



# Standard Test Method for Thermal Stability of Organic Heat Transfer Fluids<sup>1</sup>

This standard is issued under the fixed designation D6743; 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 covers the determination of the thermal stability of unused organic heat transfer fluids. The procedure is applicable to fluids used for the transfer of heat at temperatures both above and below their boiling point (refers to normal boiling point throughout the text unless otherwise stated). It is applicable to fluids with maximum bulk operating temperature between 260 °C (500 °F) and 454 °C (850 °F). The procedure shall not be used to test a fluid above its critical temperature. In this test method, the volatile decomposition products are in continuous contact with the fluid during the test. This test method will not measure the thermal stability threshold (the temperature at which volatile oil fragments begin to form), but instead will indicate bulk fragmentation occurring for a specified temperature and testing period. Because potential decomposition and generation of high pressure gas may occur at temperatures above 260 °C (500 °F), do not use this test method for aqueous fluids or other fluids which generate high-pressure gas at these temperatures.

1.2 DIN Norm 51528 covers a test method that is similar to this test method.

1.3 The applicability of this test method to siloxane-based heat transfer fluids has not been determined.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.5 *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.* For specific warning statements, see 7.2, 8.8, 8.9, and 8.10.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.L0.06 on Non-Lubricating Process Fluids.

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## 2. Referenced Documents

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

D2887 Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography

D4175 Terminology Relating to Petroleum, Petroleum Products, and Lubricants

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

### 2.2 DIN Norms:<sup>3</sup>

51528 Determination of the Thermal Stability of Unused Heat Transfer Fluids

## 3. Terminology

### 3.1 Definitions:

3.1.1 *thermal stability, n*—the resistance to permanent changes in properties caused solely by heat. **D4175**

### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *decomposition products that cannot be vaporized, n*—materials from the thermally stressed heat transfer fluid, from which those fractions that can be vaporized are removed by distillation procedures, that are quantitatively determined as residues in a bulb tube distillation apparatus.

3.2.2 *fluid within the unstressed fluid boiling range, n*—any fluid components with boiling point between the initial boiling point and final boiling point of the unstressed fluid.

3.2.3 *gaseous decomposition products, n*—materials with boiling points below room temperature, at normal pressure, such as hydrogen and methane, that escape upon opening the test cell and that can be determined by measuring the mass immediately thereafter.

3.2.4 *high boiling components, n*—materials from the thermally stressed heat transfer fluid, with boiling points above the final boiling point of the unstressed heat transfer fluid, but

<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 Deutsches Institut für Normung e.V.(DIN), Burggrafenstrasse 6, 10787 Berlin, Germany, http://www.din.de.

which can still be separated by distillation from the heat transfer fluid by means of classical separation procedures.

3.2.5 *low boiling components, n*—materials from the thermally stressed heat transfer fluid, with boiling points below the initial boiling point of the unstressed heat transfer fluid.

3.2.6 *mass percentage of high boiling components, n*—the percentage of thermally stressed heat transfer fluid with a boiling point above the final boiling point of the unstressed fluid.

3.2.7 *mass percentage of low boiling components, n*—the percentage of thermally stressed heat transfer fluid with a boiling point below the initial boiling point of the unstressed fluid.

3.2.8 *test cell, n*—an ampoule constructed from stainless steel tubing and sealed with compression fittings at each end.

3.2.9 *thermally stressed, adj*—subjected to heating, as described in this test method.

#### 4. Summary of Test Method

4.1 Charge the test fluid in a thermal stability test cell purged with nitrogen and tightly seal the test cell to remove and preclude introduction of oxygen and water from the atmosphere. Heat the fluid in an oven at a given temperature and for a given period of time. Determine the boiling range of the heated fluid by gas chromatography (GC) analysis and compare it to the boiling range of pure, unused fluid.

#### 5. Significance and Use

5.1 Heat transfer fluids degrade when exposed to sufficiently high temperatures. The amount of degradation increases as the temperature increases or the length of exposure increases, or both. Due to reactions and rearrangement, degradation products can be formed. Degradation products include high and low boiling components, gaseous decomposition products, and products that cannot be evaporated. The type and content of degradation products produced will change the performance characteristics of a heat transfer fluid. In order to evaluate thermal stability, it is necessary to quantitatively determine the mass percentages of high and low boiling components, as well as gaseous decomposition products and those that cannot be vaporized, in the thermally stressed heat transfer fluid.

5.2 This test method differentiates the relative stability of organic heat transfer fluids at elevated temperatures in the absence of oxygen and water under the conditions of the test.

5.3 The user shall determine to his own satisfaction whether the results of this test method correlate to field performance. Heat transfer fluids in industrial plants are exposed to a variety of additional influencing variables. Interaction with the plant's materials, impurities, heat build-up during impaired flow conditions, the temperature distribution in the heat transfer fluid circuit, and other factors can also lead to changes in the heat transfer fluid. The test method provides an indication of the relative thermal stability of a heat transfer fluid, and can be considered as one factor in the decision-making process for selection of a fluid.

5.4 The accuracy of the results depends very strongly on how closely the test conditions are followed.

5.5 This test method does not possess the capability to quantify or otherwise assess the formation and nature of thermal decomposition products within the unstressed fluid boiling range. Decomposition products within the unstressed fluid boiling range may represent a significant portion of the total thermal degradation.

#### 6. Apparatus

6.1 *Test Cell*—The test cell shall be a new, clean ampoule made from ASTM A-269 grade 316L stainless steel tubing, 25 mm (1 in.) outside diameter, 2 mm (0.083 in.) wall thickness. The test cell shall be 0.152 m  $\pm$  0.003 m (6 in.  $\pm$  0.125 in.) in length and sealed with compression fittings at each end.

NOTE 1—Where tubing with SI dimensions is not readily available, the use of tubing with inch-pound dimensions is acceptable.

6.2 *Heating Oven*—The oven shall be capable of being controlled within  $\pm 1$  °C ( $\pm 1.8$  °F) at test temperature. The test temperature selected will typically be between 260 °C (500 °F) and 427 °C (800 °F), depending on the fluid being tested.

6.3 *Bulb Tube Distillation Apparatus*—This apparatus shall be capable of heating to at least 250 °C (482 °F) and pressure down to at least 0.1 mm Hg.

6.4 *Dewar Flask*—The flask is used to hold the test cells during cooling after removal from the heating oven.

6.5 *Balance*—The balance shall be capable of measuring mass to the nearest 0.01 g.

#### 7. Preparation of Apparatus

7.1 *Test Cell*—The test cell used shall always be a clean, new ampoule. Reuse of ampoules is not permitted.

7.2 *Cleaning of Test Cell*—A new test cell shall be cleaned by washing with a suitable volatile solvent such as acetone and dried. (**Warning**—Use adequate safety precautions with all solvents and cleaners.)

#### 8. Procedure

8.1 Determine the initial boiling point (IBP) and final boiling point (FBP) of the unstressed heat transfer fluid by GC, in accordance with Test Method **D2887** with the following requirements: the column shall be wall-coated open tubular type of 7.5 m to 10 m length with a 100 % polydimethylsiloxane film thickness of 0.88  $\mu$ m, the detector shall be flame ionization type, the initial oven temperature shall be set to 35 °C (95 °F) eliminating cryogenic cooling, the calibration mixture shall cover the boiling range from *n*-C<sub>5</sub> to *n*-C<sub>60</sub>. The following GC parameters are recommended: oven temperature rate 10 °C (18 °F) per minute, oven final temperature 375 °C (707 °F), time at oven final temperature 3 min, injector initial temperature 100 °C (212 °F), injector temperature rate 10 °C (18 °F) per minute, injector final temperature 375 °C (707 °F), detector temperature 375 °C (707 °F).

8.2 Measure the mass of a clean, dry test cell including compression fittings to the nearest 0.01 g. Pour the unstressed

heat transfer fluid into the clean, dry test cell in a vertical position. The quantity of heat transfer fluid transferred to the test cell shall be  $27 \text{ g} \pm 0.2 \text{ g}$ . Invert the test cell in a vertical position and allow it to drain until all free-flowing material has been removed. More viscous fluids may require as long as 15 min to drain completely. At the end of the draining period, tap the test cell to remove a drop clinging to the open end of the test cell—do not wipe away any fluid. Measure the mass of the test cell and its remaining contents including compression fittings to the nearest 0.01 g.

NOTE 2—The intent is to perform this step only once for each heat transfer fluid being tested at this time.

8.3 Measure the mass of a clean, dry test cell including compression fittings to the nearest 0.01 g. Introduce high purity nitrogen using tubing at the bottom of the clean, dry test cell for 2 min at 60 mL/min to 70 mL/min.

NOTE 3—To ensure accurate results, at least three test cells containing samples of the same heat transfer fluid should be heated simultaneously.

8.4 Pour the thermally unstressed heat transfer fluid into the clean, dry test cell. The quantity of heat transfer fluid transferred to the test cell shall be  $27 \text{ g} \pm 0.2 \text{ g}$ .

8.5 Completely displace the air remaining in the gas space in the test cell by introducing high purity nitrogen using tubing just above the liquid surface of fluid inside the test cell at 30 mL/min to 35 mL/min for 12 min at ambient temperature.

8.6 Carefully seal the test cell and measure its mass to the nearest 0.01 g.

8.7 Insert the test cell vertically in the oven. Adjust the heating oven to the proper test temperature. The time to achieve proper test temperature should be approximately 3 h. The test temperature shall be maintained throughout the entire test duration and controlled in such a way that the temperature of the test liquid does not deviate by more than  $\pm 1 \text{ }^\circ\text{C}$  ( $\pm 1.8 \text{ }^\circ\text{F}$ ) at any location, including the heated wall. Temperature shall be measured and recorded throughout the test at least once per day. If test cells containing different fluids are tested at the same time, the test cells shall be distributed symmetrically inside the oven to minimize the effect of oven temperature variation on the results. The test duration shall be the time from attaining the test temperature to the time the heat supply is cut off. The test duration at the specified test temperature shall be a minimum of 500 h. The preferred test duration is  $500 \text{ h} \pm 1 \text{ h}$ , however, a longer test duration may be used. Thermal degradation cannot be assumed to be linear with time. Therefore, the stability of two fluids can only be compared at the same test temperature and test duration.

8.8 Protect the oven from heat transfer fluid that may spill in case of damage by placing a collecting pan under the test cell. (**Warning**—If fluid leaks out due to improper sealing of the test cell, there may be the potential of flammable vapors inside the oven. The oven design and installation should consider this possibility. )

8.9 At the conclusion of the heating period, shut off the oven. Do not immediately remove the test cell. Leave the oven closed and allow the oven and the test cell to cool to ambient

temperature to reduce the internal pressure. (**Warning**—Pressure inside the test cell may reach several thousand kPa during the test.)

8.10 Remove the test cell from the oven. (**Warning**— Use adequate safety precautions when removing the test cells from the oven in case some portion of the equipment is still hot.)

8.11 Carefully measure the mass of the test cell to the nearest 0.01 g. If the evaporation loss of gaseous decomposition products is calculated at greater than 0.5 mass %, the test should be repeated since this would indicate tube leakage.

8.12 Place the test cell in a Dewar flask containing a cooling mixture of acetone or isopropanol and dry ice. Allow the test cell to cool to at least  $-55 \text{ }^\circ\text{C}$  ( $-67 \text{ }^\circ\text{F}$ ). The duration of cooling is approximately 5 min to 10 min. Stand the test cell in a vertical position and allow it to reach ambient temperature, then exercise care to remove any condensed water on the exterior of the test cell. Stand the test cell in a vertical position and open the top of the test cell. Then measure the mass of the test cell including compression fittings and its contents to the nearest 0.01 g. Put a portion of the fluid into sample bottles for analytical evaluation and store the remainder for additional measurement in a glass bottle that is hermetically sealed. Invert the test cell and allow it to drain until all free-flowing material has been removed. More viscous fluids may require as long as 15 min to drain completely. At the end of the draining period, tap the test cell to remove a drop clinging to the open end of the test cell—do not wipe away any fluid. Measure the mass of the test cell and its remaining contents including compression fittings to the nearest 0.01 g.

8.13 Visually observe the appearance of the fluid sample for any insolubles, or other changes in the fluid. Examples include high pressure upon opening the test cell, appearance of fouling in the head space of the test cell and evidence of a leak from the test cell. Observations shall be noted in the report.

8.14 Determine the mass percentage of low and high boiling components in the thermally stressed sample, in accordance with Test Method D2887 using the same equipment and requirements as specified in 8.1.

8.15 The decomposition products that cannot be vaporized are determined separately in a bulb tube distillation apparatus. Measure approximately 4 g of the thermally stressed heat transfer fluid into the distillation flask. Record the mass to the nearest 0.01 g. Apply vacuum slowly by means of a vacuum pump. Pressure shall be  $0.1 \text{ mm Hg} \pm 0.01 \text{ mm Hg}$  at the end of distillation. Heat the bulb tube distillation apparatus slowly to  $250 \text{ }^\circ\text{C}$  ( $482 \text{ }^\circ\text{F}$ ). Avoid any delays in boiling. Continue distillation for at least 30 min after constant mass of distillation residue is achieved. Measure the mass of the residue in the distillation flask to the nearest 0.01 g.

NOTE 4—The heat transfer fluid is not further thermally damaged by the distillation process.

8.16 Compare the GC test results from the thermally stressed sample to those of the unstressed heat transfer fluid.

## 9. Calculation

9.1 The distillation curves of the heated samples and of the original heat transfer fluid are determined by way of simulated

distillation by gas chromatography, in accordance with Test Method **D2887** (with the exceptions noted in **8.1**). Determine the initial boiling point and the final boiling point of the thermally stressed and unstressed heat transfer fluid.

9.2 The components of the heated samples are subdivided as follows:

- 9.2.1 Gaseous decomposition products (G).
- 9.2.2 Low boiling components (LB).
- 9.2.3 Fluid within the unstressed fluid boiling range (F).
- 9.2.4 High boiling components (HB).
- 9.2.5 Decomposition products that cannot be vaporized (R).
- 9.2.6 Unstressed fluid remaining in the test cell (FR).
- 9.2.7 Material remaining in the test cell after heating (MR).
- 9.2.8 Decomposition products remaining in the test cell (DR).

9.3 The mass percentage  $m(G)$  is determined by subtracting the mass of the opened test cell measured in **8.12** from the mass of the sealed test cell in **8.6**, dividing by the mass of fluid measured into the test cell in **8.4**, and then multiplying by 100.

9.4 The mass percentage  $m(R)$  is determined by dividing the mass of the residue measured in **8.15** by the mass of thermally stressed heat transfer fluid measured into the distillation flask, and then multiplying by 100.

9.5 The mass percentage  $m(FR)$  is determined in **8.2** by subtracting the mass of the clean, dry test cell from the mass of the test cell and its remaining contents, dividing by the mass of fluid measured into the test cell, and then multiplying by 100.

9.6 The mass percentage  $m(MR)$  is determined by subtracting the mass of the clean, dry test cell measured in **8.3** from the mass of the test cell and its remaining contents measured in **8.12**, dividing by the mass of fluid measured into the test cell in **8.4**, and then multiplying by 100.

9.7 The mass percentage  $m(DR)$  is determined by subtracting  $m(FR)$  from  $m(MR)$ . The material represented by  $m(DR)$  is considered to consist of decomposition products.

9.8 Mass percentages  $m(LB)$  and  $m(HB)$  can be obtained from the boiling graphs, directly from the gas chromatogram, or by using simulated distillation software.

9.9 To take into account the mass percentages  $m(G)$ ,  $m(DR)$  and  $m(R)$ , the mass percentages  $m(LB)$  and  $m(HB)$  must be corrected in accordance with **Eq 1 and 2**.

$$m_{corr}(LB) = m(LB) \cdot \left[ \frac{100 - m(G) - m(DR) - m(R)}{100} \right], \text{ in } \% \quad (1)$$

where:

$m_{corr}(LB)$  = corrected mass percentage of low boiling components.

$$m_{corr}(HB) = m(HB) \cdot \left[ \frac{100 - m(G) - m(DR) - m(R)}{100} \right], \text{ in } \% \quad (2)$$

where:

$m_{corr}(HB)$  = corrected mass percentage of high boiling components.

9.10 The degree to which secondary products are formed is equated with the degree of decomposition, as mass percentage

of heat transfer fluid, in accordance with **Eq 3 and 4**. Mass percentage  $m(DL)$  represents the total low boiling decomposition products. Mass percentage  $m(DH)$  represents the total high boiling decomposition products.

$$m(DL) = m(G) + m_{corr}(LB), \text{ in } \% \quad (3)$$

$$m(DH) = m_{corr}(HB) + m(R) + m(DR), \text{ in } \% \quad (4)$$

9.11 Test temperature, test temperature variation and test duration shall be recorded for each test. The smaller the degree of decomposition (at the same test temperature and test duration) of a heat transfer fluid, the higher is the product's thermal stability.

## 10. Report

10.1 The test results shall be reported as the average value of samples taken from all test cells as follows:

10.1.1 Name and chemical composition of heat transfer fluid.

10.1.2 Test duration, in hours.

10.1.3 Test temperature, in °C, and amount of variation.

10.1.4 Initial boiling point and final boiling point of thermally stressed fluid, in °C.

10.1.5 Initial boiling point and final boiling point of unstressed fluid, in °C.

10.1.6 Gaseous decomposition products, in mass percentage.

10.1.7 Low boiling components, in mass percentage, as calculated by **Eq 1**.

10.1.8 High boiling components, in mass percentage, as calculated by **Eq 2**.

10.1.9 Decomposition products that cannot be vaporized, in mass percentage.

10.1.10 Decomposition products remaining in the test cell, in mass percentage.

10.1.11 Total low boiling decomposition products, in mass percentage, as calculated by **Eq 3**.

10.1.12 Total high boiling decomposition products, in mass percentage, as calculated by **Eq 4**.

10.1.13 Visual appearance of thermally stressed fluid and test cell as compared to the unstressed fluid and clean test cell, particularly noting the presence of solid deposits.

10.1.14 Conditions not in accordance with those specified in this test method.

10.1.15 Date and time at beginning of test and end of test.

10.1.16 Number of test cells heated.

## 11. Precision and Bias<sup>4</sup>

11.1 *Precision*—The precision of this test method is based on a single laboratory study conducted in 2010. The precision

<sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1733.

**TABLE 1 Material A (Mass %)**

	Average, $\bar{x}$	Repeatability Standard Deviation, $s_r$	Repeat- ability Limit, $r$
Low boiling decomposition	0.6890	0.1065	0.2981
High boiling decomposition	3.9094	0.2804	0.7850

statement was determined through statistical examination of 12 results, from a single laboratory, on these two materials:

Material A: Synthetic organic heat transfer fluid

Material B: Mineral oil heat transfer fluid

Every “test result” represents an individual determination. The laboratory reported three replicate test results for each material/analysis combination. Except for the use of only one laboratory, Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report No. RR:D02-1733.

11.1.1 The repeatability standard deviation and repeatability limit values have been determined to be the values shown in Tables 1 and 2.

11.1.2 Any judgment in accordance with the values in Tables 1 and 2 would normally have an approximate 95 % probability of being correct, however the precision statistics obtained in this ILS must not be treated as exact mathematical quantities which are applicable to all circumstances and uses. The limited number of laboratories reporting replicate results guarantees that there will be times when differences greater

**TABLE 2 Material B (Mass %)**

	Average, $\bar{x}$	Repeatability Standard Deviation, $s_r$	Repeat- ability Limit, $r$
Low boiling decomposition	7.6233	0.2040	0.5712
High boiling decomposition	4.2952	0.0419	0.1173

than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95 % probability limit would imply. Consider the repeatability limit as a general guide, and the associated probability of 95 % as only a rough indicator of what can be expected.

11.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

## 12. Keywords

12.1 heat transfer fluids; thermal degradation; thermal fluids; thermal stability

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