



Designation: E 1858 – 03

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

NOTE 1—Since all electronic data treatments are not equivalent, the user shall verify equivalency to this method.

1.3 *Test Method A*— A differential scanning calorimeter (DSC) is used at ambient pressure, for example, about 100 kPa 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 SI values are the standard.

1.6 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.

1.7 *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.* Specific precautionary statements are given in Note 6 and Note 14.

2. Referenced Documents

2.1 ASTM Standards:

D 3350 Specification for Polyethylene Plastic Pipe and Fitting Materials²

D 3895 Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry³

D 4565 Test Method for Physical Environmental Performance Properties of Insulations and Jackets for Telecom-

munications Wire and Cable⁴

D 5482 Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry⁵

D 5885 Test Method for Oxidative Induction Time of Polyolefin Geosynthics By High Pressure Differential Scanning Calorimetry⁶

D 6186 Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC) Polyolefin Geosynthics By High Pressure Differential Scanning Calorimetry⁷

E 473 Terminology Relating to Thermal Analysis⁸

E 691 Practice for Conducting and Interlaboratory Study To Determine the Precision of a Test Method⁸

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters⁸

E 1860 Test Method for Elapsed Time Calibration of Thermal Analyzers⁸

2.2 Other Standards:

ISO 11357–6 Plastics-Differential Scanning Calorimetry (DSC) — Part 6: Oxidation Induction Time⁹

CEC L-85–T Hot Surface Oxidation¹⁰

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

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

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² *Annual Book of ASTM Standards*, Vol 08.03.

³ *Annual Book of ASTM Standards*, Vol 08.02.

⁴ *Annual Book of ASTM Standards*, Vol 10.02.

⁵ *Annual Book of ASTM Standards*, Vol 05.03.

⁶ *Annual Book of ASTM Standards*, Vol 04.09.

⁷ *Annual Book of ASTM Standards*, Vol 05.04.

⁸ *Annual Book of ASTM Standards*, Vol 14.02.

⁹ Available from ANSI, 11 W. 42nd Street, 13th Floor, New York, NY 10036.

¹⁰ Available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096.

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 D 3895, D 4565, D 5482, D 6186, and Specification D 3350).

NOTE 2—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 ± 0.4 °C.

6.1.1.3 *Differential Sensors*, to detect a heat flow difference between specimen and reference with a sensitivity of 5 μ 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 °C/min constant to 1 % and an isothermal temperature constant to ± 0.4 °C

NOTE 3—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 *Recording Device*, capable of recording and displaying any fraction of the heat flow signal on the Y-axis and time

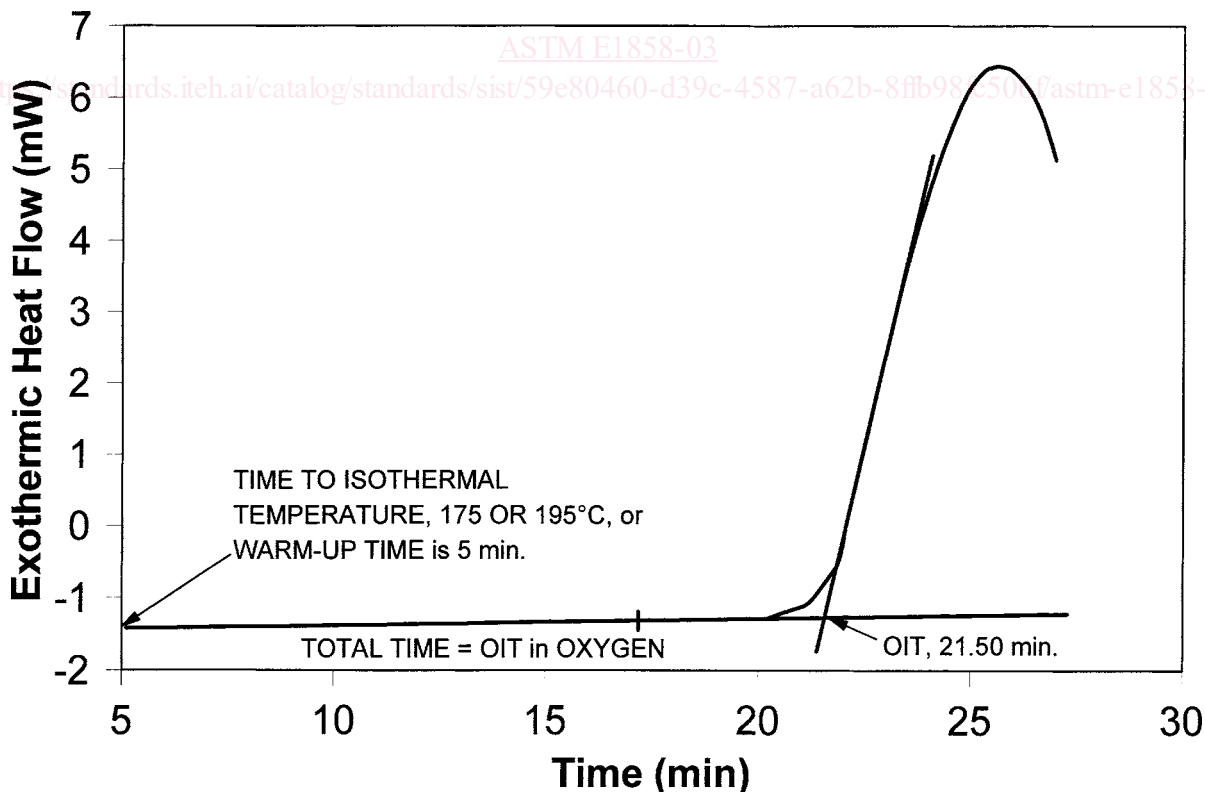


FIG. 1 Hydrocarbon Oxidation by DSC

on the *X*-axis (see Fig. 1). Time base shall be accurate to ± 0.1 min and be readable to 0.1 min.

NOTE 4—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 ± 0.2 MPa, including any temperature dependence of the transducer.

NOTE 5—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 ± 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 ± 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 13, following Section 11.4.

NOTE 6—**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 7—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 8—**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 9—**Caution:** Oxygen is a strong oxidizer and vigorously accelerates combustion. Keep surfaces clean.

NOTE 10—**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 11—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 12—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.