Designation: D6186 – 08

Standard Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)[1]

This standard is issued under the fixed designation D6186; 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 covers the determination of oxidation induction time of lubricating oils subjected to oxygen at 3.5 MPa (500 psig) and temperatures between 130 and 210°C.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.2.1 *Exception*—Pressure measurement appears in MPa with psig provided in parentheses for information only.

1.3 *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. Terminology

2.1 *Definitions of Terms Specific to This Standard:*

2.1.1 *extrapolated onset time*, *n*—a time determined on a thermal curve, as the intersection of the extrapolated baseline and a line tangent to the oxidation exotherm constructed at its maximum rate.

2.1.2 *oxidation induction time, (OIT)*, *n*—a period of time during which the oxidation rate accelerates from zero to a maximum and which corresponds to the extrapolated onset time.

2.1.3 *thermal curve*, *n*—a graph of sample heat flow versus time.

3. Summary of Test Method

3.1 A small quantity of oil is weighed into a sample pan and placed in a test cell. The cell is heated to a specified temperature and then pressurized with oxygen. The cell is held at a regulated temperature and pressure until an exothermic reaction occurs. The extrapolated onset time is measured and reported as the oxidation induction time for the lubricating oil at the specified test temperature.

4. Significance and Use

4.1 Oxidation induction time, as determined under the conditions of this test method, may be used as an indication of oxidation stability.[2] This test method is faster than other oil oxidation tests and requires a very small amount of sample. It may be used for research and development, quality control, and specification purposes. However, no correlation has been established between the results of this test method and service performance.

5. Apparatus

5.1 *Pressure Differential Scanning Calorimeter (PDSC)*, equipped with the following items:

5.1.1 *Sample Enclosure*, with capability to 3.5 ± 0.2 MPa (500 ± 25 psig) at 210°C and pressure gauge graduated at intervals of 200 KPa (28.6 psig) or less.

5.1.2 *Thermal Analyzer.*

5.1.3 *Aluminum Solid Fat Index (SFI) Sample Pan*—See Note 1.

5.1.4 *Oxidation Stability Software.*

5.1.5 *Calibration Software.*

5.1.6 *Calibrated Flowmeter*, with a capacity of at least 200 mL/min and graduated in intervals of 5 mL or less.

5.1.7 *Sample Encapsulation Press*.

NOTE 1—It has been found that when oil samples are prepared with SFI pans which have more consistent surface areas than standard flat bottom pans, reproducibility is improved.

NOTE 2—Stainless steel or copper tubing is compatible with oxygen.

NOTE 3—See Fig. 1 for a diagram of a typical test unit.

6. Reagents and Materials

6.1 *Oxygen*, a minimum purity of 99.5 % oxygen by volume. (**Warning—**Oxidizer. Gas under pressure.)

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

7. Calibration

7.1 *Sample Temperature Calibration*:

7.1.1 Weigh approximately 10 mg of indium into an aluminum sample pan, insert a lid and crimp the lid to the pan using

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.09.0D on Oxidation of Lubricants.

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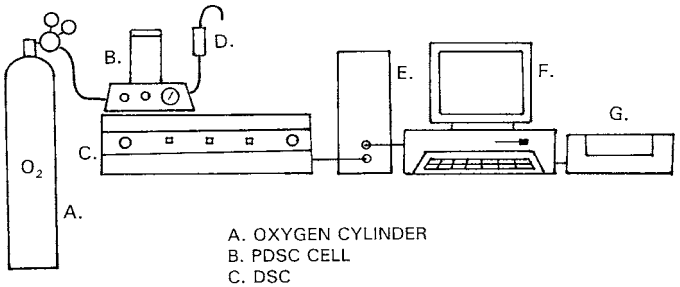
[2] Rhee, In-Sik, "Development of New Oxidation Stability Test Method for Lubricating Oils Using a Pressure Differential Scanning Calorimeter (PDSC)," *NLGI Spokesman*, Vol 65, No. 3, June 2001, pp. 16–23.

***A Summary of Changes section appears at the end of this standard.**



A. OXYGEN CYLINDER
B. PDSC CELL
C. DSC
D. FLOWMETER
E. MODULE INTERFACE
F. MICROPROCESSOR
G. PLOTTER

FIG. 1 PDSC Test Unit

the encapsulation press. Place the crimped pan onto the sample platform in the pressure cell. Seal an empty pan in the same manner and place it on the reference platform. Set the cell cover in place and close the cell.

7.1.2 Open the oxygen cylinder valve slightly and set a pressure of 3.5 ± 0.2 MPa (500 ± 25 psig) on the cell inlet line with the pressure regulator. Partially open the inlet valve on the cell and allow the pressure to slowly build up in the cell. This requires approximately 2 min. Using the outlet valve, adjust and maintain the oxygen purge rate through the flowmeter at 100 ± 10 mL/min.

7.1.3 Set the thermal analyzer to heat from ambient temperature (approximately 22°C) to 180°C at a programmed rate of 10°C/min. After completion of the run measure the melting temperature of the indium. If the melting temperature differs from 157.4 ± 0.2°C (see Note 4) correct the difference by using either the hardware or software calibration procedure described in the manufacturer's instruction manual. If the hardware calibration procedure is used, perform the temperature correction under 3.5 MPa (500 psig) oxygen pressure with a 100 mL/min purge rate. A typical melting calibration curve is shown in Fig. 2.

NOTE 4—The melting temperature of indium is 156.6°C at atmospheric pressure, but has been found to be elevated to 157.4°C under the conditions of this test method, 3.5 MPa (500 psig) of oxygen.

7.2 *Temperature Controller Calibration*:

7.2.1 Remove both the sample pan and the reference pan from the cell, then close the cell. Slowly pressurize the cell with 3.5 ± 0.2 MPa (500 ± 25 psig) oxygen and adjust the purge rate to 100 ± 10 mL/min using the cell outlet valve. Select the desired test temperature (either 210, 180, 155, or 130°C).

7.2.2 Program the cell to maintain the selected test temperature. If, after 10 min, the displayed cell temperature differs by more than ± 0.2°C from the selected temperature, slowly adjust the temperature controller until they agree. After making an adjustment, wait at least 5 min to make certain that the temperature is stable before continuing. If the PDSC equipment does not have this function, the control calibration shall be followed according to the equipment manufacturer's recommendations.

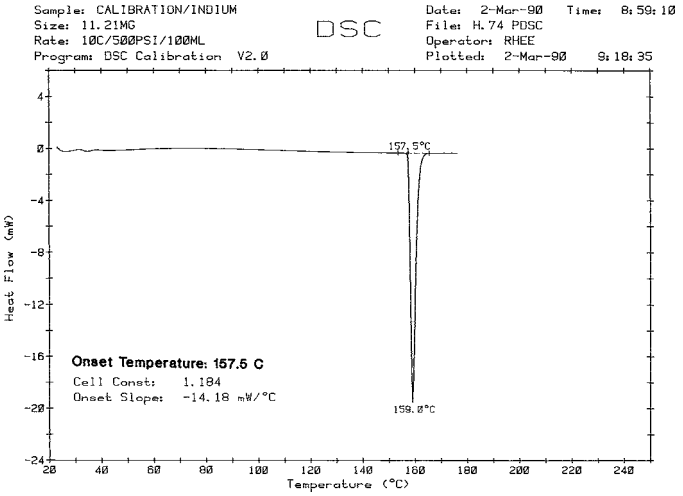


FIG. 2 Calibration Curve for PDSC

7.3 *Cell Base Pressure Gauge Calibration*—Conduct the calibration using a calibrated pressure transducer or a previously calibrated gauge according to the pressure cell manufacturer's instructions.

8. Procedure

8.1 Before starting a test, the control thermocouple calibration shall be conducted at the test temperature (either 210, 180, 155, or 130°C) according to 7.2.1 and 7.2.2. When the test temperature is not known, conduct the calibration at 210°C.

8.2 Weigh 3.0 ± 0.2 mg of oil into a new sample pan. Spread the sample evenly upon the flat portion. Do not spill any of the sample into the trough portion of the pan. A flat bottom pan can be used if the sample is placed upon a 0.5 cm diameter circle in the center of the pan.

8.3 Place the uncovered pan containing the sample onto the platform of the cell according to the PDSC manufacturer's instructions for placing the sample pan. Place a new empty pan of the same configuration onto the cell platform according to the PDSC manufacturer's instructions for placing the reference pan. Close the cell and the pressure release valve.

8.4 Beginning at ambient temperature (approximately 22°C), program the sample temperature to increase at a rate of 100°C/min to the test temperature.

8.5 Allow the sample to equilibrate at the test temperature for 2 min.

8.6 Open the oxygen valve and slowly pressurize the cell to 3.5 ± 0.2 MPa (500 ± 25 psig). This requires approximately 2 min to reach maximum pressure. Measure the oxidation induction time from the time when the oxygen valve is opened.

8.7 As soon as the pressure has equilibrated, check the cell purge rate and adjust and maintain at 100 ± 10 mL/min with the outlet valve.

8.8 After a duration of 120 min from the time when the oxygen valve was opened, close the oxygen valve and slowly release the cell pressure by opening the cell pressure release valve. In the case of a sample for which the approximate oxidation induction time is known, the test can be stopped after the oxidation exotherm has occurred.

8.9 Plot the thermal curve and measure the extrapolated onset time for the oxidation exotherm. Report this time, to the

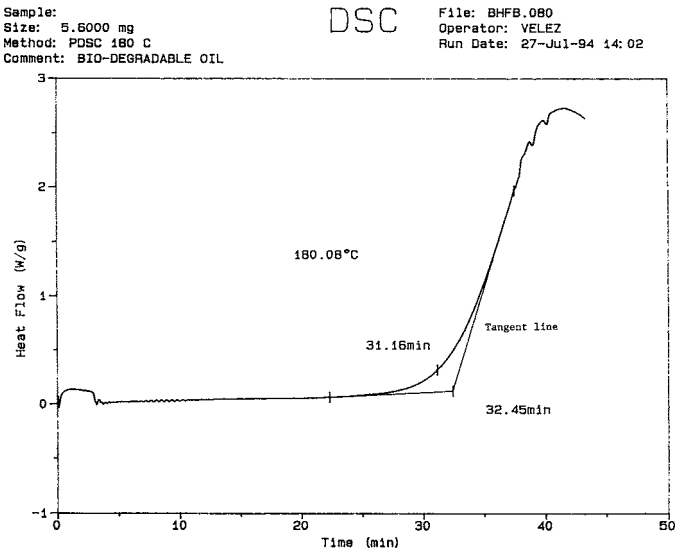


FIG. 3 A Typical Thermal Curve From PDSC Test

nearest 1 min, as the oxidation induction time for the sample. If more than one oxidation exotherm is observed, report the oxidation induction time for the largest exotherm.

NOTE 5—A typical thermal curve is shown in Fig. 3.

8.10 If the induction time is less than 10 min, rerun the test at the next lower temperature, starting at 8.2. Allow the cell to cool to ambient temperature before running the test at the next lower temperature.

9. Report

9.1 Report, to the nearest minute, the oxidation induction time (OIT) for the sample.

9.2 Report the test temperature.

10. Precision and Bias

10.1 *Precision*—The precision of this test method was determined in accordance with currently accepted guidelines in Committee D02's "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants." Eight laboratories evaluated thirteen samples at four different test temperatures (130, 155, 180, and 210°C) in the round robin and reported oxidation induction times ranged from 10 to 119 min. Appendix X2 lists round robin data and PDSC equipment used by cooperators.

10.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only one case in twenty:

$$r = 0.17\,m \tag{1}$$

where

m = average of the two test results.

10.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material, would in the long run, in normal and correct operation of the test method, exceed the following values only one case in twenty:

$$R = 0.35\,m \tag{2}$$

where:

m = average of the two test results.

10.2 *Bias*—The procedure in this test method has no bias because the value of oxidation induction time can be defined only in terms of a test method.

11. Keywords

11.1 differential scanning calorimetry; lubricating oil; OIT; onset temperature; oxidation; oxidation coefficient; oxidation induction time; PDSC; thermal analysis

APPENDIXES

(Nonmandatory Information)

X1. CALCULATION OF INDUCTION TIMES

X1.1 The following kinetic equation can be used to predict induction times of lubricating oils at various test temperatures:

$$t = (4.6/k_o) \times e^{E/RT} \tag{X1.1}$$

where:

t = calculated oxidation induction time, min,
E = activation energy, J/mol,
k_o = frequency factor,
R = universal gas constant, 8.314 J/mol K, and
T = temperature, K (for desired temperature).

X1.1.1 Activation energy, E, can be calculated using the following equation:

$$E = R\,(T_1T_2\,/\,(T_1 - T_2)) \times ln\,(t_1/t_2) \tag{X1.2}$$

X1.1.2 Eq X1.2 requires two induction times (t_1, t_2) from two different test temperatures (T_1, T_2).

X1.1.3 Calculate k_o from the following equation:

$$k_o = (4.6/t) \times e^{E/RT} \tag{X1.3}$$

X2. PDSC ROUND ROBIN DATA

TABLE X2.1 Round Robin Cooperators and PDSC Instruments

LAB	Instrument	Sample pan
1	TA 2200 and 961	SFI
2	TA 2100 and 961	SFI
3	TA 2100 and 961	SFI
4	TA 961	SFI
5	TA 912 (dural sample cell)	SFI
6	Mettler DSC 27HP	Mettler sample pan
7	Mettler DSC	Mettler sample pan
8	thermal science	thermal science pan

TABLE X2.2 PDSC Round Robin Data

LAB	D-11	D-12	D-13	D-14	D-15	D-16	D-17	D-18	D-19	D-20	D-21	D-22	D-23
1	42.6	52.7	44.3	86.6	77.9	36.7	26.8	15.8	20.5	118	85.1	29.7	33.9
	40.8	46.9	45.7	77.5	85.1	38.6	26.3	15.4	19.6	116	79.9	29.1	35.6
2	42.2	65.0	51.5	92.1	56.9	37.8	27.0	14.1	10.2	111	88.8	27.2	28.2
	41.5	60.5	53.9	87.6	60.2	41.4	25.3	16.6	10.1	116	94.7	26.1	30.3
3	37.4	48.7	39.0	105	90.7	39.8	26.5	16.8	18.9	112	79.0	24.1	32.6
	40.1	52.0	41.0	102	86.2	41.6	26.3	16.7	17.5	109	79.9	21.6	28.0
4	44.0	55.8	47.4	97.4	69.6	38.7	23.6	17.9	15.2	109	75.6	26.8	34.3
	43.4	45.7	46.0	88.8	67.9	34.0	22.5	13.9	13.2	105	68.1	28.8	34.2
5	37.0	53.0	41.6	84.6	63.8	38.9	30.1	14.0	14.6	95.8	79.2	26.9	26.1
	36.1	52.2	39.4	85.3	62.9	40.0	31.3	15.6	13.6	96.9	79.0	28.4	26.2
6	38.8	47.0	39.3	122	57.9	23.3	31.4	18.1	17.9	100	103	32.7	37.2
	38.6	51.8	39.4	121	56.6	27.7	33.6	16.8	17.4	102	103	30.1	38.8
7	41.7	55.9	42.1	92.3	76.7	30.3	28.7	19.8	13.8	117	94.6	25.0	31.6
	41.4	59.5	41.9	97.7	81.9	34.8	22.2	16.6	13.6	116	93.5	20.1	33.0
8	38.4	52.4	46.5	81.5	47.5	33.9	26.1	14.5	18.2	118	83.9	25.6	25.8
	37.8	47.4	44.1	77.2	49.9	35.8	26.5	16.6	20.2	119	79.4	26.0	26.9
Test Temperature, °C	180	130	180	180	180	180	210	210	180	210	155	155	210

TABLE X2.3 Round Robin Samples

Sample	Type of Oil	Description
D-11	engine oil	mineral oil
D-12	vegetable based hydraulic fluid	rapeseed oil
D-13	heavy duty diesel oil	mineral oil
D-14	hydraulic fluid with Zn	mineral oil
D-15	hydraulic fluid without Zn	mineral oil
D-16	turbine oil	mineral oil
D-17	gear oil	mineral oil
D-18	engine oil	synthetic
D-19	hydraulic fluid	PAO
D-20	aviation turbine oil	polyol ester
D-21	gear oil	synthetic
D-22	vegetable based hydraulic fluid	sunflower
D-23	synthetic biodegradable oil	polyol ester

SUMMARY OF CHANGES

Subcommittee D02.09.0D has identified the location of selected changes to this standard since the last issue (D6186–98(2003)$^{\varepsilon 1}$) that may impact the use of this standard.

(*1*) Replaced kinetic model in Appendix X1.