Designation: ~~D7689 – 20~~ D7689 – 21

Standard Test Method for Cloud Point of Petroleum Products and Liquid Fuels (Mini Method)[1]

This standard is issued under the fixed designation D7689; 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 the cloud point of petroleum products, biodiesel, and biodiesel blends that are transparent in layers 40 mm in thickness, using an automatic instrument.

1.2 This test method covers the range of cloud point temperatures from –50 °C to +6 °C.

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

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2500 Test Method for Cloud Point of Petroleum Products and Liquid Fuels
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
D6751 Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels

2.2 *Energy Institute Standard:*[3]

IP219 Test Method for Cloud Point of Petroleum Products

3. Terminology

3.1 *Definitions:*

[1] 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 D02.07 on Flow Properties.

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[2] 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.

[3] Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., http://www.energyinst.org.

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

3.1.1 *biodiesel, n*—fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

3.1.1.1 *Discussion*—

Biodiesel is typically produced by a reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-alkyl esters and glycerin, which is removed. The finished biodiesel derives approximately 10 % of its mass from the reacted alcohol. The alcohol used in the reaction may or may not come from renewable resources.

3.1.2 *biodiesel ~~blend,~~ blend (BXX), n—~~blend of biodiesel fuel with diesel fuels and fuel oils.~~*a homogeneous mixture of hydrocarbon oils and mono-alkyl esters of long chain fatty acids.

3.1.2.1 *Discussion*—

In the abbreviation, BXX, the XX represents the volume percentage of biodiesel fuel in the blend.

3.1.2.2 *Discussion*—

The mono-alkyl esters of long chain fatty acids (that is, biodiesel) used in the mixture shall meet the requirements of Specification D6751.

3.1.2.3 *Discussion*—

Diesel fuel, fuel oil, and non-aviation gas turbine oil are examples of hydrocarbon oils.

3.1.3 *biodiesel fuel, n*—synonym for biodiesel.

3.1.4 *cloud point, n—in petroleum products and biodiesel fuels*, the temperature of a liquid specimen when the smallest observable cluster of wax crystals first occurs upon cooling under prescribed conditions.

3.1.4.1 *Discussion*—

The cloud point occurs when the temperature of the specimen is low enough to cause wax crystals to precipitate. In a homogeneous liquid, the cloud is always noted first at the location in the specimen where the specimen temperature is the lowest. The cloud point is the temperature at which the crystals first occur, regardless of their location in the specimen, and not after extensive crystallization has taken place. The wax crystals that precipitate at lower temperatures are typically, but not excluded to, straight-chain hydrocarbons and lipids.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *D2500/IP219 equivalent cloud point, n*—temperature of a specimen, in integers, calculated by applying a bias and rounding the results of this test method to the next lower integer (see 12.2).

3.2.1.1 *Discussion*—

This test method produces results with 0.1 °C resolution. Should the user wish to provide results with a similar format to Test Method D2500, then this calculation can be performed. Some apparatus can perform this calculation automatically.

3.2.2 *mini method, n—in cloud point test methods*, automatic test procedure using a small sample size, prescribed cooling rate, specimen receptacle, and optical system for detection of crystal formation.

3.2.2.1 *Discussion*—

The prescribed cooling rate is described in 4.1, the specimen receptacle is described in 7.1, and the optical system for detection of crystal formation is described in 4.1.

4. Summary of Test Method

4.1 After inserting the test specimen into the automatic apparatus, and initiation of the program, the test specimen is heated, if necessary, to a starting temperature and then cooled by prescribed rates (11.5 and 11.6). The test specimen is continuously monitored for appearance of hydrocarbon crystals with opposing light emitter and optical receiver (Annex A1). When the crystallization in the specimen is detected by the optical system, the temperature is recorded to within 0.1 °C resolution. The specimen is then heated to facilitate the start of the next test.

5. Significance and Use

5.1 The cloud point of petroleum products and biodiesel fuels is an index of the lowest temperature of their utility for certain applications. Wax crystals of sufficient quantity can plug filters used in some fuel systems.

5.2 Petroleum blending operations require precise measurement of the cloud point.

5.3 This test method can determine the temperature of the test specimen at which wax crystals have formed sufficiently to be observed as a cloud with a resolution of 0.1 °C.

5.4 This test method provides results that, when corrected for bias and rounded to the next lower integer (see 12.2), have been found equivalent to Test Method D2500.

5.5 This test method determines the cloud point in a shorter time period than required by Test Method D2500.

6. Apparatus

6.1 *Automated Apparatus*[4]—The apparatus consists of a microprocessor-controlled test specimen chamber that is capable of heating and cooling the test specimen at required rates, optically observing the first appearance of hydrocarbon wax crystals, and recording the temperature of the test specimen chamber. A detailed description of the apparatus is provided in Annex A1.

6.2 The apparatus shall be equipped with a thermostatically controlled specimen chamber, digital display, cooling and heating systems, optical detection system, and a specimen chamber temperature measuring device.

6.3 The temperature-measuring device in the specimen chamber shall be capable of measuring the temperature, at minimum, from –60 °C to 60 °C at a resolution of 0.1 °C.

7. Reagents and Materials

7.1 *Specimen Vial*—Disposable, clear glass cylinder with closed flat bottom, 1 mL capacity.

NOTE 1—Standard NWV type vial is suitable.
Dimensions:
Outer diameter: ~~8.0~~8.0 mm to 8.3 mm
Wall thickness: ~~0.75~~0.75 mm to 0.85 mm
Outer length: ~~39.25~~39.25 mm to 40.25 mm

7.2 *Specimen Vial Stopper*[4]—Disposable, proprietary designed for use in this apparatus.

7.3 *Micropipette*—Capable of delivering 0.5 mL ± 0.1 mL of sample. Positive displacement-type micropipette with capillary piston is preferred for use. Air displacement-type micropipettes are not recommended for viscous samples.

8. Sampling

8.1 Obtain a sample in accordance with Practice D4057 or D4177.

8.2 At least 1 mL of sample is required for each test.

8.3 Samples of very viscous materials may be warmed until they are reasonably fluid before they are tested. However, no sample should be heated more than is absolutely necessary.

8.4 The sample shall not be heated above 60 °C. When the sample is heated above 60 °C, allow the sample to cool below 60 °C before filtering or inserting into the apparatus.

8.5 When moisture is present, remove the moisture by a method such as filtration through dry, lint-free filter paper until the oil is perfectly clear, but make such filtration at a temperature at least 14 °C above the expected cloud point.

[4] The sole source of supply of the apparatus (ISL Model MPP 5Gs analyzer) known to the committee at this time is ISL, B.P. 70825 14653, Verson, France. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

NOTE 2—Moisture will be noticed in the sample as a separate phase or as a haze throughout the entire sample. Generally, a slight haze will not interfere with the detection of the wax cloud.

9. Preparation of Apparatus

9.1 Prepare the instrument for operation in accordance with the manufacturer's instructions.

10. Calibration and Standardization

10.1 Ensure that all of the manufacturer's instructions for calibrating, checking, and operating the apparatus are followed.

10.2 A sample with a well-documented cloud point can be used to verify the performance of the automatic apparatus. Alternatively, a sample that has been extensively tested in a cloud point cross-check program can be used. Such verification materials can also be prepared from intracompany cross-checks.

11. Procedure

11.1 Draw 0.5 mL ± 0.1 mL of sample into a micropipette and transfer the specimen into a new clean, dry specimen vial. When necessary, heat the sample in a water bath or oven until it is just sufficiently fluid to transfer. Samples with an expected cloud point (ECP) above 25 °C or which appear solid at room temperature can be heated above 45 °C but shall not be heated above 60 °C.

11.2 Place a new clean, dry specimen vial stopper on the specimen vial and insert the assembly into the apparatus. Start the operation of the apparatus according to the manufacturer's instructions.

11.3 When the expected cloud point of the specimen is known, program it in the apparatus as ECP (expected cloud point) and start test sequence. From this point up to and including the termination of the test, recording and reporting of the result, the apparatus automatically controls the procedure.

11.4 The apparatus shall adjust the specimen chamber to a preselected starting temperature. By default, the preselected starting temperature is 25 °C. Alternatively, the operator can preprogram a defined starting temperature between 25 °C and 60 °C, if desired. When the expected cloud point is known and programmed in the apparatus, the starting temperature shall be at least 10 °C warmer than the expected cloud point. In the event that the preselected starting temperature is programmed lower than 10 °C above the programmed expected cloud point, the apparatus shall heat the specimen chamber to a starting temperature at least 10 °C above the expected cloud point, but not more than 60 °C. (**Warning—**Exercise care when selecting starting temperatures above 40 °C. Samples which are fluid at ambient room temperature can also have a low temperature flash point. Use higher start temperatures only on samples known to be solid near ambient room temperature.)

11.5 When the expected cloud point of the specimen is not known, once the starting temperature is reached (see 11.4) cool the specimen chamber at a rate of 1.5 °C ± 0.15 °C/min, while the optical system monitors for the appearance of the crystals.

11.6 When the expected cloud point of the specimen is known and programmed into the apparatus, once the starting temperature (see 11.4) is reached, cool the specimen chamber at a rate of 10 °C ± 1 °C/min until 10 °C warmer than the programmed expected cloud point, then adjust the cooling rate to 1.5 °C ± 0.15 °C/min, while the optical system monitors for appearance of the crystals.

11.7 When a cloud point is detected prematurely, during the fast cooling rate, as determined by the apparatus, reheat the specimen to a higher starting temperature, at least 30 °C warmer than the temperature of premature detection, and then cool as described in 11.5, while the optical system monitors for appearance of the crystals.

11.8 At the detection of the cloud point, record the temperature the specimen attained, to within 0.1 °C, which is held on the digital display. Reheat the specimen to the preselected starting temperature.

12. Report

12.1 Report the temperature recorded in 11.8 to 0.1 °C as the cloud point D7689 (Mini Method).

TABLE 1 Typical Repeatability and Reproducibility at Various Cloud Point (valid range –50 °C to +6 °C)

Cloud Point, °C	Repeatability, °C	Reproducibility, °C
5	0.5	1.4
0	0.6	1.7
-5	0.7	2.0
-10	0.8	2.2
-15	0.9	2.5
-20	1.0	2.8
-25	1.1	3.1
-30	1.2	3.4
-35	1.3	3.6
-40	1.4	3.9

12.2 When specified, correct the temperature recorded in 11.8 with the relative bias in accordance with 13.3, round the result to the next lower integer (a colder temperature), and report as the Test Method D2500 equivalent cloud point per Test Method D7689.

13. Precision and Bias[5]

13.1 *Precision*—The precision of this test method as determined by the statistical examination of the interlaboratory test results is as follows:

13.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator using the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method, exceed Eq 1 only in one case in twenty (see Table 1).

~~0.0206(30 °C − X) valid range − 50 to +6 °C (1)~~

$$0.0206(30\ °C - X) \quad \text{valid range} - 50\ °C \text{ to } +6\ °C \tag{1}$$

where:

X = cloud point (mini method).

13.1.2 *Reproducibility*—The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in normal and correct operation of this test method, exceed Eq 2 only in one case in twenty (see Table 1).

~~0.0561(30 °C − X) valid range − 50 to +6 °C (2)~~

$$0.0561(30\ °C - X) \quad \text{valid range} - 50\ °C \text{ to } +6\ °C \tag{2}$$

where:

X = cloud point (mini method).

13.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, bias has not been determined.

13.3 *Relative Bias (the Degree of Agreement Between Results by Test Method D7689 and Test Method D2500/IP219)*—Results on the same materials produced by Test Method D7689 and Test Method D2500 have been assessed in accordance with procedures outlined in Practice D6708. The findings are:

13.3.1 The degree of agreement between results from Test Method D7689 and Test Method D2500/IP219 can be further improved by applying the bias correction outlined in Eq 3. Sample-specific bias, as defined in Practice D6708, was observed for some samples after applying the bias correction.

$$\text{Bias} - \text{corrected X} = \text{predicted Y} = \text{X} + 1.27\ °C \tag{3}$$

[5] Supporting data (the results of the 2009 Interlaboratory Cooperative Test Program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1726. Contact ASTM Customer Service at service@astm.org.