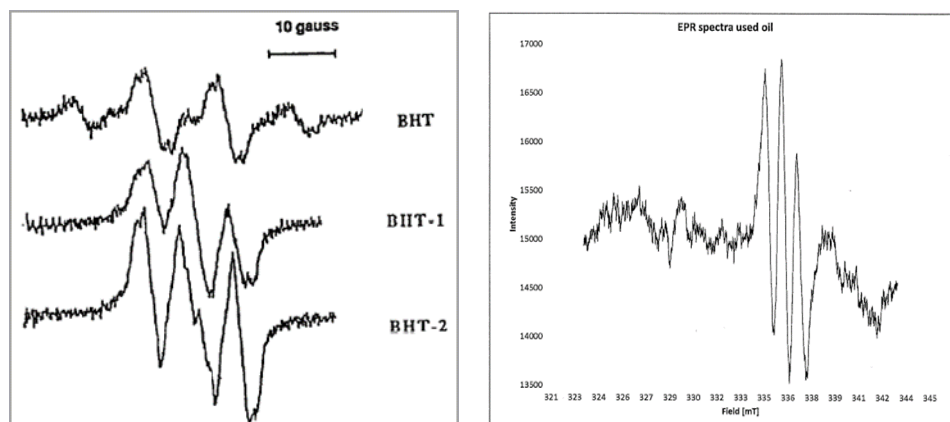


Fig. 6. Comparison of the literature ESR spectra of BHT radicals and derivatives (left) against collected ESR spectrum of the “suspect” BHT radical

Rys. 6. Porównanie opublikowanych ESR spektrów wolnych rodników BHT i pochodnych z otrzymanym spektrum „prawdopodobnego” wolnego rodnika BHT

The imperfect scaling of the spectra displayed above in **Figure 6** precludes the direct comparison of the signal traces, including the location of the signal, its width, shape, the free electron value ($g = 2.0356$) and essentially all other features are consistent with the fact that the collected spectrum belongs to the BHT radical [L. 7]. Similarly, this interpretation is consistent with the fact that BHT or one of its close derivatives is very likely to be employed in this turbine lube oil formulation.

CONCLUSION

The data presented herein provide conclusive evidence for the formation of free radical species that occurs as a result of electrostatic arcing which can take place within turbine lubricating systems under certain operating conditions. The free radical identified by the collected ESR spectrum has been shown to be BHT, a common antioxidant additive frequently employed in turbine lubricating oil formulations. As a result of these investigations, ESD has been clearly shown to be responsible at least for initiating the free radical formation mechanism. Consequently, its active role in accelerating and promoting the oil and additive oxidative breakdown processes has likewise been demonstrated. Collectively, these findings strongly suggest that all steps necessary to eliminate the occurrence of ESD in turbine lubricating systems be undertaken in order to prevent damage to the lubricant and/or its additive package components.

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Streszczenie

Wyladowania elektrostatyczne zostały wygenerowane w typowym oleju ISO VG 46 cSt stosowanym jako olej smarny w turbinach gazowych w trakcie przepływu oleju przez element filtracyjny na bazie włókien szklanych przy obciążeniu hydraulicznym wynoszącym $0,06 \text{ L} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$. Przewodowość oleju wynosiła $8 \text{ pS} \cdot \text{m}^{-1}$ przy temperaturze 25°C . Eksperyment został przeprowadzony w temperaturze pokojowej. Maksymalna amplituda wyladowań elektrostatycznych osiągnęła -500 V . Amplituda wyladowań była wystarczająca, by doprowadzić do powstawania wolnych rodników BHT stosowanym jako antyutleniacz w typowych formułacjach turbinowych olejów smarnych. Obecność wolnego rodnika BHT została zarejestrowana za pomocą X-Band MiniScope MS100 spektrometru z częstotliwością rezonansową $9,43 \text{ GHz}$ o maksymalnym zasięgu pola magnetycznego 400 mT . Zarejestrowane wyniki wskazują, że ESD może być źródłem powstawania wolnych rodników i prowadzić do wolnorodnikowych procesów polimeryzacyjnych odpowiedzialnych za tworzenie się zanieczyszczeń osadowych w turbinowych olejach smarnych.