Designation: D7527 – 10

Standard Test Method for Measurement of Antioxidant Content in Lubricating Greases by Linear Sweep Voltammetry[1]

This standard is issued under the fixed designation D7527; 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 antioxidants in new or in-service lubricating greases in concentrations from 0.0075 weight percent up to concentrations found in new greases by measuring the amount of current flow at a specified voltage in the produced voltammogram.

1.2 This test method is intended to monitor the antioxidant content in lubricating greases; it cannot be applied for lubricating greases that do not contain antioxidants.

1.3 This test method is designed to allow the user to monitor the antioxidant depletion rate of in-service greases through its life cycle as part of condition monitoring programs. This test method is performed in order to collect and trend early signs of deteriorating lubricant grease, and it may be used as a guide for the direction of any required maintenance activities. This will ensure a safe, reliable, and cost-effective operation of the monitored plant equipment.

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]

D942 Test Method for Oxidation Stability of Lubricating Greases by the Oxygen Pressure Vessel Method

D1193 Specification for Reagent Water

D5483 Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry

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

3. Summary of Test Method

3.1 A measured quantity of sample is weighed into a vial containing a measured quantity of acetone based electrolyte solution and containing a layer of sand. When the vial is shaken, the dissolved 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 antioxidants dissolved in the solution are quantified by voltammetric analysis.

NOTE 1—Voltages are 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. Significance and Use

4.1 The quantitative determination of antioxidants in new greases measures the amount of the chemical compounds that were added to the base oil as protection against grease oxidation. For in-service oil greases, the voltammetric test method measures the amount of original (individual) antioxidants remaining after grease oxidation have reduced its concentration. Before making final judgment on the remaining useful life of the in-service grease, which might result in the replacement of the grease reservoir, it is advised to perform additional analytical techniques, such as Test Method D942 and D5483, which may be used to measure the remaining oxidative life of the used grease.

4.1.1 This test method is applicable to mineral oil-based and synthetic oil-based greases, based on all type of applied thickeners. This test method is applicable to greases containing at least one type of antioxidant. The presence of other types of additives like corrosion inhibitors or metal deactivators will not interfere with this test method.

[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.G0.07 on Research Techniques.

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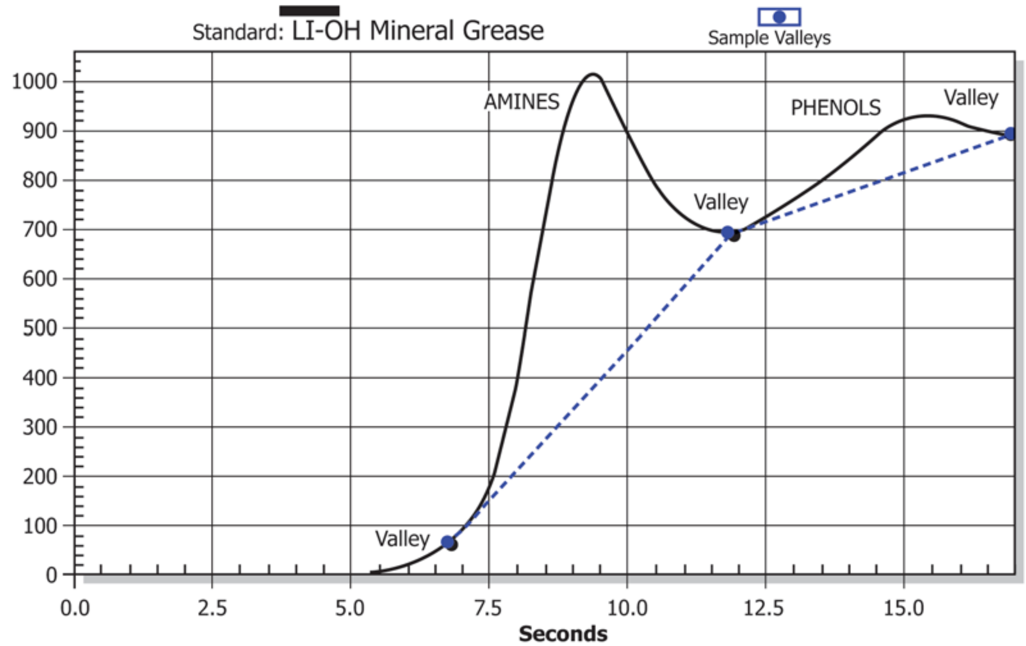
[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.



NOTE 1—X-axis represents time (seconds) and Y-axis represents current (arbitrary units). Upper line curve in Fig. 1 is voltammogram of a fresh Li-OH mineral grease showing valley indicators (dotted lines) before and after a antioxidant additives.

FIG. 1 Aromatic Amine and Hindered Phenol Voltammetric Response in Neutral Test Solution with Blank Response Zeroed

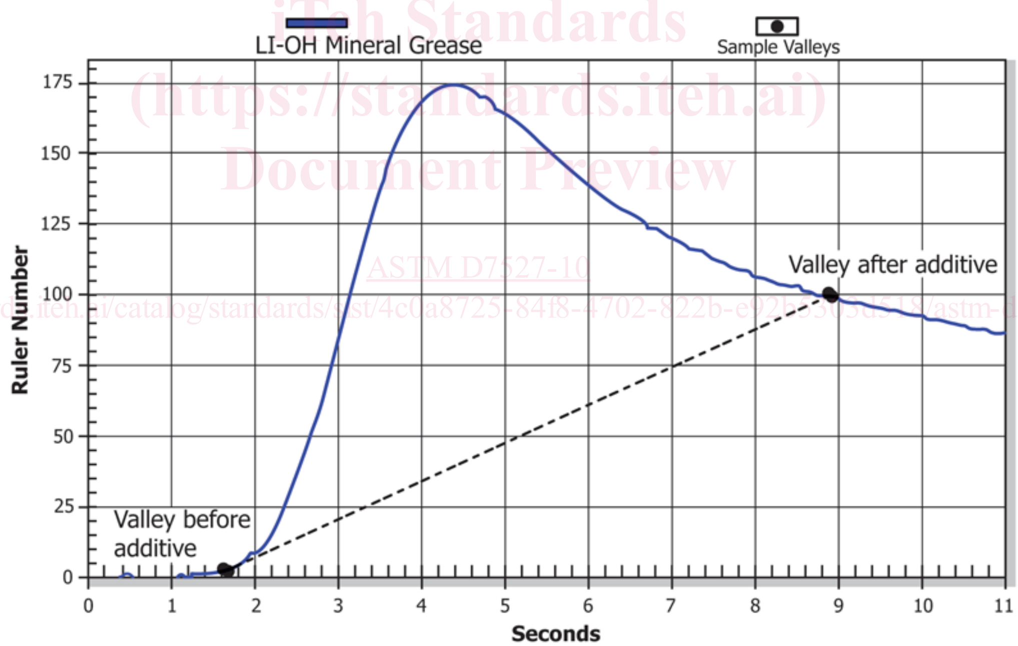


FIG. 2 Hindered Phenol Voltammetric Response in Basic Alcohol Test Solution with Blank Response Zeroed

4.2 When a voltammetric analysis is obtained using a neutral acetone test solution for a grease inhibited with a typical synergistic mixture of hindered phenol and aromatic amine antioxidants, there is an increase in the voltammogram current between 8 to 12 s (or 0.8 to 1.2 V applied voltage), see Note 1, for the aromatic amines, and an increase in the voltammogram current of the produced voltammogram between 13 to 16 s (or 1.3 to 1.6 V applied voltage), see Note 1, for the hindered phenols. In Fig. 1, x-axis = 1 s = 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). Aromatic amine antioxidants detected by voltammetric analysis include, but are not limited to, phenyl alpha naphthylamines, and alkylated diphenylamines.

4.3 For greases containing only aromatic amines as antioxidants, there will only be an increase in the current of the produced voltammogram between 8 to 12 s (or 0.8 to 1.2 V applied voltage) for the aromatic amines, by using the neutral acetone test solution (first peak in Fig. 1).

4.4 For greases containing ZDDP as antioxidants, there shall be an increase in the voltammogram current between 6 to 10 s (or 0.6 to 1.0 V applied voltage), see Note 1, for the ZDDP, when evaluated in the neutral acetone test solution.

4.5 For greases containing only hindered phenolic antioxidants, basic alcohol test solutions are recommended for use as described in Test Method D6810. In basic alcohol test solutions, the voltammogram current for phenols increases between 3 to 6 s (or 0.3 to 0.6 V applied voltage), see Note 1. In Fig. 2, x-axis = 1 s = 0.1 V are as described in Test Method D6810, where x-axis = time (seconds) and y-axis is current (arbitrary units). Top line in Fig. 2 is fresh grease.

5. Apparatus

5.1 *Voltammograph*—The instrument used to quantify the antioxidants is a voltammograph equipped with a three-electrode system and a digital or analog output. The three-electrode system consists of a glassy 3 mm diameter carbon disc working electrode, a platinum wire (0.5 mm diameter) auxiliary electrode, and a 0.5 mm diameter platinum wire (reference electrode, as described in Test Method D6810 and D6971). During operation, the voltammograph applies a linear voltage ramp (0 to -1.8 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 the working electrode is converted to voltage by the voltammetric analyzer, using the gain ratio of 1V/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.

5.2 *Vortex Mixer*—With a 2800 to 3000 r/min motor and a pad suitable for mixing test tubes and vials.

5.3 *Spatula*—Or equivalent laboratory tool, capable of delivering samples from 50 to 300 mg.

5.4 *Microbalance*—Capable of weighing 50 to 300 ± 1 mg samples.

5.5 *Solvent Dispenser*—Or equivalent, capable of delivering volumes of analysis solution (see 6.3) required in the test method, such as 5.0 ± 0.1 mL.

5.6 *Glass Vials with Caps*—4 or 7 mL capacity, and containing 1 g of sand white quartz suitable for chromatography, within the particle size range of 200 to 300 ± 100 microns.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, where applicable reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[3] 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.

6.2 *Purity of Water*—Unless otherwise specified, water that shall conform to Specification D1193, Type II.

6.3 *Analysis Materials:*

6.3.1 *Acetone Test Solution (Neutral)*—Proprietary Green[4] test solution, acetone solvent (1:10 distilled water/acetone solution) containing a dissolved neutral electrolyte. (**Warning—**Corrosive, Poison, Flammable, and Skin Irritant. Harmful if inhaled.)

6.3.2 *Alcohol Test Solution (Basic)*—Proprietary Yellow[4] test solution, Ethanol solvent (1:10 distilled water/ethanol solution) containing a dissolved base electrolyte. (**Warning—**Corrosive, Poison, Flammable, and Skin Irritant. Harmful if inhaled.)

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

7. Sampling

7.1 It is important to accurately sample the in-service grease. Since sample composition may depend upon sampling position, it is recommended that samples be collected from more than one location.

7.2 Samples of an in-service grease can be non-homogeneous. It should be agreed with the customer how to prepare the lubricating grease samples for analysis.

8. Procedure

8.1 The voltammograph used in this test method gives linear results between 2 to 50 mmol/kg for different types of antioxidants using a grease sample size of 250 mg and 5.0 mL of the test solution. The corresponding range of weight percents depends on the molecular weight of the antioxidants like hindered phenol and aromatic amine, and the density of the grease. For instance, the weight percent range of 0.044 to 1.1 is equal to 2 to 50 mmol/kg for a hindered phenol containing one hydroxyl group and with a molecular weight of 220 g/mole (2,6-di-*tert*-butyl-4-methylphenol) and an oil density of 1g/mL. Below 2 mmol, the noise to signal ratio becomes large

[3] *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.

[4] The sole source of supply known to the committee at this time is Fluitec, 2850 Scherer Dr., Suite 500, St. Petersburg, FL 33716; Friendship Building, Rijnkaai 37, B.2000 Antwerp, Belgium. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.