Designation: D7590 − 09 (Reapproved 2014)

Standard Guide for
Measurement of Remaining Primary Antioxidant Content In In-Service Industrial Lubricating Oils by Linear Sweep Voltammetry[1]

INTRODUCTION

Under normal thermal and oxidative working conditions, which degrade the chemical composition of the oil's basestock and gradually deplete the oil's additive package, good oil condition monitoring procedures are necessary to determine and planning corrective actions before the oil properties changes have passed their warning limits. Antioxidant monitoring practices are a vital part of modern oil condition monitoring practices to achieve lubrication excellence. This guide addresses the correct guidelines for voltammetric data interpretation.

1. Scope

1.1 This guide covers the voltammetric analysis for qualitative measurements of primary antioxidants in new or in-service type industrial lubricants detectable in concentrations as low as 0.0075 mass percent up to concentrations found in new oils by measuring the amount of current flow at a specified voltage in the produced voltammogram.

1.2 This guide can be used as a resource for a condition monitoring program to track the oxidative health of a range of industrial lubricants which contain primary antioxidants. In order to avoid excessive degradation of the base-oil, these primary antioxidants play a major role to protect the lubricants against thermal-oxidative degradation. This guide can help users with interpretation and troubleshooting results obtained using linear sweep voltammetry (LSV).

1.3 When used as part of oil condition monitoring practices, it is important to apply trend analysis to monitor the antioxidant depletion rate relative to a baseline sample rather than use voltammetry for an absolute measurement of the antioxidant concentration. The trending pattern provides a proactive means to identify the level of oil degradation or abnormal changes in the condition of the in-service lubricant.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4378 Practice for In-Service Monitoring of Mineral Turbine Oils for Steam, Gas, and Combined Cycle Turbines
D6224 Practice for In-Service Monitoring of Lubricating Oil for Auxiliary Power Plant Equipment
D6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration
D6810 Test Method for Measurement of Hindered Phenolic Antioxidant Content in Non-Zinc Turbine Oils by Linear Sweep Voltammetry
D6971 Test Method for Measurement of Hindered Phenolic and Aromatic Amine Antioxidant Content in Non-zinc Turbine Oils by Linear Sweep Voltammetry
D7214 Test Method for Determination of the Oxidation of Used Lubricants by FT-IR Using Peak Area Increase Calculation

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[1] This guide is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.09.0C on Oxidation of Turbine Oils.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

2.2 *ISO Standards:*[3]

ISO 4406.2 Hydraulic fluid power—Fluids—Method for coding the level of contamination by solid particles

2.3 *Other Standards:*[4]

VGB Guideline VGB-M 416 M In-Service Monitoring of Turbine Oils

3. Oil Condition Monitoring Programs

3.1 Most industrial lubricants consist of mineral or synthetic oils compounded with oxidation and rust inhibitors. Depending upon their application and the performance level desired, specific required amounts of other additives such as metal deactivators, pour depressants, extreme pressure additives, and foam suppressants can also be present.

3.2 With modern formulations of industrial lubricants, the antioxidants play a major role in protecting the base-oil against excessive degradation. To prevent this base-oil degradation, resulting in the eventual build-up of deposits, varnish and sludge, the monitoring of the antioxidants represents a proactive information on the remaining oxidative health of the in-service lubricant. Oxidation is a chemical reaction between oxygen atoms with the base oil hydrocarbon molecules, which are converting the hydrocarbon molecules into oxidation products and subsequently weak organic acids. The rate of oxidation depends on the presence of antioxidant additives, which controls the speed of oxidation, but eventually the antioxidants are consumed. Consequently as part of modern proactive maintenance strategies, it is vital to know at any time during the operating cycle of the lubricants, its condition by assessing the remaining activity of antioxidants, to prevent the oxidative degradation of the base oil.

3.3 Antioxidant monitoring guidelines have been part of International Standards such as Practice D4378, Practice D6224, and VGB Guideline VGB-M 416 M, as well International OEM Maintenance Specifications. This guide presents guidelines for the lubricant professionals using voltammetric techniques as part of their regular maintenance strategies, such as data interpretation, oil analysis frequency, combination with other condition monitoring tests, etc.

4. Summary of Linear Sweep Voltammetric (LSV) Test Method

4.1 Linear Sweep Voltammetric (LSV) test can be performed on any type of industrial lubricant containing at least one type of antioxidant. The voltammetric test is a comparative test method. By establishing a comparison between its reference oil (fresh oil or standard) and its used oil, this guide can be used without the specific knowledge on the category to which the antioxidants belong.

4.2 ASTM International has two standards, Test Method D6810 and D6971, that shall enable the measurement of the remaining phenolic and aminic type of antioxidants. No standard test method has been developed for the detection of other type of antioxidants by linear voltammetry, although LSV also has detection capabilities for these types of secondary antioxidants (such as zinc dialkyl dithiophosphates).[5]

4.3 A measured quantity of sample is dispensed into a vial containing a measured quantity of a selected test solution and containing a layer of sand. When the vial is shaken, the antioxidants and other solution soluble oil components present in the sample are extracted into the electrolytic test solution and the remaining droplets suspended in the test solution are agglomerated by the sand. The sand/droplet suspension is allowed to settle out and the antioxidants dissolved in the test solution are quantified by voltammetric analysis. The results are calculated and reported as mass percent of antioxidant or as millimoles (mmol) of antioxidant per litre of sample for prepared and fresh oils and as a percent remaining antioxidant for in-service oils.

4.4 Voltammetric analysis is a technique that applies electroanalytic methods wherein a sample to be analyzed is mixed with an electrolyte and a solvent (acetone or ethanol based), and placed within an electrolytic cell. Data is obtained by measuring the current passing through the cell as a function of the potential applied, and test results are based upon current, voltage and time relationships at the cell electrodes. The cell consists of a fluid container into which is mounted a small, easily polarized working electrode, and a large non-polarizable reference electrode. The reference electrode should be massive relative to the working electrode so that its behavior remains essentially constant with the passage of small current; that is, it remains unpolarized during the analysis period. Additional electrodes, auxiliary electrodes, can be added to the electrode system to eliminate the effects of resistive drop for high resistance solutions. In performing a voltammetric analysis, the potential across the electrodes is varied linearly with time, and the resulting current is recorded as a function of the potential. As the increasing voltage is applied to the prepared sample within the cell, the various additive species under investigation within the oil are caused to electrochemically oxidize. The data recorded during this oxidation reaction can then be used to determine the remaining useful life of the oil type. A typical current-potential curve produced during the practice of the voltammetric test can be seen by reference to Fig. 1. Initially the applied potential produces an electrochemical reaction having a rate so slow that virtually no current flows through the cell. As the voltage is increased, as shown in Fig. 1, the electroactive species (for example, substituted phenols) begin to oxidize at the working electrode surface, producing an anodic rise in the current. As the potential is further increased, the decrease in the electroactive species concentration at the electrode surface and the exponential increase of the oxidation rate lead to a maximum in the current-potential curve shown in Fig. 1.

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[3] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, http://www.iso.org.

[4] Available from VGB PowerTech e.V., P. O. Box 10 39 32, D-45039 Essen, Klinkestraße 27 - 31, D-45136 Essen, http://www.vgb.org.

[5] "Remaining Useful Life Measurements of Diesel Engine Oils, Automotive Engine Oils, Hydraulic Fluids, and Greases Using Cyclic Voltammetric Methods," STLE, *Lubrication Engineering*, Vol 51, 3, pp. 223 –229.

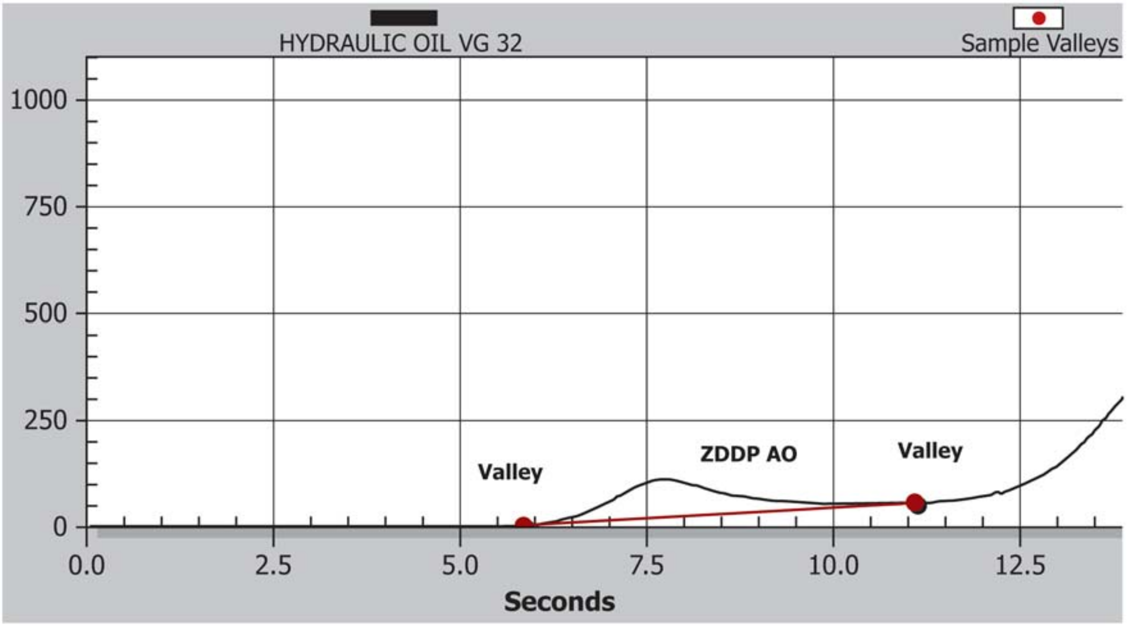

FIG. 1 Zinc Dialkyl Dithiophosphate (ZDDP) Voltammetric Response in the Neutral Test Solution with Blank Response Zeroed

5. Significance and Use

5.1 The quantitative determination of remaining antioxidants for in-service industrial oils by measuring the amount of these additives that have been added to the oil as protection against oxidation. Industrial lubricants, such as turbine oils, compressor oils, gear oils, hydraulic oils, bearing lubricants and greases can be formulated with a wide variety of antioxidants types such as phenols and amines (as primary antioxidants), which are working synergistically and therefore all important to be monitored individually. For in-service oils, the LSV determines and compares the amount of original primary antioxidants remaining after oxidation have reduced its initial concentration.

5.2 This guide covers procedures for primary antioxidants such as amines and phenols, as described by Test Method D6971 and D6810.

5.3 LSV is not designed or intended to detect all of the antioxidant intermediates formed during the thermal and oxidative stressing of the oils, which are recognized as having some contribution to the remaining useful life of the used or in-service oil. In order to measure the overall stability of an oil (including contribution of intermediates present), and before making final judgment on the remaining useful life of the used oil (which might result in the replacement of the oil reservoir), it is advised to perform additional analytical techniques (in accordance with Practice D4378 and Practice D6224).

5.4 This guide is applicable to a wide range of industrial oils, both mineral or synthetic based, which can contain rust and oxidation inhibitors, antiwear additives such as zinc dialkyl dithiophosphates on gear oils, circulating oils, transmission oils and other industrial lubricating oils.

5.5 The test is also suitable for manufacturing control and specification acceptance.

5.6 When a voltammetric analysis is obtained for a industrial lubricant inhibited with at least one type of antioxidant, there is an increase in the current of the produced voltammogram between 5 to 8 s (or 0.5 to 0.8 V applied voltage) (see Note 1) for the zinc dialkyl dithiophosphate type of antioxidant (Fig. 1), an increase in the current of the produced voltammogram between 8 to 12 s (or 0.8 to 1.2 V applied voltage) (Fig. 2) (see Note 1) for the aromatic amines, and increase in the current of the produced voltammogram between 13 and 16 s (or 1.3 to 1.6 V applied voltage) (see Note 1) for the hindered phenols or carbamates in the neutral acetone solution (Fig. 2: x-axis 1 s = 0.1 V), or both. Hindered phenol antioxidants detected by voltammetric analysis include, but are not limited to, 2,6-di-*tert* -butyl-4-methylphenol; 2,6-di-*tert*-butylphenol and 4,4'-Methylenebis(2,6-di- *tert*-butylphenol). Aromatic amine antioxidants detected by voltammetric analysis include, but are not limited to, phenyl alpha naphthylamines, and alkylated diphenylamines.

NOTE 1—Voltages listed with respect to reference electrode. The voltammograms shown in Figs. 1-6 were obtained with a platinum reference electrode and a voltage scan rate of 0.1 V/s.

5.7 For industrial lubricants containing zinc dialkyl dithiophosphate type of antioxidants, there is an increase in the current of the produced voltammogram between 5 to 8 s (or 0.5 to 0.8 V applied voltage) (see Note 1) by using the neutral acetone test solution (see Fig. 1). There is no corresponding ASTM International standard describing the test method procedures for measuring zinc dialkyl dithiophosphates type of antioxidants in industrial lubricants.

5.8 For industrial lubricants containing only aromatic amines as antioxidants, there is an increase in the current of the produced voltammogram between 8 to 12 s (or 0.8 to 1.2 V applied voltage) (see Note 1) for the aromatic amines, by using

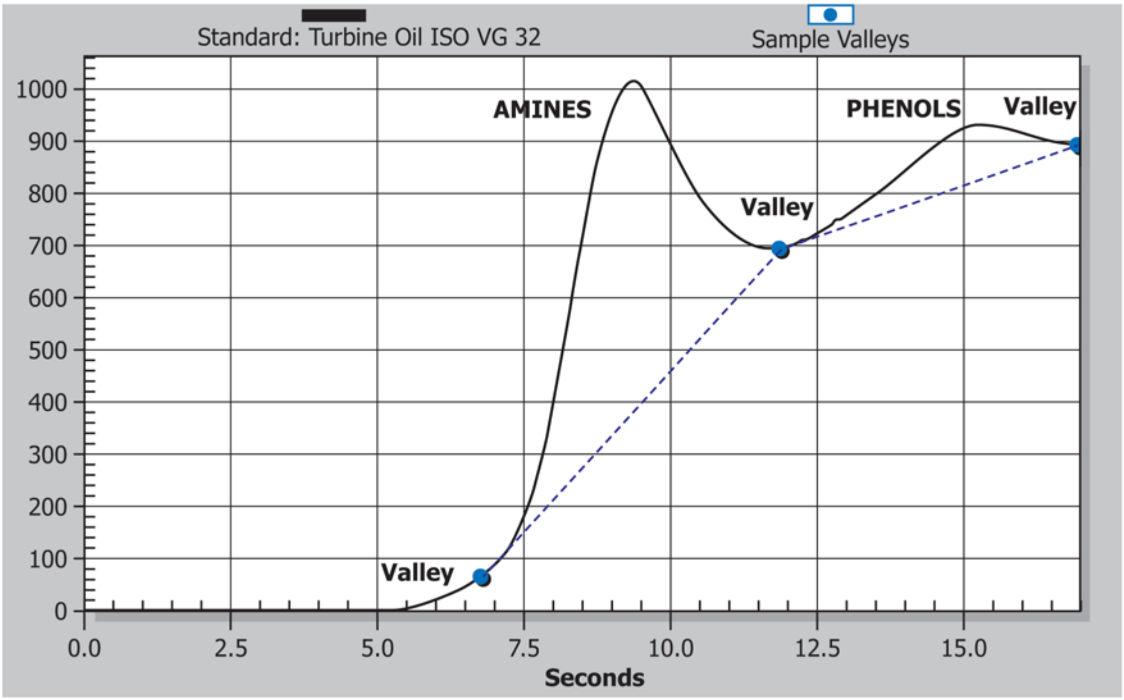

FIG. 2 Aromatic Amine and Hindered Phenol Voltammetric Response in the Neutral Test Solution with Blank Response Zeroed

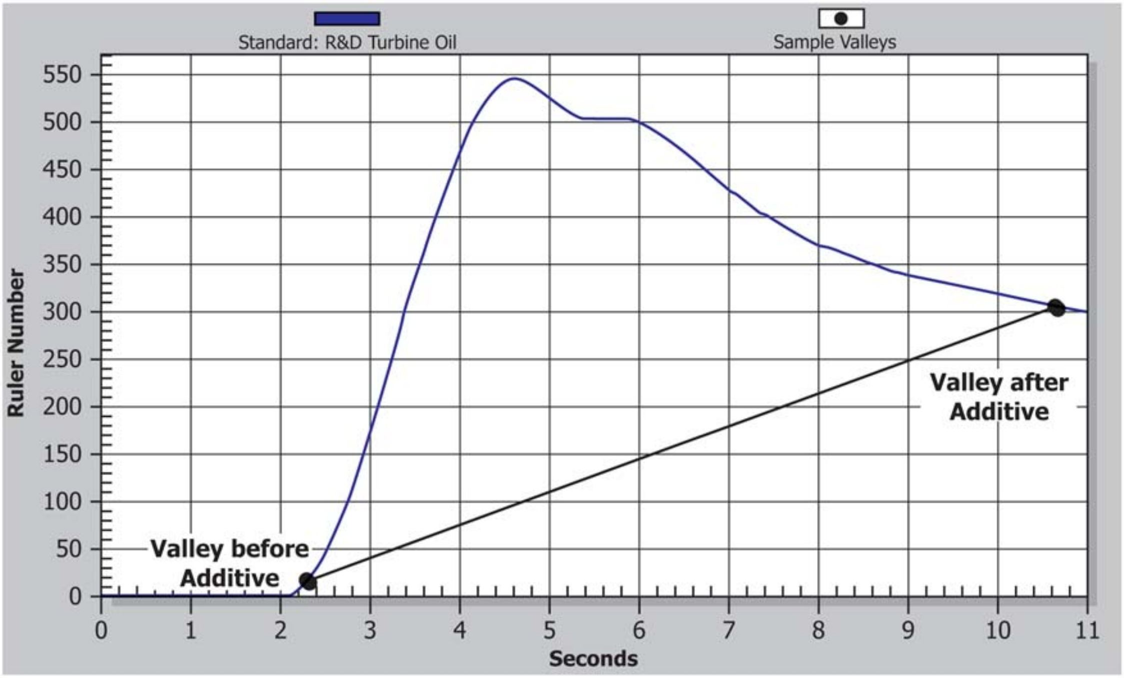

FIG. 3 Hindered Phenol Voltammetric Response in Basic Test Solution with Blank Response Zeroed

the neutral acetone test solution (first peak in Fig. 2) as described in Test Method D6971.

5.9 For industrial lubricants containing only hindered phenolic antioxidants, it is preferable to use a basic alcohol solution rather than the neutral acetone solutions, to achieve an increase in the current of the produced voltammogram between 3 to 6 s (or 0.3 to 0.6 V applied voltage) (see Note 1) in basic alcohol solution (Fig. 3: x-axis 1 s = 0.1 V) as described in Test Method D6810.

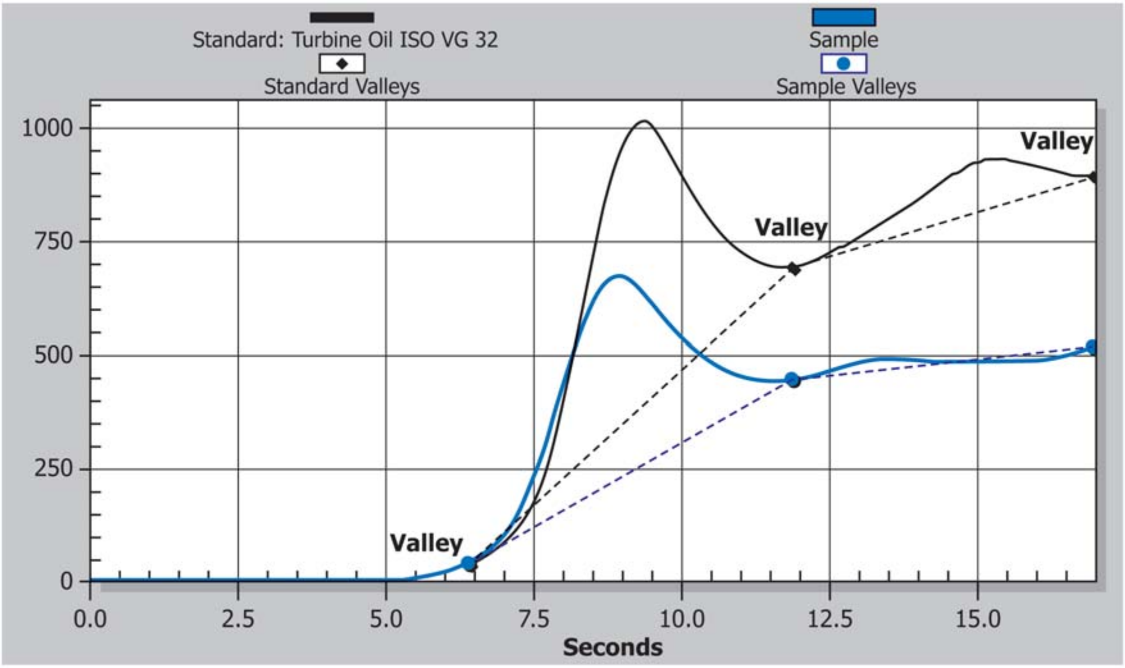

FIG. 4 Voltammetric Reading for an In-service Oil Sample Comparing Aromatic Amines (additive #1) and Hindered Phenols (additive #2) Peaks (in the Neutral Test Solution)—Standard (top line) and Sample In-Service Oil (lower line)

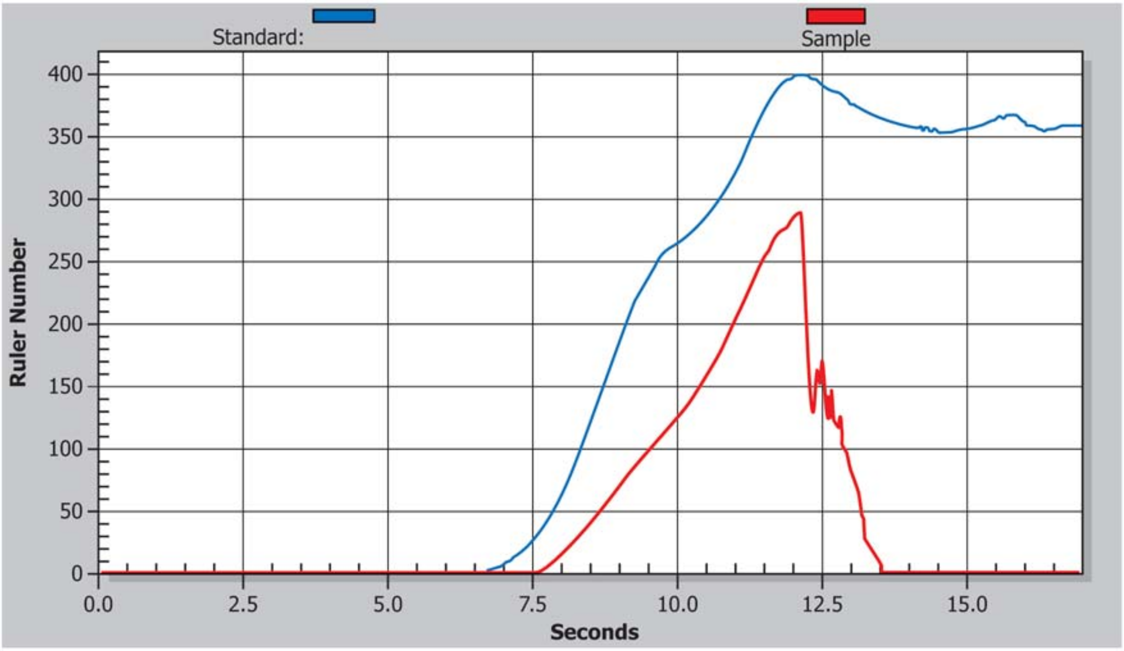

FIG. 5 a Filming Problems Due to Oil Solubility

6. Voltammetric Test Apparatus

6.1 *Voltammetric Analyzer*[6]—Specifically designed to perform antioxidant determinations of industrial oils. The instrument used to quantify the hindered phenol and aromatic amine antioxidants is a voltammograph equipped with a three-electrode system (referred further to as the probe) and a digital or analog output. The combination electrode system consists of a glassy carbon disc (3 mm diameter) working electrode, a platinum wire (0.5 mm diameter) auxiliary electrode, and a platinum wire (0.5 mm diameter) reference electrode, as described in Test Method D6810 and D6971. The voltammetric analyzer applies a linear voltage ramp (0 to –1.7 V range with respect to the reference electrode) at a rate of 0.01 to 0.5 V/s (0.1 optimum) to the auxiliary electrode. The current output of

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[6] Trademark of Fluitec International, 1997 Newborn Rd. Rutledge, GA 30663 (USA), Nieuwbrugstraat 73 B-1830, Machelen, Belgium (Europe), www.fluitec.com.

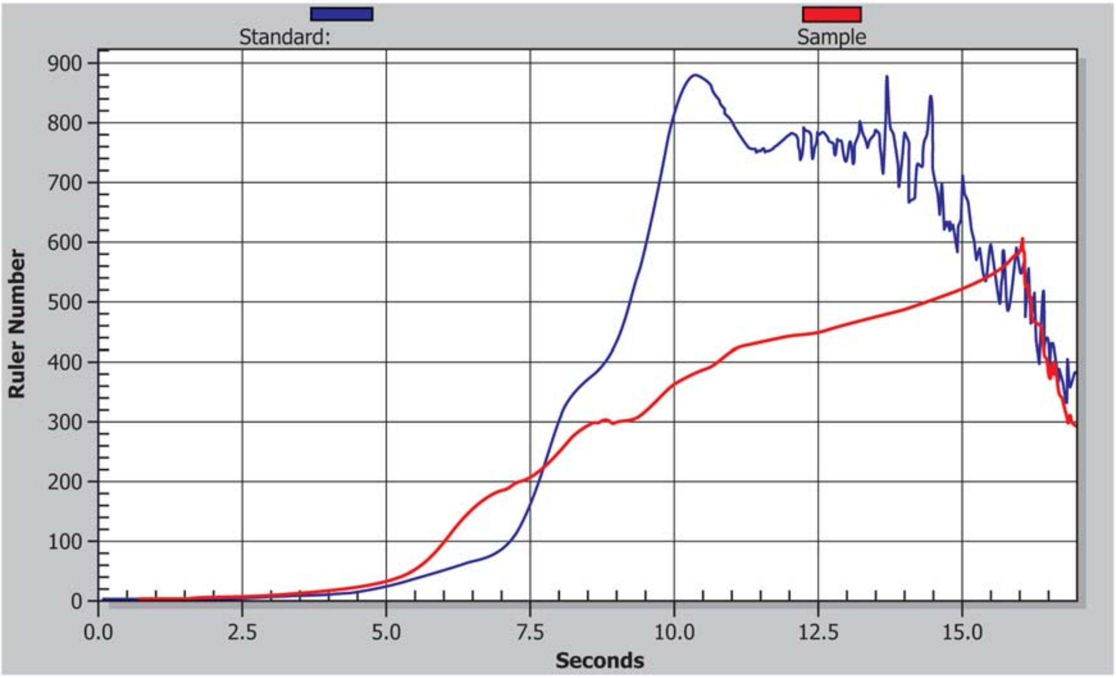

FIG. 5 b Filming Due to Additive Concentration *(continued)*

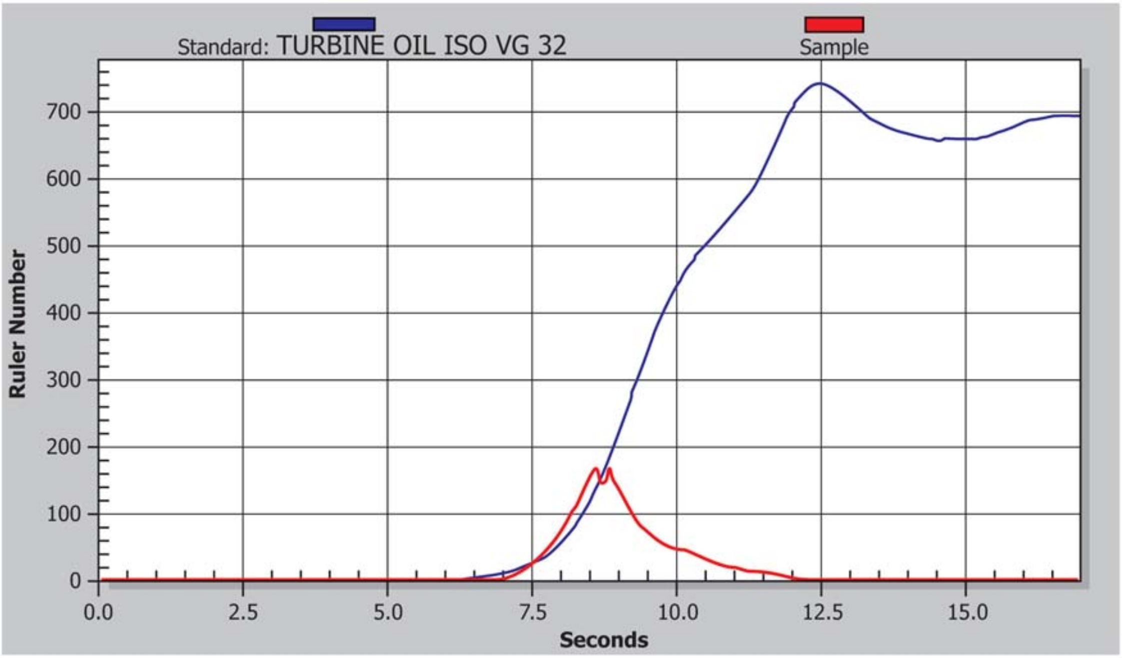

FIG. 5 c Filming Problems Due to Oil Solubility *(continued)*

the working electrode is converted to voltage by the voltammetric analyzer, using the gain ratio of 1 V/20 µA, and is outputted to an analog or digital recording device (0 to 1 V full scale) as shown in Figs. 1 and 2.

6.2 *Vortex Mixer*—A vortex mixer with a 2800 to 3000 r/min motor and a pad suitable for mixing test tubes and vials. Ultrasonic shakers may also be used to achieve a quick and efficient shaking of the prepared test solution.

6.3 *Pipet*—or equivalent, capable of delivering sample volumes required in this guide from 0.10 to 0.50 mL.

6.4 *Solvent Dispenser*—or equivalent, capable of delivering volumes of analytical test solution (see 6.3) required in this guide, such as 3.0 and 5.0 mL.

6.5 *Glass Vials with Caps*—4 or 7 mL capacity, and containing 1 g of sand.

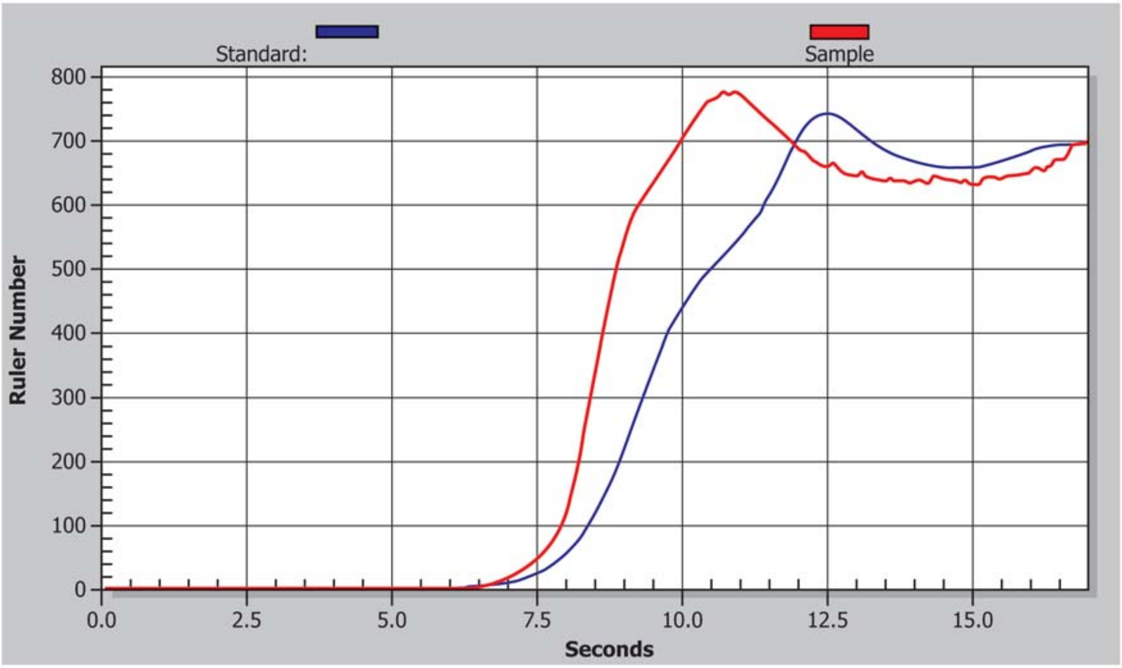

FIG. 6 Shifting of Antioxidant Peaks Due to Oil Solubility

6.6 *Sand*—Required to be white quartz suitable for chromatography within the size range of 200 to 300 ± 100 microns.

7. Sampling

7.1 Obtain the sample in accordance with Practice D4057.

8. Test Solutions – Reagents and Selection

8.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent's purity suffices to permit its use without lessening the accuracy of the determination.[7]

8.2 *Purity of Water*—Unless otherwise specified, references to water that conforms to Specification D1193, Type II water.

8.3 *Analysis Materials:*

8.3.1 *Acetone–Based Test Solution (Neutral)*—Proprietary Green Analytical Test Solution, acetone solvent (1:10 water/acetone solution) containing dissolved neutral electrolytes.

8.3.2 **Warning—**Corrosive, Poison, Flammable, and Skin Irritant. Harmful if inhaled.

8.3.3 *Alcohol–Based Test Solution (Basic)*—Proprietary Yellow Analytical Test Solution, ethanol solvent (1:10 water/ethanol solution) containing dissolved base electrolytes.

8.3.4 **Warning—**Corrosive, Poison, Flammable, and Skin Irritant. Harmful if inhaled.

8.3.5 *Alcohol Cleansing Pads*—70% isopropyl alcohol saturated cleansing pads (alcohol prepared skin cleansing pads, for the preparation of the skin prior to injection (antiseptic).

9. Procedure

9.1 The voltammetric analyzer used in the LSV method gives linear results between 2 to 50 mmol for all type of antioxidants using an oil sample size of 0.40 mL and 5.0 mL of the analytical test solutions. The corresponding range of mass percents depends on the molecular weight of the type of antioxidant, and the density of the base oil. For instance, the mass percent range of 0.044 to 1.1 is equal to 2 to 50 mmol/L for a hindered phenol containing one hydroxyl group and with a molecular weight of 220 g/mol (2,6-di-*tert*-butyl-4-methylphenol) and an oil density of 1 g/mL. Below 2 mmol, the noise to signal ratio becomes large decreasing the accuracy of the measurements. For measurements below 2 mmol or for fresh oils with high noise to signal ratios, the sample size should be increased to 0.60 mL and the volume of analysis test solutions remains at 5.0 mL.

9.2 *General Voltammetric Test Procedure*—The test procedure for voltammetric analysis consists of the blank reading (calibration), followed by a standard reading and finally the sample (in-service oil) reading.

9.2.1 *Blank Reading (0 mmol/L = 0 mass percent)*—The blank reading (voltammetric number) is a measurement of the analytical test solution by itself. The blank measurement gives a reference number with no antioxidants present (the zero baseline).

9.2.2 *Standard Reading (30 to 150 mmol/L – mass percent dependent on density of fresh oil and molecular weight of*

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[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

antioxidant)—The standard reading is a measurement of a fresh, unused oil (containing at least one type of antioxidant) mixed with an appropriate analytical test solution. This measurement gives you a voltammetric reading (standard reading) that corresponds with the voltammetric response for the 100% of antioxidant's concentration (Additive RUL% = 100%) oil being tested or analyzed.

9.2.3 *Sample (In-Service Oil), Reading*— The sample reading is a measurement of an in-service oil sample mixed with the same type of analytical test solution as the standard. This measurement provides voltammetric readings that normally range between the blank and standard measurements, and reflect the concentration of remaining antioxidants present in the in-service oil sample. Voltammetric readings for in-service oils decrease as the different types of antioxidants present in the industrial oil are depleted or consumed.

9.3 *Voltammetric Reading—Test Result Interpretation by the Graph Valley Indicators:*

9.3.1 After the operator has selected the valleys before and after the antioxidant peaks (as shown in Fig. 1) for the standard (reference oil), the software package (R-DMS)[6] automatically identifies and calculates the area above the baseline between the two valley indicators. This calculated area is then used for the sample reading (in-service oil), which is established by comparing the used oil area to its standard (see Fig. 4), and to establish remaining antioxidant calculations.

9.3.2 If the valley indicators for the in-service oil have shifted with less than 1.5 s to the left and do not correspond with the valley indicators from the corresponding standard, the operator shall perform the following actions:

9.3.2.1 Clean the probe carefully, and perform a second voltammetric test in the same prepared test solution vial.

9.3.2.2 Once the valley indicators and additive peaks are aligned, the remaining useful life calculation is performed automatically and correctly.

9.3.2.3 If the shift from the valley indicators remain, the operator shall drag the valley indicators of the in-service oil to their appropriate location. This location corresponds with the point where the valley starts (lowest point) after the antioxidant peak. (see Fig. 5).

9.3.3 If the valley indicators for the in-service oil show a shift of more than 1.5 s, the operator shall select another in-service oil sample and perform a new voltammetric test. When the large shift is persisting, this is most probably due to a problem with the reference oil or standard.

9.4 *Calibration (Blank Reading) Procedure:* Pipet 5.0 mL of analysis solution into a 7 mL vial or other suitable container containing 1g of sand.

9.4.1 Insert the probe of the voltammetric analyzer into the analytical test solution to wet the bottom surface of the electrodes, remove, and rub dry the bottom electrodes surface with a lint free paper towel.

9.4.2 Insert the probe into the test solution vial so that the bottom of the probe and its electrodes are submerged in the analytical test solution without resting on the sand layer on the bottom of the test solution vial.

9.4.3 Place the test solution vial/probe upright into rack or foam block for testing. Perform the voltammetric analysis (see 6.1).

9.4.4 Record the voltammetric reading in the neutral test solution for the individual voltage ranges of zinc dialkyl dithiophosphates (0.5 to 0.8 V) (see Note 1), aromatic amines (0.8 to 1.1 V) (see Note 1), and the phenols (1.3 to 1.6 V) (see Note 1 and Fig. 1).

9.4.5 Remove the combination electrode from the blank solution and rub dry the bottom surface of the probe with a lint free paper towel.

9.4.6 Run at least two tests of the analysis solution to ensure the electrode is clean and the minimal blank value has been obtained.

9.5 *Standard and In-Service Oil Sample Preparation Procedures:*

9.5.1 *Preparing Solution Step*—Remove seal and cap of the test solution vial. Pipet 5.0 mL of analytical test solution into a 7 mL vial or other suitable container containing 1g of sand. Pipet 0.40 mL of the selected oil sample also into the 7 mL test solution vial.

9.5.2 For measurements below 2 mmol or for fresh oils with high noise to signal ratios, the sample size should be increased to 0.60 mL and the volume of analytical test solution remains at 5.0 mL.

9.5.3 *Shaking Solution Step*—Cap the vial and shake vigorously using a vortex mixer for 20 s or by hand (between 50 and 60 shaking cycles/min), until the sand is thoroughly mixed. Ultrasonic shakers can also be used to achieve a homogeneous mixture. Place the prepared oil/test solution mixture upright in a rack or perforated foam block for a minimum time of 30 s (and a maximum time of 5 min) to allow the sand to settle on the bottom of the prepared test solutions vial with the oil.

9.5.4 *Cleaning Electrode Step*—Prepare the electrodes for analysis by cleaning the probe and its electrodes surfaces. Use an alcohol-cleansing pad to wet the bottom surface of the electrodes. These must be dried immediately with a clean lens tissue (lint free paper towel). The glassy carbon surface of the electrodes should always have a polished look before running a test. A glazed or cloudy look indicates the presence of a chemical film. If the probe tip is not cleaned properly, voltammetric readings can be distorted, and this affects the accuracy of the test method.

9.5.5 *Running Test Step*—Insert the probe into the prepared test solution vial so that the bottom of the probe and electrodes are submerged in the prepared test solution without resting on the sand layer on the bottom of the vial. Place the vial/probe upright into rack or foam block for testing. Perform the voltammetric analysis (see 6.1) for the remaining antioxidants into the in-service oil sample. Record the voltammetric reading in the neutral test solution for the individual voltage ranges of zinc dialkyl dithiophosphates (0.5 to 0.8 V) (see Note 1), aromatic amines (0.8 to 1.2 V) (see Note 1), and the phenols (1.3 to 1.6 V) (see Note 1 and Fig. 2). Remove the combination electrode from the oil solution and repeat the cleaning procedure of the electrodes surface. Run at least two tests (cleaning the electrodes between tests) of the standard or in-service oil sample to assure the value is stable and repeatable.

9.5.6 Make all measurements within 5 min after the initial mixing of the analysis solution, selected sample, and sand.

9.6 When the manufacturer of the oil is known, and the uninhibited base oil is available, use it to prepare the standards (mmol or mass percent antioxidant calculations). Prepare a standard containing in the range of 30 to 150 mmol/L of oil (0.5 to 3.0 mass percent) of the selected antioxidant(s) dissolved in an uninhibited base oil. The concentration should be selected to span the expected concentrations of the new and in-service oils.

9.7 It is generally not advised to use too high concentrations of antioxidants which may result in the filming of the voltammetric probe and even on long term damage the electrode surface(s). As a general rule of thumb we advise not to exceed the voltammetric detection level (RULER number[6]) of higher than 2000.

9.8 Standard readings should be updated whenever new batches of lubricants are stocked, and periodically to monitor the amount of natural oxidation occurring in the lubricant during storage.

9.9 For fresh or in-service oils of unknown origin, use a typical fresh turbine oil as the standard (100% remaining antioxidant calculations).

9.10 The analytical test solution and scan time should be the same for the blank, standard and in-service oil sample.

10. Troubleshooting

10.1 Here are procedures to help voltammetric test method operators when using the voltammetric analyzer for antioxidants monitoring on in-service oils.

10.2 *Filming of Voltammetric Test Probe*—When using voltammetry on lubricants which dissolve less good in the electrolytic test solutions, or when having a too high concentration of antioxidants, test results can influenced due to the filming of the test probe. Consequently the voltammetric graphs show peak shifting, irregular peak shapes (saw teeth shapes curves), and reduced reproducibility (see Fig. 5) for typical examples of probe filming problems).

10.2.1 If the oil is still floating on the test solution surface in medium size to large oil droplets, it is advised to repeat the mixing/shaking of the test solutions/oil mixture. Some hydrotreated or synthetic type of lubricants are more difficult to dissolve and will create an oil film on the voltammetric test probe. In that case it is advised to remove the oil droplet on the surface with an absorbing tissue and perform the voltammetric test again, once the floating oil droplets have been removed.

10.2.2 If the oil shows good solubility, with the oil droplets at the bottom of the vial, and the test solution becoming clear, but a graph (Fig. 5b) appears, than the concentration of the antioxidants may be too high (voltammetric test result higher than 2000). Repeat the test, and if the problems persists, it is advised to prepare a new vial with half of the oil test volume, and repeat the test.

10.3 *Voltammetric Peak Shifting*—If shifting occurs (see Fig. 6) from the voltammetric peaks, it is advised to perform the three following actions:

(1) Check/control the surface of the solution for oil droplets (see 10.2). Oil solubility (especially with synthetic oils) is the primary reason for peak shifting effects.

(2) Repeat the test, by assuring yourself that the probe surface is perfectly cleaned (see 9.5.4).

(3) Assure yourself that the tested oil belongs to the same brand of oil (10.6).

10.4 If the problem persists, the reasons for peak shifting could be explained by:

(1) Presence of oxidation products (see 10.5) increase the settling time till 5 to 10 min, and the influence of oxidation products may decrease.

(2) Damage of voltammetric test probe.

10.4.1 To check the main cause for the voltammetric peak shifting, voltammetric test operators should analyze with a new reference oil (new oil), and evaluate if peak shifting persists. If the peak shifting persists, this means probe replacement and instrument calibration are needed.

10.5 *Oxidation Products Presence and Effect on Voltammetric Graphs:*

10.5.1 When oils have been degraded severely and have consequently a low concentration of remaining antioxidants (for example on turbine oils, with less than 20% of the original antioxidants), the buildup of oxidation products can be significant. The presence of these oxidation products will, in most cases, result in a tail at the end of the voltammogram, which is due to an increase of conductivity of the test solution by the presence of polar oxidation compounds. For a voltammetric operator it is important to know that this effect can start to interfere with antioxidant's calculation (see Fig. 7).

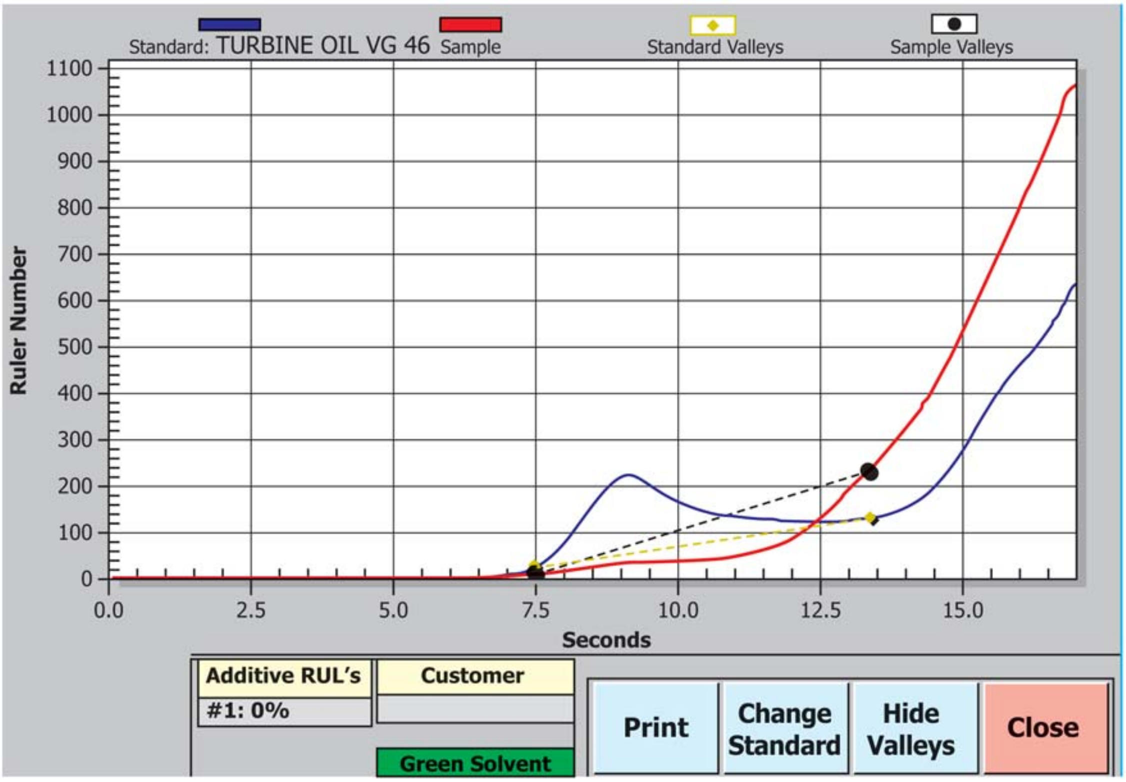
10.5.2 If oxidation products are present in in-service oils, they will be detected in the voltage/time window at 13 to 14 s, and result in a graph superseding the standard (new oil) graph. Voltammetric software calculation does not take this area increase as supplementary antioxidant activity, as calculations are based on comparison of area between the valley indicators for individual antioxidants.

10.6 *Mixtures of Oil types and Batches*—When the voltammetric graphs are not corresponding between the in-service oil and the standards, this can be due to the mixture of different type of lubricants; the voltammetric results and readings will reflect the differences in antioxidant types or concentration. Essentially, the voltammetric graphs will show the appearance of additional antioxidant peaks, change the shape of the voltammetric wave peaks, or can even increase the concentration of the antioxidants (above the 100% RUL). As the antioxidants in the different lubricant type or batch, can belong to a different class, or type of chemical compound, it is normal that the electrochemical and voltammetric response will be also different. This difference can result in:

(1) A voltammetric peak located at a different voltage/time window (Fig. 8).

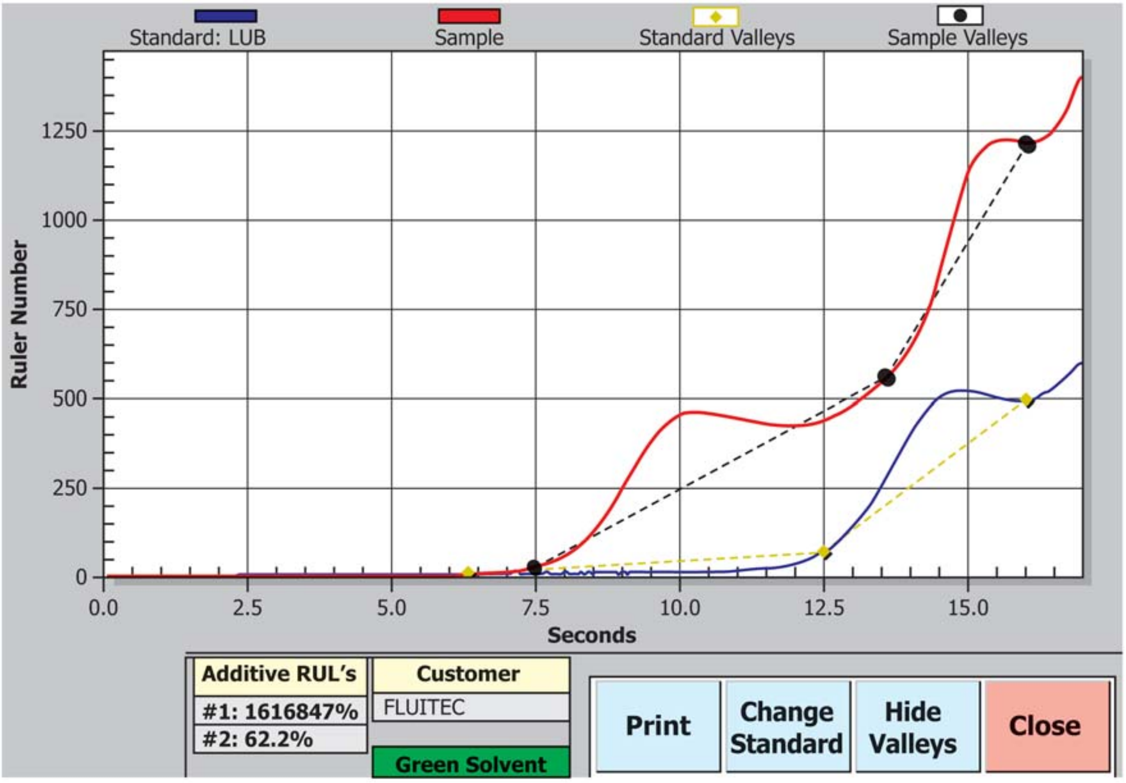
(2) A voltammetric peak with a much higher response (Fig. 9).

10.6.1 In Fig. 8, the results from the in-service oil shows one additional antioxidant (amines at 10 s), with the second antioxidant which is belonging to the same class of (phenolic)



Additive RUL's	Customer
#1: 0%	

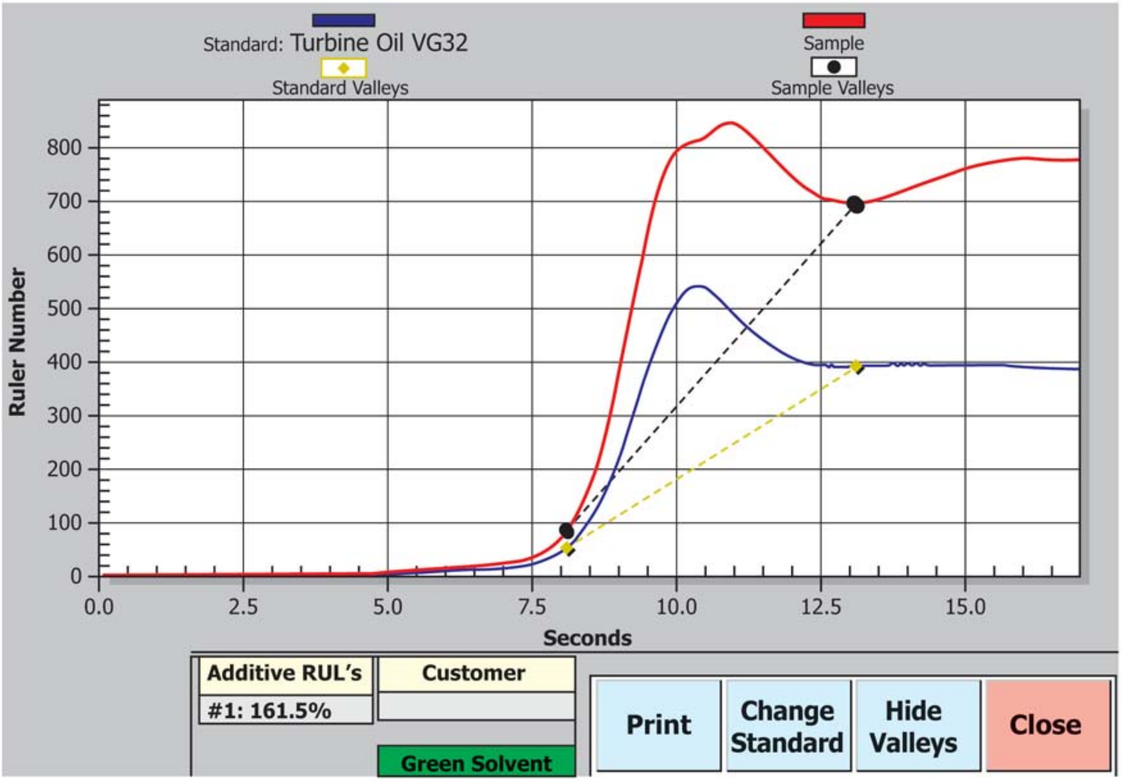
FIG. 7 Voltammetric Graph with Presence of Oxidation Products (13 to 16 s) Due to Oil Oxidation



Additive RUL's	Customer
#1: 1616847%	FLUITEC
#2: 62.2%	

FIG. 8 Voltammetric Graph from a Mixture of Two Different Lubricants and Appearance of New Voltammetric Peak

antioxidants. Voltammetric analytical data can consequently be monitored, but the operator needs to address this lubricant mixture problem, as a possible root cause for improper lubrication. In Fig. 9, we see a significant increase of peak, due



Additive RUL's
#1: 161.5%

FIG. 9 Voltammetric Graph from a Mixture of Different Lubricants with the In-service Oil (upper line) Resulting in a Higher Response than the Standard Fresh Oil (lower line)

to the mixture with a new brand of oil, having higher concentrations of antioxidants in its reference oil. Logically RUL% values exceed the 100% and will have to be used as the new reference baseline. It is up to the operator to check their lubricant supplies, as well the oil addition procedures. To check and confirm the presence of different antioxidants, it is also possible for operators to run the in-service oil samples in other voltammetric test solutions. As in modern additive packages, different additives can have different depletion trends, and therefore it is advised to select the most appropriate solution for each antioxidant (see Fig. 10a and b). From Fig. 10a and b, the user can conclude that the second antioxidant (phenols) in this turbine oil has totally depleted, whereas the oil has 66 % remaining amines (Fig. 10a). This can be confirmed by analyzing the oil in the Yellow test solution (Fig. 10b) with the same results as with the neutral test solutions (Green).

10.7 *Too Low Voltammetric Reading*—When voltammetric readings are too low (Fig. 11), with voltammetric RULER number less than 100, the voltammetric graphs are difficult to use, and consequently data interpretation will be limited. It is advised to increase the oil sample volume, to a maximum of 600µl, which shall result in a voltammetric response for the standard (reference oil) with a number of minimum 100. The oil sample volume is limited due to the solubility of the oil in to the small prepared test solution vials of 5 mL. For greases, there is no specific limit of weight, as the thickeners do not interfere with the probe surface.

10.8 *Too High RULER Reading*—When the voltammetric instrument measures a voltammetric current, with corresponding RULER number higher than 2000, it is advised to reduce the oil sample volume (half). A too high concentration of antioxidants may result in less accuracy, and as well create an irreversible filming on the test probe. The operator shall prepare a new test solution vial, as well modify the test sample information, and repeat the test.

10.9 *Cleaning Difficulties*—When a voltammetric test can not be duplicated or repeated, and cleaning problems persists, the operator shall check if the proper cleaning materials are used. It is possible that with highly contaminated and oxidized oil samples a cleaning with acetone (in place of isopropyl alcohol) will have to be executed, in order to remove some of the more harsh deposits and films created by the oxidation products.

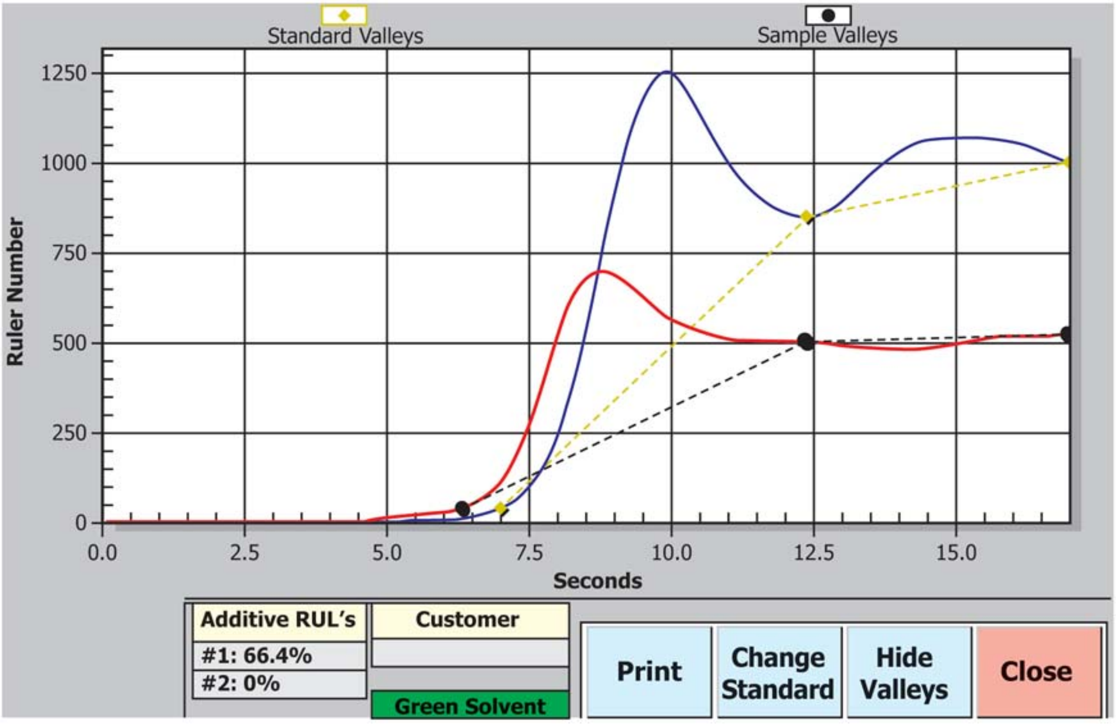
11. Calculation

11.1 *Weight Percent Remaining Antioxidant Calculation*—If the type of antioxidant present in the oil sample is known, then the percent antioxidant (% AO) in the sample can be calculated in accordance with the following equation:

$$\%\ AO = \frac{(S - B)}{(s - B)} \times w \quad (1)$$

where:

$\%\ AO$ = percent of antioxidant, %,
S = sample reading,
B = blank reading,
s = standard reading, and
w = weight percent antioxidant of standard, %.

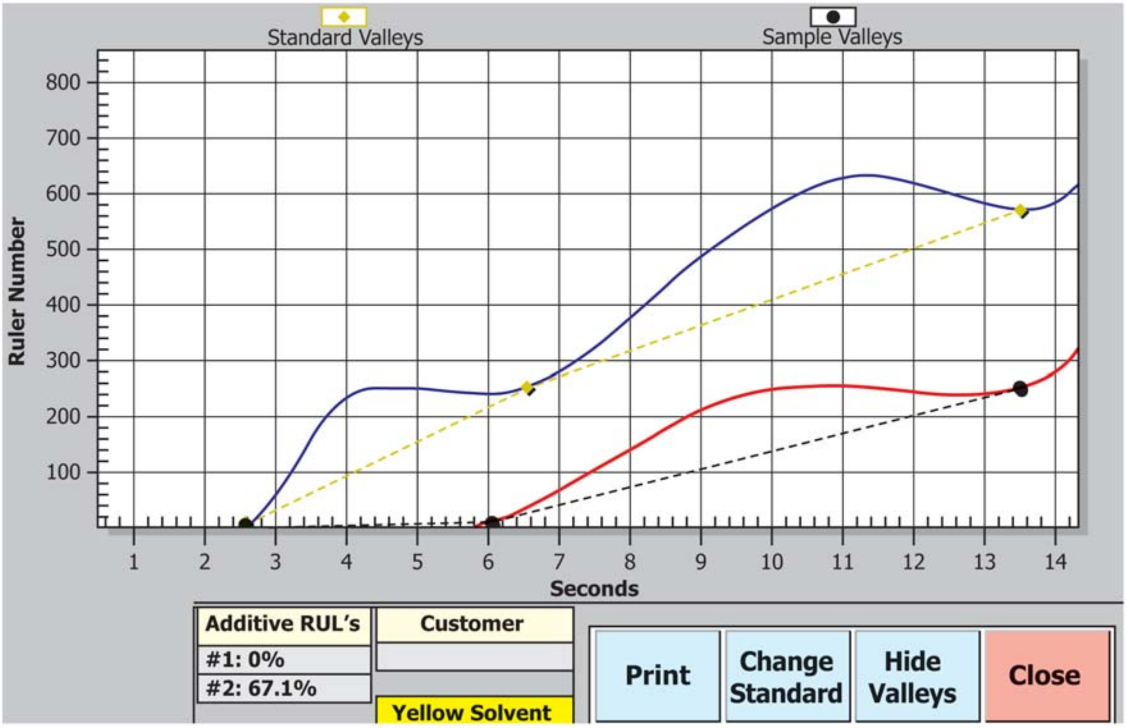


Additive RUL's
#1: 66.4%
#2: 0%

Customer

Green Solvent

FIG. 10 a Turbine Oil in Green Solution



Additive RUL's
#1: 0%
#2: 67.1%

Customer

Yellow Solvent

FIG. 10 b Same Turbine Oil in Yellow Solution *(continued)*

11.2 *Percent Remaining Antioxidant Calculation*—The percent remaining antioxidant (RUL%) in an in-service oil using the fresh oil as the RUL 100% baseline can be calculated in accordance with the following calculation:

$$RUL\% = \frac{(S - B)}{(s - B)} \times 100 \qquad (2)$$

where:

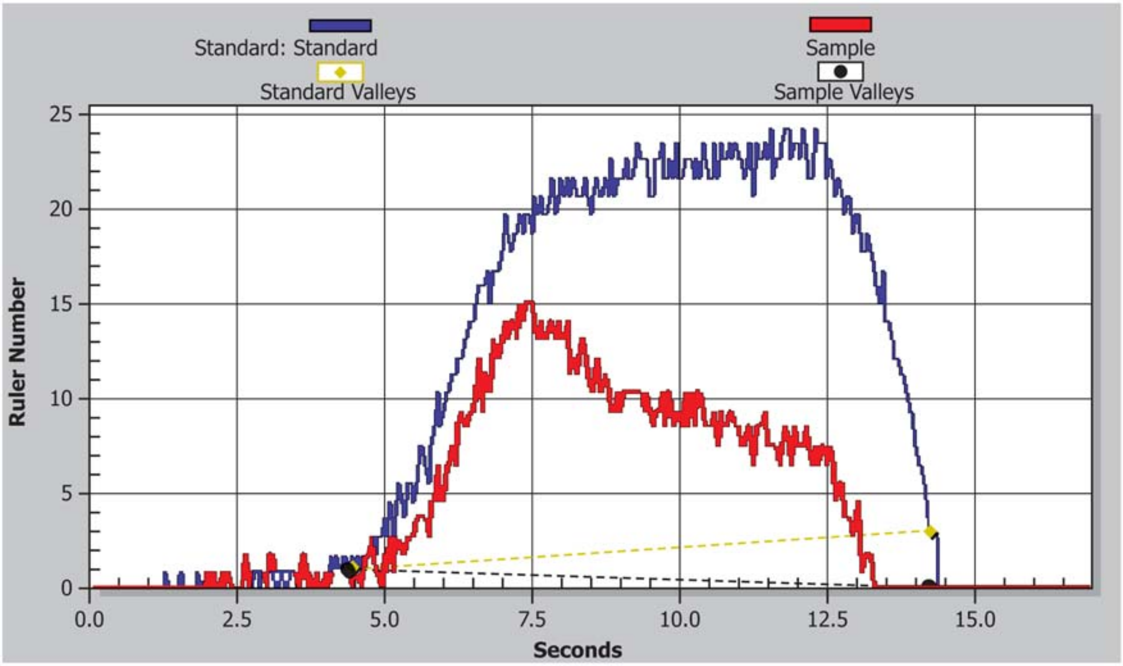


FIG. 11 Voltammetric Reading with Too Low Response

RUL% = remaining antioxidant,
S = sample reading,
B = blank reading, and
s = standard reading.

11.3 For Eq 1 and Eq 2, the reading relates to the area between the valleys as indicated by the software valley indicators (see 9.3) for antioxidants between 0.8 – 1.6 V (see Note 1).

12. Report

12.1 Results are calculated and reported as weight percent of antioxidant or as millimoles (mmole) of antioxidant per gram of sample for prepared and fresh oils (antioxidants known) and as a percent remaining antioxidant (RUL%) for in-service oils (antioxidant unknown) as described in Eq 1 and Eq 2.

13. Voltammetric Data Integration

13.1 Establish a trending curve for the individual antioxidants. After selecting and applying a regular oil analysis frequency, the end-user can establish a trending curve for the individual antioxidant's depletion versus the operating time (hours, days, months). The trend for the individual antioxidant's depletion can contain valuable information regarding root cause failures for oil degradation, such as overheating or contamination. It is important for end-users to evaluate and make interpretation of test data with their oil and additive supplier, in order to achieve the right corrective actions towards oil health management, as well decide what additional testing should be considered.

13.2 Combine voltammetric analysis with other proactive oil condition parameters.

13.2.1 *Particle Counting*—Particulate contaminants in industrial lubricants act as oxidative accelerators and therefore represent an important complementary analysis to antioxidant analysis, as part of root cause failure. Particle contamination can be performed in accordance with ISO 4406.2. It is generally advised to apply the correct sampling techniques when performing particle counting and contamination assessment.

13.2.2 *Water Contamination*—As a liquid contaminant, water contributes to the oxidative degradation of a lubricant, and is therefore an important analytical parameter complementing antioxidant analysis. Water contamination can be performed by using Test Method D6304.

13.2.3 *Insolubles*—With gas turbine applications it is be important to combine antioxidant monitoring with insolubles content, as an indication of the presence of insoluble colored bodies or deposits, or both. Membrane patch colorimetric methods (under development in ASTM Subcommittee D02.C00) qualify the oil samples by colorimetric analysis.

13.3 *Targets*—The important step is to set a target (alarm level) for the remaining antioxidant concentration. These targets help maintain an environment viable to prolonged lubricant and machine life. Control of the antioxidants conditions within these targets can be achieved by using trending graphs for voltammetric analysis on industrial lubricants. As part of proactive maintenance strategies, it is vital to keep the oils' condition, by means of monitoring their remaining antioxidants life, above these targets.

13.4 *Defining Corrective Actions:*

13.4.1 *Adapting Oil Frequency Analysis*—Table 1 summarizes the oil frequency intervals, in function of the remaining antioxidant concentrations. It is generally advised to consult

TABLE 1 Oil Frequency Intervals

Remaining Antioxidant Concentration (RUL%)	Oil analysis frequency (excluding gas turbines)	Oil analysis frequency for gas turbine lubricants
50 to 100%	Quarterly to max. every 6 months	Every 3 months
25 to 50%	Max. every 3 months	Once 1 month
< 25%	Every month	Every 2 weeks

also the OEM Specifications and Maintenance manuals to define the correct oil analysis intervals.

13.4.2 *Additional Laboratory Testing*—When using the antioxidant monitoring test for oil condition monitoring purposes, it is recommended to perform additional tests to assess the global condition of the oil sample. A very important step in lube oil analysis programs is data interpretation, in order to enable operators to take corrective actions. A good example of that strategy is when the trend of the antioxidant depletion trend is showing an increased depletion, it is be important to define corrective actions before the antioxidant concentration approaches the upper alarm level.

13.4.3 When the remaining antioxidant concentration (measured as individual additive antioxidant RUL% number since the oxidation products could result a superficially higher RUL %), the lower alarm level, and condemning limit are 25% RUL, it is advised, as in Practice D4378, to make complementary analytical testing such as FTIR, such as PAI (Test Method D7214), acid number, or RPVOT analysis, or a combination thereof.

13.4.4 *Consult with Oil and Additive Company*—Final decisions regarding oil changes or additive replenishments shall be discussed with the oil and additive companies, in order to establish their own criteria or important factors that affects the fluid's integrity.

14. Keywords

14.1 2,6-di-*tert*-butylphenol; 2,6-di-*tert*-butyl-4methylphenol; phenyl alpha naphthylamine; alkylated diphenylamine; turbine oil; linear sweep voltammetry (LSV); hindered phenol antioxidant; aromatic amine antioxidant; zinc dialkyl dithiophosphates