Designation: D6810 – 13

Standard Test Method for Measurement of Hindered Phenolic Antioxidant Content in Non-Zinc Turbine Oils by Linear Sweep Voltammetry[1]

This standard is issued under the fixed designation D6810; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the voltammetric determination of hindered phenol antioxidants in new or in-service non-zinc turbine oils in concentrations from 0.0075 weight % up to concentrations found in new oils by measuring the amount of current flow at a specified voltage in the produced voltammogram.

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

1.3 *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

D6447 Test Method for Hydroperoxide Number of Aviation Turbine Fuels by Voltammetric Analysis

D6971 Test Method for Measurement of Hindered Phenolic and Aromatic Amine Antioxidant Content in Non-zinc Turbine Oils by Linear Sweep Voltammetry

3. Summary of Test Method

3.1 A measured quantity of sample is dispensed into a vial containing a measured quantity of alcohol-based electrolyte solution and containing a layer of sand. When the vial is shaken, the hindered phenol antioxidants and other solution soluble oil components present in the sample are extracted into the solution and the remaining droplets suspended in the solution are agglomerated by the sand. The sand/droplet suspension is allowed to settle out and the hindered phenol antioxidants dissolved in the solution are quantified by voltammetric analysis. The results are calculated and reported as weight 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 used oils.

3.2 Voltammetric analysis is a technique that applies electro-analytic methods when a sample to be analyzed is mixed with an electrolyte and a solvent 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 nonpolarizable 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

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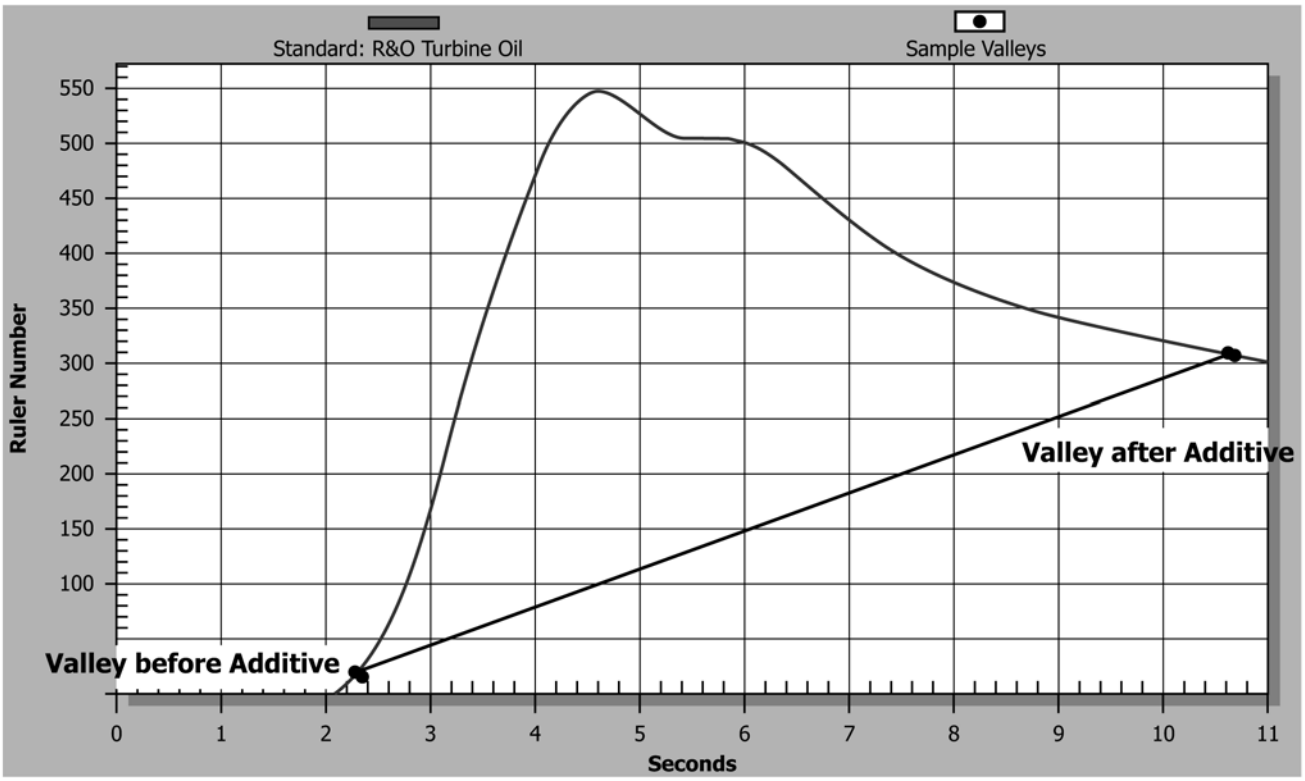
[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

***A Summary of Changes section appears at the end of this standard**



NOTE 1—*x*-axis = time (seconds) and *y*-axis is current (arbitrary units). Top line in Fig. 1 is voltammogram of a fresh R&O turbine oil showing valley indicator before and after standard.

FIG. 1 Hinderd Phenol Voltammetric Response in Basic Test Solution with Blank Response Zeroed

electro-active 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 electro-active 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.

4. Significance and Use

4.1 The quantitative determination of hindered phenol antioxidants in a new turbine oil measures the amount of this material that has been added to the oil as protection against oxidation. Beside phenols, turbine oils can be formulated with other antioxidants such as amines which can extend the oil life. In used oil, the determination measures the amount of original (phenolic) antioxidant remaining after oxidation have reduced its initial concentration. This test method 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. Nor does it measure the overall stability of an oil, which is determined by the total contribution of all species present. 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 Practices D6224 and D4378), having the capability of measuring remaining oxidative life of the used oil.

4.1.1 This test method is applicable to non-zinc turbine oils. These are refined mineral oils containing rust and oxidation inhibitors, but not antiwear additives. This test method has not yet been established with sufficient precision for antiwear oils.

4.2 This test method is also suitable for manufacturing control and specification acceptance.

4.3 When a voltammetric analysis is obtained for a turbine oil inhibited with a typical hindered phenol antioxidant, there is an increase in the current of the produced voltammogram between 3-5 s (or 0.3 to 0.6 V applied voltage) (see Note 1) in the basic test solution (Fig. 1—*x*-axis 1 second = 0.1 V). 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).

NOTE 1—Voltages listed with respect to reference electrode. The voltammograms shown in Figs. 1 and 2 were obtained with a platinum reference electrode and a voltage scan rate of 0.1 V/s.

4.4 For non-zinc turbine oils containing aromatic (aryl) amine compounds (antioxidants and corrosion inhibitors), there is an increase in the current of the produced voltammogram between 7-11 s (0.7 to 1.1 V applied voltage in Fig. 2) (see Note 1) which does not interfere with the hindered phenol measurement in the basic test solution. For the measurement of these aromatic amine antioxidants, refer to Test Method D6971, where the neutral test solution shall be used.