



Designation: E2009 – 23

# Standard Test Methods for Oxidation Onset Temperature of Hydrocarbons by Differential Scanning Calorimetry<sup>1</sup>

This standard is issued under the fixed designation E2009; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods describe the determination of the oxidative properties of hydrocarbons by differential scanning calorimetry or pressure differential scanning calorimetry under linear heating rate conditions and are applicable to hydrocarbons, which oxidize exothermically in their analyzed form.

1.2 *Test Method A*—A differential scanning calorimeter (DSC) is used at ambient pressure of one atmosphere of oxygen.

1.3 *Test Method B*—A pressure DSC (PDSC) is used at high pressure (e.g., 3.5 MPa (500 psig) of oxygen).

1.4 *Test Method C*—A differential scanning calorimeter (DSC) is used at ambient pressure of one atmosphere of air.

1.5 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee E37 on Thermal Measurements and are the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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<sup>2</sup> 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.

- D3350 Specification for Polyethylene Plastics Pipe and Fittings Materials
- D3895 Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry
- D4565 Test Methods for Physical and Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable
- D5483 Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry
- E473 Terminology Relating to Thermal Analysis and Rheology
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
- E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers
- E1858 Test Methods for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry
- E3142 Test Method for Thermal Lag of Thermal Analysis Apparatus

## 3. Terminology

### 3.1 Definitions:

3.1.1 For definitions of terms used in these test methods, refer to Terminology E473.

### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *oxidation (extrapolated) onset temperature (OOT)*—a relative measure of oxidative stability at the cited heating rate is determined from data recorded during a DSC scanning temperature test. The temperature at which the onset to the observed oxidation is taken as the OOT.

## 4. Summary of Methods

4.1 In thermal analysis, a physical property of a material is measured either as a function of time at a specified constant temperature, or more frequently, as a function of temperature under conditions of a fixed rate of temperature change. The measured property is the dependent variable, and the measured temperature is the independent variable.

4.2 The test specimen in an aluminum container and an empty reference aluminum container or pan are heated at a

specified constant heating rate in an oxygen (or air) environment. Heat flow out of the specimen is monitored as a function of temperature until the oxidative reaction is manifested by heat evolution on the thermal curve. The oxidation (extrapolated) onset temperature (OOT), a relative measure of oxidative stability at the cited heating rate, is determined from data recorded during the scanning temperature test. The OOT measurement is initiated upon reaching the exothermic reaction and measuring the extrapolated onset temperature.

4.3 For some particularly stable materials, the OOT may be quite high ( $> 300\text{ }^{\circ}\text{C}$ ) at the specified heating rate of the experiment. Under these circumstances, the OOT may be reduced by increasing the pressure of oxygen purge gas. Conversely, reducing the partial pressure of oxygen (such as by the use of air) may retard reactions that proceed too rapidly, with a corresponding increase of the OOT. By admixing oxygen gas with a suitable diluent, for example, nitrogen, the OOT will be increased (see Specification D3350 and Test Methods D3895, D4565, and D5483).

NOTE 1—For some systems, the use of copper pans to catalyze oxidation will reduce the oxidation onset temperature. The results, however, will not necessarily correlate with non-catalyzed tests.

## 5. Significance and Use

5.1 Oxidation onset temperature is a relative measure of the degree of oxidative stability of the material evaluated at a given heating rate and oxidative environment (e.g., oxygen); the higher the OOT value the more stable the material. The OOT is described in Fig. 1. The OOT values can be used for comparative purposes and are not an absolute measurement, like the oxidation induction time (OIT) at a constant temperature (see Test Method E1858). The presence or effectiveness of antioxidants may be determined by these test methods.

5.2 Typical uses of these test methods include the oxidative stability of edible oils and fats (oxidative rancidity), lubricants, greases, and polyolefins.

## 6. Interferences

6.1 This test method involves the continuous monitoring of the specimen temperature within the test chamber's enclosed environment of a flowing, static, or self-generated gaseous atmosphere (or vacuum) during execution of the stipulated procedure. In DSC apparatus, the sensor employed to measure the specimen temperature is not in direct contact with the specimen but is in fixed close thermal contact assumed to be representative of the specimen, such that the measured temperature is that of the sensor itself and the actual specimen temperature will lag behind this measured temperature during heating or cooling (see Test Method E3142). The magnitude of this temperature offset depends upon a number of systematic and random factors including, but not limited to, type and size of sensor, rate of temperature change, size and thermal conductance of the specimen, specimen container, and thermal contact between the specimen and the specimen container during the measurement. To obtain the correct specimen temperature, the DSC apparatus must be temperature calibrated at equivalent experimental conditions so that the recorded temperature correctly indicates the specimen temperature.

6.2 Temperature sensors are subject to degraded performance with age and exposure to the DSC test chamber atmosphere. Therefore, it is imperative that the apparatus is temperature calibrated regularly. At a minimum, annual calibration is recommended for all instrument signals.

## 7. Apparatus

7.1 *Differential Scanning Calorimeter (DSC) or Pressure Differential Scanning Calorimeter (PDSC)*—Multiple generations of DSCs from numerous commercial suppliers, as well as in-house custom apparatus, utilizing a variety of sensor configurations may be available to the user. While all such apparatus capabilities may not be equivalent, for purposes of this test method, any DSC that meets the following criteria should be able to generate acceptable results.

7.1.1 A DSC test chamber composed of: a furnace to provide uniform controlled heating of a specimen and a reference to a constant heating rate of at least  $10\text{ }^{\circ}\text{C}/\text{min}$  within the applicable temperature range for these test methods; a temperature sensor to provide an indication of the specimen temperature readable to  $\pm 0.1\text{ }^{\circ}\text{C}$ ; a differential sensor to detect heat flow (power) difference between the specimen and the reference to  $0.1\text{ mW}$ ; and the instrument should have the capability of measuring heat flow of at least  $6\text{ mW}$ , with provision for less sensitive ranges.

NOTE 2—In certain cases when the sample under study is of high volatility (e.g., low molecular weight hydrocarbons), the use of pressures  $\geq 0.1\text{ MPa}$  (1 atmosphere) is needed. The operator is cautioned to verify (with apparatus designer) the maximum oxygen pressure at which the apparatus may be safely operated. A PDSC is used in Method B.

7.2 A data collection device to provide a means of acquiring, storing, and displaying measured or calculated signals, or both. The minimum output signals required for DSC are heat flow, temperature, and time.

7.3 A high-pressure gas regulator or similar device to adjust the applied pressure in the test chamber to less than  $\pm 5\%$ , including any temperature dependence on the transducer, is used in Method B. (**Warning**—Use metal free of organic matter or fluoropolymer tubing with oxygen rather than the commonly used rubber or polyvinyl chloride plastic tubing. There have been hazardous situations with prolonged use of certain polymer tubing with oxygen.)

NOTE 3—Gas delivery tubing should be kept as short as possible to minimize dead volume. The link between the test chamber and pressure transducer should allow fast pressure equilibration to ensure accurate recording of the pressure above the specimen during testing.

7.4 Specimen containers are aluminum sample pans and should be inert to the specimen and reference material as well as the oxidizing gas. The specimen containers should be of suitable structural shape and integrity to contain the specimen and reference in accordance with the specific requirements of these test methods, including a pressure system consisting of a pressure vessel or similar means of sealing the test chamber at any applied pressure within the pressure limits required for these test methods. The specimen containers should be clean, dry, and flat. A typical cylindrical specimen container has the following dimensions: height, (1.5 to 2.5) mm and outer diameter, (5.0 to 7.0) mm.

**DSC**

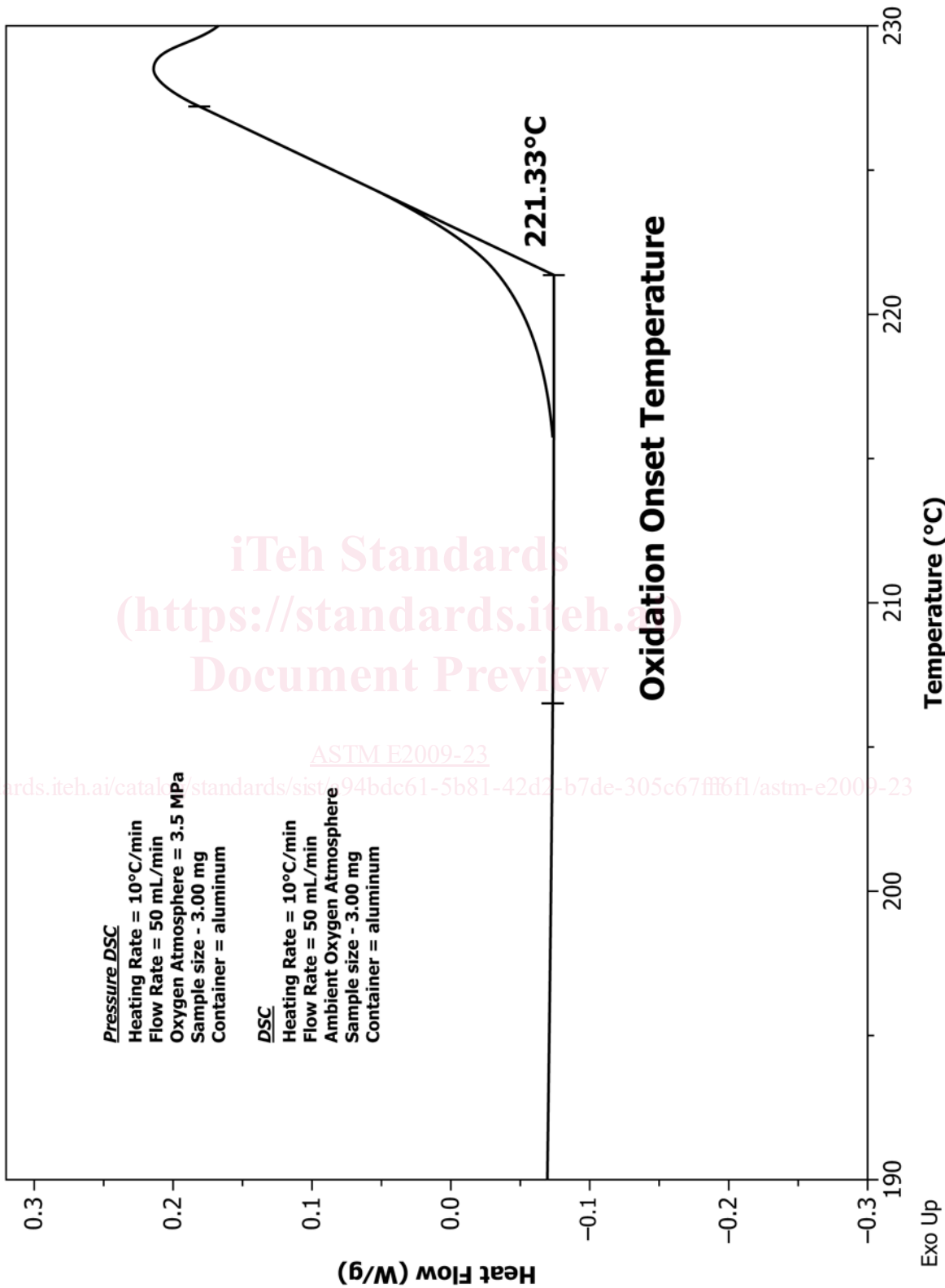


FIG. 1 DSC Oxidation (Extrapolated) Onset Temperature (OOT)

iTeh Standards  
 (https://standards.iTeh.org)  
 Document Preview  
 ASTM E2009-23  
 https://standards.iTeh.org/catalog/standards/sist/94bdc61-5b81-42d2-b7de-305c67ff6f1/astm-e2009-23

7.5 Flow meter capable of reading 50 mL/min, or another selected flow rate, accurate to within  $\pm 5\%$ . Ensure the flowmeter is calibrated for oxygen. Contact a flow meter supplier for specific details on calibration (see warning statement in 7.3).

7.6 Use an *analytical balance* with a capacity of at least 100 mg and capable of weighing to the nearest 0.01 mg, or less than 1 % of the specimen or containers' masses, or both. Recommended procedure for new sample pan cleaning can be found in **Annex A1**.

## 8. Reagents and Materials

8.1 *Oxygen*, extra dry, of  $\geq 99.5\%$  purity by volume. (**Warning**—Oxidizer. Gas under pressure.)

8.2 *Air*, extra dry.

8.3 *Indium*, of  $\geq 99.9\%$  purity by mass.

8.4 *Tin*, of  $\geq 99.9\%$  purity by mass.

## 9. Sampling

9.1 If the sample is a liquid or powder, mix thoroughly prior to sampling.

9.2 In the absence of information, samples are to be analyzed as received. If some heat or mechanical treatment is applied to the sample prior to analysis, this treatment shall be in nitrogen and noted in the report. If some heat treatment is used prior to oxidative testing, then record any mass loss as a result of the treatment.

## 10. Precautions

10.1 **Warning**—Oxygen is a strong oxidizer and vigorously accelerates combustion. Keep surfaces clean.

10.2 If the specimen is heated to decomposition, toxic or corrosive products may be released.

10.3 For certain types of PDSC, it is recommended that the flow be set up with a reverse flow implementation to ensure there is no contact of decomposed hydrocarbons with incoming oxygen within the instrument. See instrument designer's recommendation on reverse flow.

10.4 Certain synthetic lubricants showed explosion-like onset of oxidation. Aluminum containers were melted. Care must be taken to avoid damage to the sensor and cell.

## 11. Calibration and Standardization

11.1 Calibrate the temperature output of the instrument using Test Method **E967**, using a heating rate of 10 °C/min. Use indium and tin calibration material to bracket typical OOTs determined in these test methods. Calibration shall be performed under ambient pressure conditions.

## 12. Procedure

12.1 Weigh (3.00 to 3.30) mg of sample, to a precision of  $\pm 0.01$  mg, into a clean specimen container. Do not place lid on specimen pan or container.

NOTE 4—Other specimen sizes may be used if used consistently. However, the OOT values obtained may differ from those obtained with a

3 mg sample. Also, vented specimen covers may be used, but OOT values may differ from those obtained in open containers. The following procedure assumes the use of open containers.

12.2 Place the uncovered container with the prepared specimen in the sample position of the instrument and an empty specimen container, without lid, in the reference position. Be sure that the containers are centered on the sensors.

12.3 Replace all covers in accordance with appropriate manufacturer's recommendations.

12.4 Adjust flow rate of oxygen gas at ambient pressure to  $(50 \pm 5)$  mL/min, accurate to  $\pm 5\%$ .

NOTE 5—Other flow rates may be used but shall be noted in the report. Many flowmeters are not rated for high pressure operation and may burst if excess pressure is applied. In these cases, the flow rate should be measured at atmospheric pressure (0.1 MPa) at the exit of the DSC cell, if recommended by the instrument designer.

12.5 Set the instrument sensitivity as required to retain the oxidation exotherm within the recorded range. A preanalysis may be required to determine this value. A sensitivity of 2 W/g, or less than 6 mW full scale, is typically acceptable.

12.6 Purge the specimen area for (3 to 5) min to ensure exchange of air with oxygen at atmospheric pressure. Check the flow rate at elevated pressure, and readjust to  $(50 \pm 5)$  mL/min, if required.

12.7 Commence programmed heating at 10 °C/min from ambient temperature to the onset of the exothermic heat flow. Record the heat flow and sample temperature. The OOT is measured in oxygen from the baseline to the extrapolated onset temperature of the exothermic process.

### 12.8 Test Methods:

12.8.1 When using DSC Test Method A, maintain a flow rate of 50 mL/min of oxygen at ambient pressure.

12.8.2 When using PDSC Test Method B, pressurize slowly, adjust and maintain a pressure of oxygen at  $3.5 \pm 0.2$  MPa ( $500 \pm 25$  psig), and maintain flow rate of 50 mL/min.

12.8.3 When using DSC Test Method C, maintain a flow rate of 50 mL/min of air at ambient pressure.

12.9 Continue the scanning DSC operation until the peak of the oxidation exotherm is observed or until an inflection point is observed and the total displacement from the initial baseline exceeds 3 mW or 1 W/g.

12.10 When the experiment is completed, cool the instrument to ambient temperature (25 °C).

NOTE 6—When using Test Method B, allow the instrument to cool before releasing the pressure. Failure to do so may result in injury to the user or damage to the instrument.

12.11 OOT values less than 50 °C are not precise. OOT values greater than 300 °C can be expedited through the use of a higher oxygen pressure.

## 13. Calculation

13.1 Determine the OOT (see **Fig. 1**).

13.1.1 Extend the recorded temperature baseline beyond the oxidation reaction exotherm.

13.1.2 Extrapolate the slope of the oxidation exotherm from the inflection point on the curve to the extended baseline.