



Standard Test Method for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry¹

This standard is issued under the fixed designation E 1858; 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 describes 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 This test method is related to **ISO 11357-6** but is different in technical content. This test method is 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 **Note 5** and **Note 13**.

2. Referenced Documents

2.1 ASTM Standards:²

- D 3350** Specification for Polyethylene Plastics Pipe and Fittings Materials
- D 3895** Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry
- D 4565** Test Methods for Physical and Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable
- D 5482** Test Method for Vapor Pressure of Petroleum Products (Mini Method—Atmospheric)
- D 5885** Test Method for Oxidative Induction Time of Poly-

olefin Geosynthetics by High-Pressure Differential Scanning Calorimetry

D 6186 Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)

E 473 Terminology Relating to Thermal Analysis and Rheology

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E 967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E 1860 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 Time³

CEC L-85-T Hot Surface Oxidation⁴

3. Terminology

3.1 Definitions:

3.1.1 Specific technical terms used in this test method are given in Terminology **E 473**.

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 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

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² Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: E37-1018.

³ Available from ANSI, 11 W. 42nd Street, 13th Floor, New York, NY 10036.

⁴ Available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096.

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 [D 3895](#), [D 4565](#), [D 5482](#), [D 6186](#), and Specification [D 3350](#)).

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 this test method 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 this test method.

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 manufacturer) 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 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 this test method.

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 $\pm 0.2\ \text{MPa}$, 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 $\pm 0.2\ \text{MPa}$ of the desired value.

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

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 10](#), following Section [11.4](#).

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.

NOTE 6—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.

NOTE 7—**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

NOTE 8—**Caution:** Oxygen is a strong oxidizer and vigorously accelerates combustion. Keep surfaces clean.

NOTE 9—**Caution:** Oxygen is a strong oxidizer and may react with aluminum pans.

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

8.2 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 E 967 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 10—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 E 1860.

11. Procedure

11.1 Weigh 3.00 to 3.30 mg of sample to a precision of ± 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 11—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 ± 2 mL/min accurate to ± 4 %. Other flow rates may be used, but shall be noted in the report.

NOTE 12—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 ± 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 ± 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 ± 0.4 °C.

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

NOTE 13—**Caution:** 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.

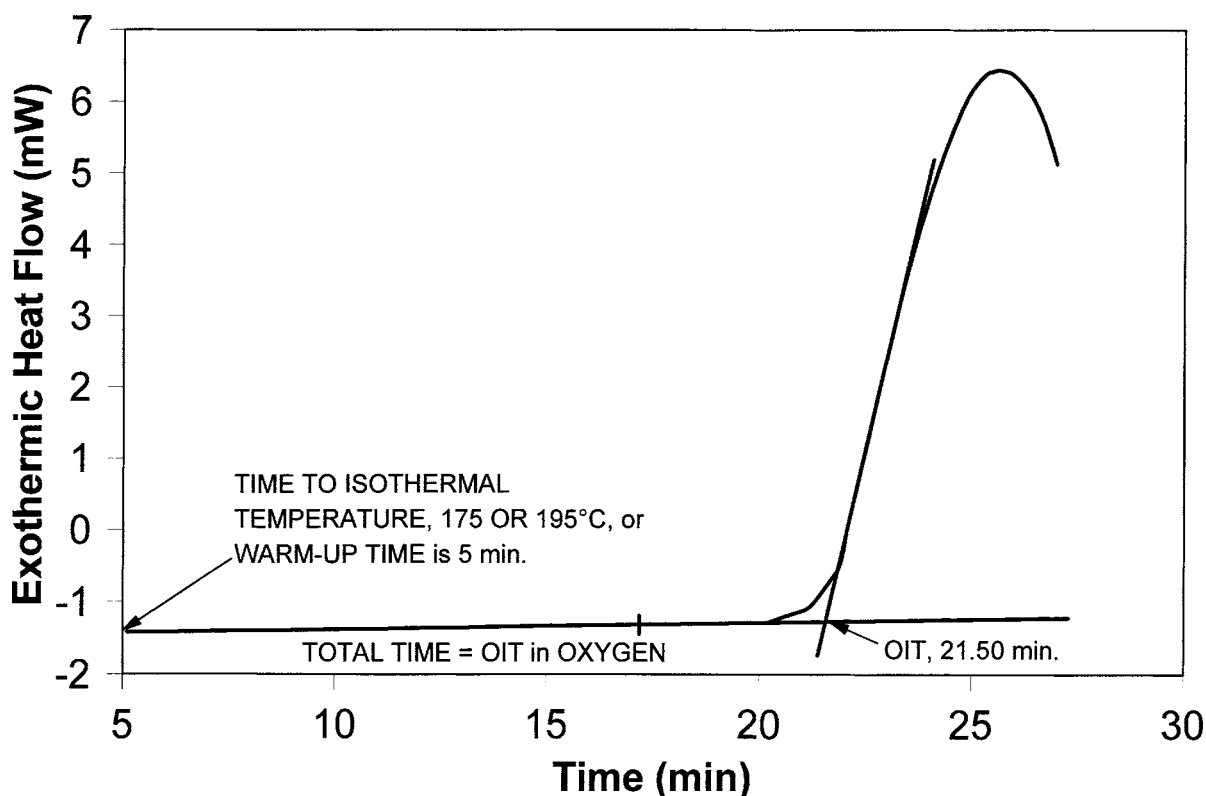


FIG. 1 Hydrocarbon Oxidation by DSC

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, (± 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 this test method used.

14. Precision and Bias

14.1 An interlaboratory study using this test method 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 E 691.

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

TABLE 1 Within and Between Laboratory Precision

Material	Oxygen Pressure	Temp. (°C)	OIT Mean (min)	S_r (min) ^A	RS_r (%) ^B	S_R (min) ^C	RS_R (%) ^D
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

^A S_r = within laboratory repeatability standard deviation.

^B RS_r = between laboratory reproducibility standard deviation.

^C RS_r = within laboratory repeatability relative standard deviation = S_r /mean OIT

^D RS_R = between laboratory reproducibility relative standard deviation = S_R /mean OIT.

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

14.2.1.1.1 *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.

14.3.1.1.1 The same polyethylene sample was also tested in 1993 by Section 17 of Test Method **D 4565** performed at 200

°C at 100 kPa (15 psia) oxygen pressure, condition different than those used in this test method. 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 freedom⁵. The same polyethylene sample was also tested in 1995 by Test Method **D 5885** performed at 150 °C and 3.4 MPa (500 psig) oxygen pressure, condition different than those used in this test method. In that test the mean OIT value was 231 min with a reproducibility standard deviation of 5.7 min (2.5 %) and a reproducibility standard deviation of 18 min (7.6 %) with 18 degrees of freedom.

NOTE 14—The difference between the results presented in **14.3.1.1** and 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

⁵ 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.

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_2 at 150 to 200 mL/min over “wet” pans to drive off the solvent.

A1.12 Rotate flask as N_2 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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