



# Standard Test Methods for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry<sup>1</sup>

This standard is issued under the fixed designation E1858; 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.

<sup>ε1</sup> NOTE—Warning notes were editorially updated throughout in May 2015.

## 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 and is applicable to hydrocarbons that oxidize exothermically in their analyzed form.

1.2 *Test Method A*—A differential scanning calorimeter (DSC) is used at ambient pressure, for example, about 100 kPa of oxygen.

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

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 These test methods are related to ISO 11357–6 but is different in technical content. These test methods are related to CEC L-85–T but includes additional experimental conditions.

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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 6.4 and 11.10.

## 2. Referenced Documents

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

D3350 Specification for Polyethylene Plastics Pipe and Fittings Materials

D3895 Test Method for Oxidative-Induction Time of Poly-

olefins by Differential Scanning Calorimetry

D4565 Test Methods for Physical and Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable

D5482 Test Method for Vapor Pressure of Petroleum Products (Mini Method—Atmospheric)

D5885 Test Method for Oxidative Induction Time of Polyolefin Geosynthetics by High-Pressure Differential Scanning Calorimetry

D6186 Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)

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

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

2.2 *Other Standards:*

ISO 11357–6 Plastics-Differential Scanning Calorimetry (DSC) — Part 6: Oxidation Induction Time<sup>3</sup>

CEC L-85–T Hot Surface Oxidation<sup>4</sup>

## 3. Terminology

3.1 *Definitions:*

3.1.1 Specific technical terms used in these test methods are given in Terminology E473.

## 4. Summary of Test Method

4.1 The test specimen in an aluminum pan and the reference aluminum pan are heated to a specified constant test temperature in an oxygen environment. Heat flow out of the specimen is monitored at an isothermal temperature until the oxidative

<sup>1</sup> These test methods are under the direct jurisdiction of Committee E37 on Thermal Measurements and is 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.

<sup>3</sup> Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

<sup>4</sup> Available from SAE International (SAE), 400 Commonwealth Dr., Warrendale, PA 15096-0001, http://www.sae.org.

reaction is manifested by heat evolution on the thermal curve. The oxidative induction time (OIT), a relative measure of oxidative stability at the test temperature, is determined from data recorded during the isothermal test. The OIT measurement is initiated upon reaching the isothermal test temperature.

4.2 For some particularly stable materials, the OIT may be quite long (>120 min) at the specified elevated temperatures of the experiment. Under these circumstances, the OIT may be reduced by increasing the isothermal temperature or increasing the pressure of oxygen purge gas, or both. Conversely, reactions that proceed too rapidly, with a short OIT, may be extended by decreasing the test temperature or reducing the partial pressure of oxygen, or both. By admixing oxygen gas with a suitable diluent, for example, nitrogen, the OIT will be increased (see Test Methods [D3895](#), [D4565](#), [D5482](#), [D6186](#), and Specification [D3350](#)).

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

## 5. Significance and Use

5.1 Oxidative induction time is a relative measure of the degree of oxidative stability of the material evaluated at the isothermal temperature of the test. The presence, quantity or effectiveness of antioxidants may be determined by this method. The OIT values thus obtained may be compared from one hydrocarbon to another or to a reference material to obtain relative oxidative stability information.

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

## 6. Apparatus

6.1 *Differential Scanning Calorimeter or Pressure Differential Scanning Calorimeter*, the essential instrumentation required to provide the minimum differential scanning calorimetric capability for these test methods include:

6.1.1 *DSC Test Chamber*, composed of:

6.1.1.1 *A Furnace(s)*, to provide uniform controlled heating of a specimen and reference to a constant temperature or at a constant rate within the applicable temperature range of these test methods.

6.1.1.2 *A Temperature Sensor*, to provide an indication of the specimen/furnace temperature to  $\pm 0.4^\circ\text{C}$ .

6.1.1.3 *Differential Sensors*, to detect a heat flow difference between specimen and reference with a sensitivity of  $5\ \mu\text{W}$ .

6.1.1.4 A means of sustaining a *Test Chamber Environment* of a purge gas of 50 mL/min within 5 %.

6.1.2 *Temperature Controller*, capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits at a rate of temperature change of  $40^\circ\text{C}/\text{min}$  constant to 1 % and an isothermal temperature constant to  $\pm 0.4^\circ\text{C}$

NOTE 2—In certain cases when the sample under study is of high volatility (for example, low molecular weight hydrocarbons), either the use of pressures in excess of one atmosphere or lower temperatures may be required. The operator is cautioned to verify (with apparatus manufac-

turer) the maximum oxygen pressure at which the apparatus may be safely operated.

6.1.3 *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.

NOTE 3—The capability to record the first derivative of the heat flow curve will be helpful in cases where the baseline is not constant.

6.2 *Containers (pans, crucibles, etc.)*, that are inert to the specimen and reference materials and that are of a suitable structural shape and integrity to contain the specimen and reference materials.

6.3 For use in Test Method B.

6.3.1 *Pressure System*, consisting of:

6.3.1.1 *A Pressure Vessel*, or similar means of sealing the test chamber at any applied oxygen pressure within the pressure limits of these test methods.

6.3.1.2 A source of pressurized oxygen or air capable of sustaining a regulated gas pressure in the test chamber of up to 3.2 MPa.

6.3.1.3 *A Pressure Transducer*, or similar device to measure the pressure inside the test chamber to  $\pm 0.2$  MPa, including any temperature dependence of the transducer.

NOTE 4—The link between the test chamber and the pressure transducer should allow for fast pressure equilibrium to ensure accurate recording of the pressure above the specimen during testing.

6.3.1.4 *A Pressure Regulator*, or similar device to adjust the applied pressure in the test chamber to  $\pm 0.2$  MPa of the desired value.

6.3.1.5 *A Ballast*, or similar means to maintain the applied pressure in the test chamber constant to  $\pm 0.2$  MPa.

6.3.1.6 *Valves*, to control the gas in the test chamber or to isolate components of the pressure system.

6.4 *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 6](#), following [Section 11.4](#). (**Warning**—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.)

NOTE 5—Gas delivery tubing should be kept as short as possible to minimize “dead” volume.

6.5 *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 mass.

6.6 *Specimen Containers*, and sample holders are the aluminum sample pans and should be inert to the sample and the oxidizing gas. The pans shall be clean, dry, and flat. A typical cylindrical pan has the following dimensions: height, 1.5 to 2.5 mm and outer diameter, 5.0 to 6.0 mm.

6.6.1 New sample pans shall be cleaned by the procedure found in [Annex A1](#).

## 7. Materials

7.1 *Oxygen*, extra dry, purity of not less than 99.50 % by volume. (**Warning**—Oxidizer. Gas under pressure.)

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

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

## 8. Precautions

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

8.2 **Warning**—Oxygen is a strong oxidizer and may react with aluminum pans.

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

8.4 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.”

## 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 should 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. Calibration

10.1 Calibrate the temperature output of the instrument using Test Method **E967** except that a heating rate of 1°C/min shall be used to approach the isothermal conditions of this test. Use indium and tin calibration material to bracket the temperature used in this test. Perform calibration under ambient pressure conditions.

NOTE 6—This assumes known temperature calibration with dependence on pressure. If the temperature calibration varies with pressure by more than 0.4°C, then the calibration should be performed at the test pressure.

10.2 Obtain the melting temperatures observed in the instrument calibration from extrapolated onset temperatures.

10.3 Confirm the time scale conformance of the differential scanning calorimeter to better than 1 % using Test Method **E1860**.

## 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 capsule. For accurate comparisons, specimens should have equivalent masses to within 10 % to avoid mass-dependent effects on the oxidative properties. Do not place lid on specimen pan or capsule.

NOTE 7—Other specimen sizes may be used if used consistently. However, the OIT values obtained may differ from those obtained with 3 mg. Also, vented specimen covers may be used, but OIT values may differ from those obtained in open pans. The following procedure assumes the use of open pans.

11.2 Place the uncovered prepared specimen in the sample position of the instrument and an empty specimen pan, without lid, in the reference position. Be sure that the pans are centered on the sensors.

11.3 Clean and replace all DSC covers in accordance with appropriate recommendations.

11.4 Adjust flow rate of oxygen gas to  $50.0 \pm 2$  mL/min accurate to  $\pm 4$  %. Other flow rates may be used, but shall be noted in the report.

NOTE 8—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 at the exit of the DSC cell, if recommended by the instrument manufacturer. If measured at elevated pressure, the flow rate should be corrected to a comparable flow rate (for example, 1.4 mL/min at 3.5 MPa).

11.5 Set the instrument sensitivity as required to retain the oxidation exotherm on the recorded range. A pre-analysis may be required to determine this value. A sensitivity of 2 W/g 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 re-adjust to  $50 \pm 2$  mL/min, if required.

11.7 Commence programmed heating at 40°C/min from ambient temperature to the isothermal temperatures, 175 or 195°C. Wait until temperature reaches isothermal conditions and record the thermal curve.

11.7.1 Continue heating until the isothermal test temperature  $\pm 0.4$ °C is reached. Discontinue programmed heating and equilibrate sample at the constant isothermal temperature. Zero time is recorded at the initiation of the OIT measurement and includes time to heat from room temperature to the specified isothermal temperature. The OIT is the total time from the start of the experiment at room temperature in oxygen to the extrapolated onset time of the exothermic process.

11.7.2 To ensure that the sample is at the proper test temperature, it is suggested that the test temperature be read and reported at 5 min into the isothermal portion of the run.

### 11.8 Test Methods:

11.8.1 When using DSC Test Method A, maintain flow rate of 50 mL/min (see **11.6**) of oxygen and isothermal temperature of  $195 \pm 0.4$ °C.

11.8.2 When using PDSC Test Method B, pressurize slowly, adjust and maintain pressure of oxygen at  $3.5 \pm 0.2$  MPa, maintain flow rate of 50 mL/min (see **11.6**) and isothermal temperature of  $175 \pm 0.4$ °C.

11.8.3 Other temperatures in the range of 170 to 210°C may be used for Test Method A and in the range of 150 to 200°C for Test Method B, but must be reported. The same temperature must be used by all participants intending to compare data and for all specimens to be compared.

11.9 Continue isothermal 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 (1 W/g).

11.10 When the experiment is completed, cool the instrument to ambient temperature. (**Warning**—Rapidly depressurizing a DSC cell may be dangerous.)

11.11 Repeat the entire test on a new specimen.

11.12 OIT values less than 15 min may be imprecise. OIT values longer than 100 min can be expedited through the use of a higher temperature or oxygen pressure.

## 12. Calculation and Measurements

### 12.1 Determination of the Oxidation Induction Time:

12.1.1 Extend the recorded baseline at the isothermal temperature (175°C (Test Method B) or 195°C (Test Method A)) 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. See Fig. 1.

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

12.1.4 The time at the intersection is the OIT.

## 13. Report

13.1 Report the following information

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

13.1.2 Test Method used, A (DSC) or B (PDSC),

13.1.3 Oxygen pressure in MPa (psig) and flow rates in mL/min,

13.1.4 Isothermal Test temperature, (175 or 195°C) as measured in 11.8,

13.1.5 Oxidative induction time in minutes, ( $\pm 0.1$ ) min,

13.1.6 Specimen mass, mg,

13.1.7 Description of the apparatus, including commercial instrument make and model (if applicable) and type of aluminum pans used, and

13.1.8 Any modifications or changes to listed conditions.

13.1.9 The specific dated version of these test methods used.

## 14. Precision and Bias

14.1 An interlaboratory study using these test methods was conducted in 1995–96 using samples of a lubricating oil and a polyethylene film. Following temperature calibration with indium, the two materials were tested with two replications using both ambient (100 kPa) oxygen atmosphere and 195°C test temperature and pressurized (3.4 MPa) oxygen atmosphere and 175°C test temperature. The test program included ten laboratories and instruments from four suppliers. The results were treated by Practice E691.

### 14.2 Precision:

14.2.1 Mean oxidative induction time, repeatability standard deviation ( $S_r$ ), relative repeatability standard deviation ( $RS_r$ ), reproducibility standard deviation ( $S_R$ ), and relative reproducibility standard deviation ( $RS_R$ ), for the two materials and two oxygen pressures are presented in Table 1. The relative standard deviation divided by the mean value.

14.2.1.1 *Within Laboratory*—Two values, each the mean of duplicate determinations, performed by the same laboratory, should be considered suspect if they differ by more than 2.8

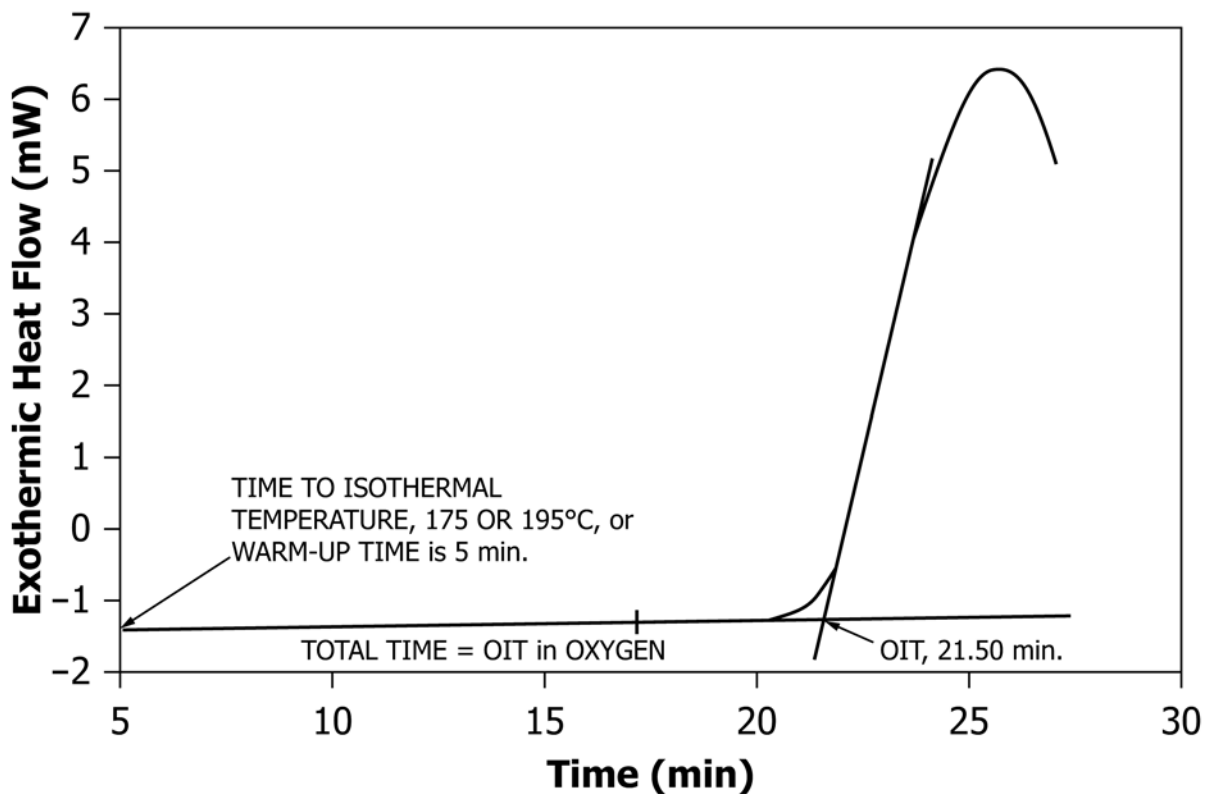


FIG. 1 Hydrocarbon Oxidation by DSC

**TABLE 1 Within and Between Laboratory Precision**

Material	Oxygen Pressure	Temp. (°C)	OIT Mean (min)	S <sub>r</sub> (min) <sup>A</sup>	RS <sub>r</sub> (%) <sup>B</sup>	S <sub>R</sub> (min) <sup>C</sup>	RS <sub>R</sub> (%) <sup>D</sup>
Oil	100 kPa	195	62.2	3.42	5.50	8.16	13.1
Oil	3.4 MPa	175	42.0	1.08	2.57	10.3	24.6
Polymer	100 kPa	195	29.0	1.26	4.34	4.49	15.4
Polymer	3.4 MPa	175	25.6	1.71	6.68	1.89	7.39

<sup>A</sup> S<sub>r</sub> = within laboratory repeatability standard deviation.

<sup>B</sup> S<sub>R</sub> = between laboratory reproducibility standard deviation.

<sup>C</sup> RS<sub>r</sub> = within laboratory repeatability relative standard deviation = S<sub>r</sub>/mean OIT

<sup>D</sup> RS<sub>R</sub> = between laboratory reproducibility relative standard deviation = S<sub>R</sub>/mean OIT.

times the repeatability standard deviation or more than 2.8 times the relative repeatability standard deviation.

(1) *Between Laboratory*—Two values, each the mean of duplicate determinations, performed in different laboratories, should be considered suspect if they differ by more than 2.8 times the reproducibility standard deviation or 2.8 times the relative reproduce deviation.

#### 14.3 Bias:

14.3.1 Since no independent calculation of oxidative induction time is possible, a comparison between measured and the true values cannot be achieved. Lack of suitable standard reference materials precludes the determination of bias.

14.3.1.1 The polyethylene sample, characterized with this standard performed at 195 °C and 100 kPa (15 psia) oxygen pressure, yielded a mean OIT value of 29.0 min with a repeatability standard deviation of 1.3 min (4.3 %) and a reproducibility standard deviation of 4.5 min (15%) with 6 degrees of freedom.

(1) The same polyethylene sample was also tested in 1993 by Section 17 of Test Method **D4565** performed at 200°C at 100 kPa (15 psia) oxygen pressure, condition different than those used in these test methods. In this test, the mean OIT was 31.4 min with a repeatability standard deviation of 1.6 min (5.1 %) and a reproducibility standard deviation of 3.1 min (9.8 %) with 44 degrees of freedom.<sup>5</sup>

NOTE 9—The difference between the results presented in **14.3.1.1** and **14.3.1.1 (1)** is not statistically significant at the 95 % confidence level.

## 15. Keywords

15.1 differential scanning calorimetry; hydrocarbons; isothermal temperature; oxidation; oxidation induction time; oxidative stability; pressure differential scanning calorimetry

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1018. Contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org).

## ANNEX

### (Mandatory Information)

#### A1. DSC 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 toluene (enough to cover pans.)

A1.3 Swirl for 0.5 to 2.0 min.

A1.4 Let stand 1 min.

A1.5 Decant toluene.

A1.6 Repeat **A1.2** through **A1.5**.

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

A1.8 Repeat **A1.3** and **A1.4**.

A1.9 Decant acetone.

A1.10 Repeat **A1.3**, **A1.4**, **A1.7**, 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 Rotate flask as N<sub>2</sub> flows in a position until no pans adhere to bottom or side of flask (approximately 5 to 6 min).

A1.13 Return pans to container (storage). Record cleaning date.

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