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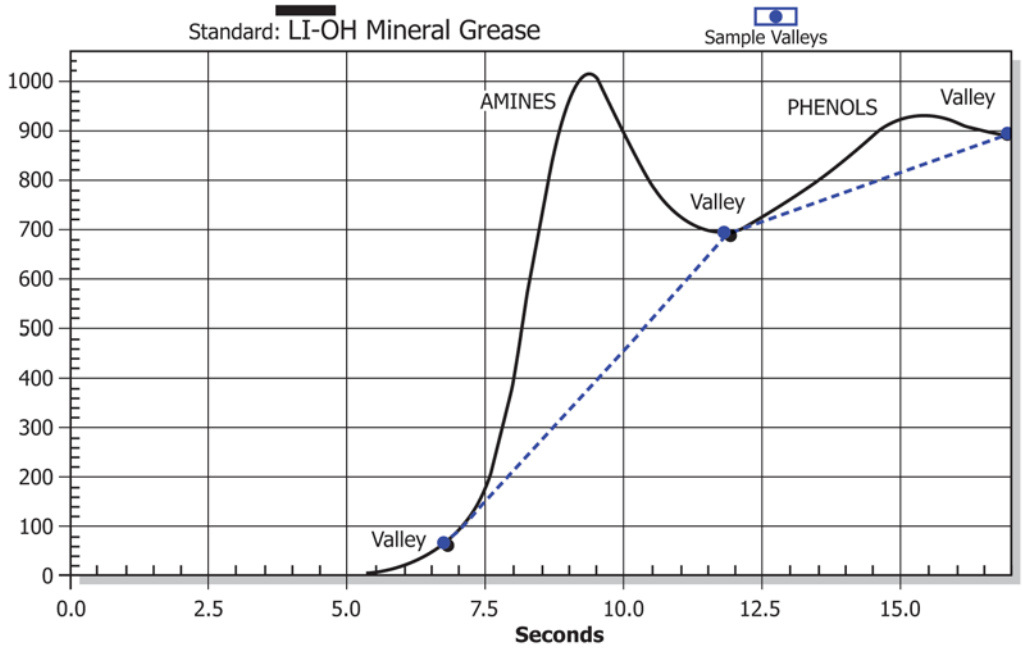
[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.



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

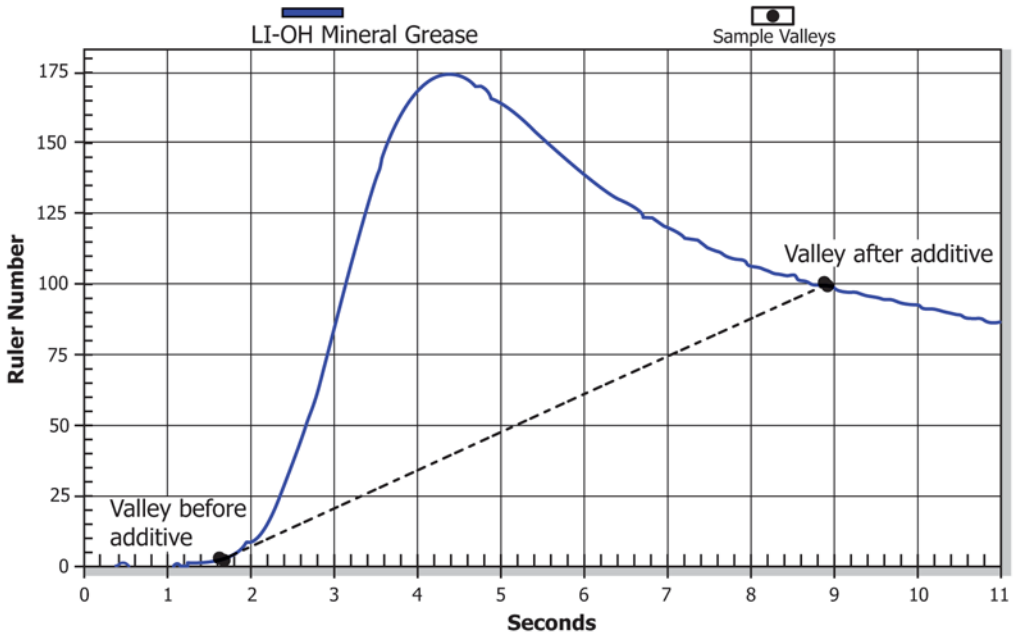


FIG. 2 Hindered Phenol Voltammetric Response in Basic Alcohol Test Solution with Blank Response Zeroed

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.

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 600 mg.

8.2 *General Voltammetric Test Procedure*—The test procedure for voltammetric analysis will consist of the blank reading (calibration), followed by a standard reading (fresh grease) and finally the reading of the (in-service or oxidized grease) sample.

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

8.2.2 *Standard Reading*—(30-150 mmol/kg). Concentration dependent on density of fresh oil and molecular weight of antioxidant). The standard reading is a measurement of a fresh, unused grease (containing one or more different types of antioxidants) mixed with an appropriate analysis solvent. This measurement gives you the voltammetric reading that indicates the response for the concentration of antioxidants in the fresh grease being tested.

8.2.3 *Sample Reading*—(Of in-service grease). The sample reading is a measurement of an in-service/ oxidized grease mixed with the same type of analysis solvent as the standard. This measurement will provide voltammetric readings that normally range between the Blank and Standard measurements, and reflects the concentration of one or more different types of antioxidants present (fresh grease) or remaining (in-service or oxidized grease) in the grease sample. Voltammetric readings for in-service or oxidized grease will decrease as the concentration of the antioxidants namely, hindered phenols, aromatic amines or ZDDP type of antioxidants are depleted.

8.3 *Voltammetric Reading*—As part of the procedure, once the operator has selected the valleys before and after the antioxidant peaks (as shown in Fig. 1), the software (R-DMS[4]) will automatically identify and calculate the area above the baseline between the two valley indicators. This calculated area is then used for the sample reading (in-service or oxidized grease), which will be established by comparing the in-service grease area to its standard (see Fig. 3) and makes the necessary calculations of remaining antioxidant concentration (see Section 9).

8.4 *Calibration (Blank Reading):*

8.4.1 Pipette 5.0 mL of analysis solution into a 7 mL vial or other suitable container containing 1 g of sand.

8.4.2 Insert the electrode of the voltammetric analyzer into the analysis solution to wet the bottom surface of the electrode, remove, and rub the bottom electrode surface dry with a lint free paper towel. Insert the electrode into the vial so that the bottom of the electrode is submerged in the analysis 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.

8.4.3 Perform the voltammetric analysis (see 5.1). Record the voltammetric reading in the voltage range of aromatic amines, 0.8 to 1.2 V, see Note 1, and the phenols, 1.3 to 1.6 V, see Note 1, in neutral test solution (Fig. 1).

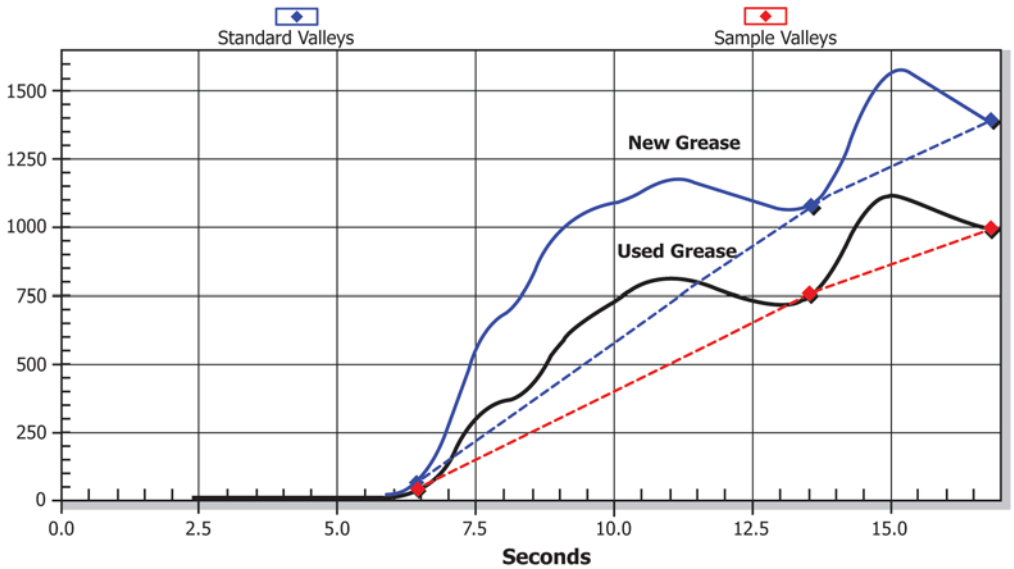
8.4.4 Remove the combination electrode from the blank solution, and rub the bottom surface dry of the electrode with a lint-free paper towel.

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

8.4.6 *Calibration Frequency*—Recalibration with freshly prepared blank test solution shall be performed before each testing session.

8.5 *Standard and In-service/Oxidized Grease Sample Preparation Procedures:*

8.5.1 *Preparing Solution:*



NOTE 1—New grease (top line) and sample in-service grease (used grease lower line).

Amines antioxidant peaks are calculated based on the area indicated by the valley indicators for the amine antioxidant peaks (6 to 13 s) and phenol antioxidant peaks (13 to 17 s)

FIG. 3 Voltammetric Reading for an In-service Grease Sample Calculating Aromatic Amines (Antioxidant #1) and Hindered Phenols (Antioxidant #2) Peaks (in the Neutral Test Solution)

8.5.1.1 Remove the seal and cap of the test solution vial, containing 1 g of sand. Tare the vial on the microbalance. In general weigh a 250 ± 5 mg of the selected grease sample into the 7 mL vial and record the weight of the grease sample.

8.5.1.2 For high temperature application greases it is advised to limit the amount of grease sample to 150 ± 0.1 mg, max, of grease.

8.5.1.3 Smear the grease with a spatula uniformly on the inside walls of the vial by mixing with the sand.

8.5.1.4 Pipette 5.0 mL of analysis solution into the 7 mL vial or other suitable container containing 1g of sand.

8.5.2 For measurements below 2 mmol or for fresh oils with high noise to signal ratios, the sample size should be increased to 400 ± 0.1 mg.

8.5.3 *Shaking/Mixing Solution (Antioxidant Extraction)*—Cap the vial and shake vigorously using a vortex mixer for 20 s or 20 s of vigorous hand shaking, until sand is thoroughly mixed. Place the prepared grease solution upright in a rack or perforated foam block for a minimum time of 30 min to allow the antioxidants to be extracted out of the oil into the test solution. This will also allow the sand to settle on the bottom of the vial with the thickeners.

8.5.4 *Cleaning Electrode*—Prepare the electrode for analysis by cleaning the electrode. Use an alcohol-cleansing pad or blank analysis solution to wet the bottom surface of the electrode. The bottom of the electrode must be dried immediately with a clean lens tissue (lint-free paper towel). The glassy carbon surface 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 may be incorrect.

8.5.5 *Running Test*—Insert the electrode into the vial so that the bottom of the electrode is submerged in the analysis 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 5.1) for hindered phenolic and aminic antioxidants. Record the valley to valley antioxidant readings in the voltage range of the amines, 0.8 to 1.2 V, see Note 1, and the phenols, 1.3 to 1.6 V, see Note 1, in neutral solution (Fig. 1). Remove the combination electrode from the prepared grease solution and repeat the cleaning procedure of the electrode. Run at least two tests (cleaning the electrode and shaking the standard for 10 s between tests) for the standard or in-service grease sample to ensure the value is stable and repeatable.

8.6 When the manufacturer of the grease is known, and the uninhibited grease is available, use the grease to prepare the standards (mmole or weight percent antioxidant calculations). Prepare a standard containing in the range of 30 to 150 mmol/kg of oil (0.5 to 3.0 weight percent) of the selected phenolic and aminic antioxidant dissolved in an uninhibited grease. The concentration should be selected to span the expected concentrations of the new and used greases.

8.7 Standard readings should be updated whenever new batches of lubricating greases are stocked, and periodically to monitor the amount of natural oxidation occurring in the stock during storage.

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

8.9 The analysis solution and scan time should be the same for the blank, standard, and in-service grease sample.

9. Calculation

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

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

where:

$\%\ AO$ = Percent of antioxidant, %,
S = Sample reading,
B = Blank reading,
s = Standard reading,
B = Blank reading, and
w = Weight percent antioxidant of standard, %.

9.2 *Molar Concentration of Antioxidant Calculation*—If the type of antioxidant in the grease sample is unknown, then the millimoles of antioxidants ([Mol AO]) in the sample can be calculated in accordance with the following equation:

$$[Mol\ AO] = \frac{(S - B)}{(s - B)} \times a \tag{2}$$

where:

$[Mol\ AO]$ = concentration of antioxidant, mmole/kg of grease,
S = Sample reading,
B = Blank reading,
s = Standard reading,
B = Blank reading, and
a = Antioxidant concentration of standard (mmole/kg of grease).

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

$$RUL\% = \frac{(S - B)}{(s - B)} \times 100\% \tag{3}$$

where:

$RUL\%$ = Remaining antioxidant,
S = Sample reading,
B = Blank reading,
s = Standard reading, and
B = Blank reading.

For Eq 1-3, the reading relates to the area between the valleys as indicated by the software valley indicators (see 8.3) for antioxidants between 0.8 to 1.6 V, see Note 1.

10. Report

10.1 Results are calculated and reported as weight percent of antioxidant or as millimoles (mmole) of antioxidant per gram of sample for prepared and fresh greases (antioxidants

known) and as a percent remaining antioxidant (RUL%) for in-service greases (antioxidant unknown) as described in equations in 9.3.

11. Precision and Bias[5]

11.1 An interlaboratory study was performed in 2007 by nine laboratories and ten grease samples (Note 2).

11.2 The following criteria should be used for judging the acceptability of results (95% of confidence), based on the ASTM research report.

11.2.1 *Repeatability*—The difference between concurrent test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials, would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in 1 case in 20:

$$\text{Repeatability} = 7.168\ \%, \text{ where x denotes mean value} \quad (4)$$

11.2.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in 1 case in 20:

$$\text{Reproducibility} = 17.818\ \%, \text{ where x denotes mean value} \quad (5)$$

NOTE 2—The precision data were established for lubricating greases using polyurea and lithium soap thickeners in combination with mineral baseoils.

11.3 *Bias*—No information can be presented on the bias, since the result of this test is defined only in the terms of this test method.

12. Keywords

12.1 2,6-di-*tert*-butyl-4methylphenol; 2,6-di-*tert*-butylphenol; alkylated diphenylamine; aromatic amine antioxidant; grease; hindered phenol antioxidant; linear sweep voltammetry; phenyl alpha naphthylamine

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1693.

APPENDIX

(Nonmandatory Information)

X1. BACKGROUND

X1.1 Voltammetric analysis is a technique that applies an electro-analytic method test device to the analysis of lubricating materials wherein 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 in which is mounted a small, easily polarized working electrode and a large non-polarizable reference electrode.

X1.2 The reference electrode should be larger 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 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 voltage. As the increasing voltage is applied to the prepared sample within the cell, the various additive species under investigation within the grease are caused to electrochemically oxidize.

X1.3 The voltammetric response recorded during this oxidation reaction can then be used to determine the remaining useful life of the grease type. A typical current-potential curve produced during the voltammetric test is presented in 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 electro-active species (for example, substituted phenols or aromatic amines) begin to oxidize at the working electrode surface, producing an anodic rise in the current. As the potential is further increased, the concentration of the electro-active species at the electrode surface decreases and the exponential increase of the oxidation rate lead to a maximum in the current-potential curve shown in Fig. 1.