



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

This standard is issued under the fixed designation E 2009; 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 This test method describes the determination of the oxidative properties of hydrocarbons by differential scanning calorimetry or pressure differential scanning calorimetry under linear heating rate conditions and is applicable to hydrocarbons, which oxidize exothermically in their analyzed form.

1.2 Computer or electronic-based instruments, techniques, or data treatment equivalent to this test method may also be used.

NOTE 1—Users of this test method are expressly advised that all such instruments or techniques may not be equivalent. It is the responsibility of the user of this standard to determine the necessary equivalency prior to use.

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

1.4 *Test Method B*—A pressure DSC (PDSC) is used at high pressure, for example, 3.5 MPa (500 psig) oxygen.

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

1.6 SI units are the standard.

1.7 *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:

D 3350 Specification for Polyethylene Plastics Pipe and Fittings Materials<sup>2</sup>

D 3895 Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry<sup>2</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Test Methods and Recommended Practices.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 08.02.

D 4565 Test Method for Physical Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable<sup>3</sup>

D 5483 Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry<sup>4</sup>

E 473 Terminology Relating to Thermal Analysis<sup>5</sup>

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>5</sup>

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers<sup>5</sup>

E 1858 Test Method for Determining Oxidative Induction Time of Hydrocarbons by Differential Scanning Calorimetry<sup>5</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 *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.

3.1.2 For definitions of terms used in this test method, refer to Terminology E 473.

## 4. Summary of Method

4.1 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

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 10.02.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.03.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 14.02.

measurement is initiated upon reaching the exothermic reaction and measuring the extrapolated onset temperature.

4.2 For some particularly stable materials, the OOT may be quite high (>300°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 D 3350 and Test Methods D 3895, D 4565, and D 5483).

NOTE 2—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, for example, 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 E 1858). The presence or effectiveness of antioxidants may be determined by this test method.

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

## 6. Apparatus

6.1 *Differential Scanning Calorimeter (DSC) or Pressure Differential Scanning Calorimeter (PDSC)*—The essential instrumentation required to provide the minimum differential scanning calorimetric capability for this test method includes: a DSC 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°C/min within the applicable temperature range for this test method; a temperature sensor to provide an indication of the specimen temperature to  $\pm 0.1^\circ\text{C}$ ; a differential sensor to detect heat flow (power) difference between the specimen and the reference to 0.1 mW; and the instrument should have the capability of measuring heat flow of at least 6 mW, with provision for less sensitive ranges.

NOTE 3—In certain cases when the sample under study is of high volatility (for example, low molecular weight hydrocarbons), the use of pressures in excess of 0.1 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.

6.2 Recorder or printer/plotter, or similar device, is used, capable of displaying heat flow on the Y-axis and temperature on the X-axis. The temperature shall be accurate to  $\pm 0.3^\circ\text{C}$  (see Practice E 967) and be readable to  $0.1^\circ\text{C}$ . The capability to record the first derivative of the heat flow curve is helpful in cases in which the baseline is not constant.

6.3 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.

NOTE 4—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.

NOTE 5—**Caution:** Use metal 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 in oxygen service.

6.4 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 this test method, 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 this test method. The specimen containers shall 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.

6.5 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 supplier of flow meters for specific details on calibration (see Note 5).

6.6 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.

## 7. Reagents and Materials

7.1 *Oxygen*, extra dry, of not less than 99.5% by volume, or,

NOTE 6—**Warning:** Oxidizer. Gas under pressure.

7.2 *Air*, extra dry.

7.3 *Indium*, of not less than 99.9% by mass.

7.4 *Tin*, of not less than 99.9% by mass.

## 8. Sampling

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

8.2 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.

## 9. Precautions

9.1 **Caution:** Oxygen is a strong oxidizer and vigorously accelerates combustion. Keep surfaces clean.

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

9.3 For certain types of PDSC, it is recommended that the flow be set up with a *reverse flow* implementation to ensure

DSC

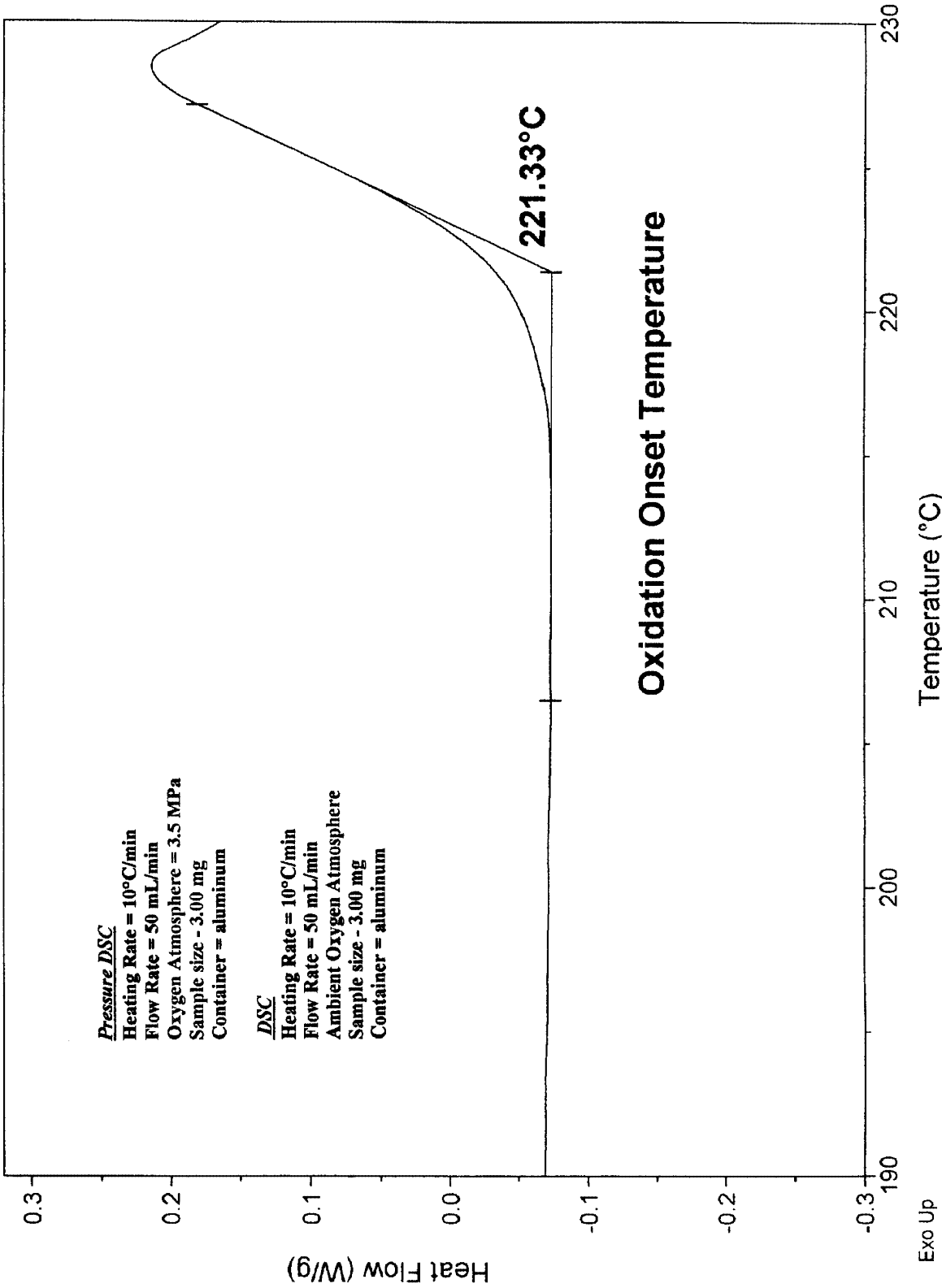


FIG. 1 DSC Oxidation Onset Temperature (OOT), Extrapolated Onset Temperature

there is no contact of decomposed hydrocarbons with incoming oxygen within the instrument. See instrument designer's recommendation on reverse flow.

9.4 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.

## 10. Calibration and Standardization

10.1 Calibrate the temperature output of the instrument using Practice E 967, using a heating rate of 10°C/min. Use indium and tin calibration material to bracket typical OOTs determined in this test method. Calibration shall be performed under ambient pressure conditions.

## 11. Procedure

11.1 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 7—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.

11.2 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.

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

11.4 Adjust flow rate of oxygen gas at ambient pressure to 50.0 ( $\pm 5$ ) mL/min, accurate to  $\pm 5\%$ .

NOTE 8—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.

11.5 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.

11.6 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.

11.7 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.

### 11.8 Test Methods:

11.8.1 When using DSC Test Method A, maintain a flow rate of 50 mL/min<sup>-1</sup> of oxygen at ambient pressure.

11.8.2 When using PDSC Test Method B, pressurize slowly, adjust and maintain pressure of oxygen at 3.5 MPa (500 psig)  $\pm 0.2$  MPa (25 psig), and maintain flow rate of 50 mL min<sup>-1</sup>.

11.8.3 When using DSC Test Method C, maintain a flow rate of 50 mL min<sup>-1</sup> of air at ambient pressure.

11.9 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.

11.10 When the experiment is completed, cool the instrument to ambient temperature, 25°C.

NOTE 9—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.

11.11 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.

## 12. Calculation

12.1 Determine the OOT, see Fig. 1.

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

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

12.1.3 Determine the temperature at the intersection of 12.1.1 and 12.1.2.

12.1.4 The temperature at the intersection is the OOT.

## 13. Report

13.1 The report shall include the following:

13.1.1 Description and identification of the sample, including any preparative treatment.

13.1.2 Method used: A (DSC in oxygen), B (PDSC in oxygen), or C (DSC in air).

13.1.3 Description of the apparatus, including commercial instrument make and model, if applicable, and specimen container.

13.1.4 Purge gas chemical composition and pressure.

13.1.5 Purge gas flow rate, mL/min.

13.1.6 OOT, ( $\pm 1^\circ\text{C}$ ) °C.

13.1.7 Specimen mass, mg.

13.1.8 Any modifications or changes to listed conditions.

13.1.9 The specific dated version of this method used.

## 14. Precision and Bias

14.1 An interlaboratory test, using Method A, was conducted in 2001 involving participation by seven (7) laboratories using two (2) instrument models from one (1) manufacturer. Each laboratory characterized in hexuplicate a commercially available polyethylene Oxidation Induction Time (OIT) reference material<sup>6,7</sup>. The results were evaluated using Practice E 691. The results of this interlaboratory test are on file at ASTM Headquarters.<sup>8</sup>

14.2 An interlaboratory test, using Method C, was conducted in 2001 involving participation by nine (9) laboratories using four (4) instrument models from one (1) manufacturer. Each laboratory characterized in hexuplicate a commercially

<sup>6</sup> Available from TA Instruments, New Castle, DE, part number 900319.901.

<sup>7</sup> The sole source of supply known to the committee at this time is TA Instruments, Inc., New Castle, DE. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

<sup>8</sup> A Research Report is available from ASTM Headquarters. Request RR:E37-1027.

available polyethylene Oxidation Induction Time (OIT) reference material<sup>6,7</sup>. The results were evaluated using Practice E 691. The results of this interlaboratory test are on file at ASTM Headquarters.<sup>8</sup>

#### 14.3 Precision—

14.3.1 Within laboratory variability may be described using the repeatability value ( $r$ ) obtained by multiplying the repeatability standard deviation by 2.8. The repeatability value estimates the 95% confidence limit. That is, two within laboratory values should be considered suspect if they differ by more than the repeatability value ( $r$ ).

14.3.1.1 The repeatability standard deviation for OOT by Method A is 1.1°C and for Method C is 0.68°C.

14.3.2 Between laboratory variability may be estimated using the reproducibility value ( $R$ ) obtained by multiplying the reproducibility standard deviation by 2.8. The reproducibility value estimates the 95% confidence limit. That is, two between

laboratory values should be considered suspect if they differ by more than the reproducibility value ( $R$ ).

14.3.2.1 The reproducibility standard deviation for OOT for Method A is 1.3°C and for Method C is 1.4°C.

#### 14.4 Bias—

14.4.1 Bias is the difference between a test result and an accepted reference value. There is no accepted reference material or value for Oxidation Onset Temperature. Therefore, no bias information can be provided.

14.4.2 The mean value for the Oxidation Onset Temperature for the OIT Reference material<sup>6,7</sup> used in this study is 236.8°C for Method A and 245.0°C for Method C.

## 15. Keywords

15.1 differential scanning calorimetry; differential thermal analysis; hydrocarbons; oxidation; oxidation induction time (OIT); oxidation onset temperature (OOT); oxidative stability; pressure differential scanning calorimetry

## ANNEX

### (Mandatory Information)

#### A1. DSC CONTAINER (PAN) CLEANING (FOR NEW PANS ONLY)

A1.1 Place 200 pans in 250 mL Erlenmeyer Flask fitted with glass stopper.

A1.2 Add approximately 150 mL of reagent grade xylene (enough to cover pans).

A1.3 Swirl for 0.5 to 2.0 min.

A1.4 Let stand 1 min.

A1.5 Decant xylene.

A1.6 Repeat A1.2-A1.5.

A1.7 Add approximately 150 mL of reagent grade acetone.

A1.8 Swirl for 0.5 to 2.0 min, and let stand for 1 min. Repeat several times.

A1.9 Decant acetone.

A1.10 Repeat A1.7, A1.3, A1.4, and A1.9.

A1.11 Flow N<sub>2</sub> at 150 to 200 mL/min over *wet* pans to drive off the solvent.

A1.12 As N<sub>2</sub> flows into the flask, rotate it so that no pans adhere to bottom or side of flask (approximately 5 to 6 min).

A1.13 Return pans to storage. Record cleaning date.

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