Designation: D 5773 – 03

An American National Standard

Designation: 446/99

Standard Test Method for Cloud Point of Petroleum Products (Constant Cooling Rate Method)[1]

This standard is issued under the fixed designation D 5773; 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.

INTRODUCTION

This test method describes an alternative procedure for the determination of cloud point of petroleum products Test Method D 2500/IP219 using an automatic apparatus. The temperature results from this test method have been found to be equivalent to Test Method D 2500/IP219. When specification requires Test Method D 2500/IP219, do not substitute this test method or any other method without obtaining comparative data and agreement from the specifier.

1. Scope*

1.1 This test method describes the determination of the cloud point of petroleum products and biodiesel fuels that are transparent in layers 40 mm in thickness by an automatic instrument using a constant cooling rate.

1.2 This test method covers the range of temperatures from −60 to +49°C with temperature resolution of 0.1°C, however, the range of temperatures included in the 1997 interlaboratory cooperative test program only covered the temperature range of –56 to +34°C.

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

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

2. Referenced Documents

2.1 *ASTM Standards:*

D 2500 Test Method for Cloud Point of Petroleum Products[2]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[3]

2.2 *IP Standard:*

IP219 Test Method for Cloud Point of Petroleum Products[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *biodiesel*, *n*—a 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 vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-esters and glycerin. The fuel typically may contain up to 14 different types of fatty acids that are chemically transformed into fatty acid methyl esters (FAME).

3.1.2 *biodiesel blend*, *n*—a blend of biodiesel fuel with petroleum-based diesel fuel designated BXX, where XX is the volume percentage of biodiesel.

3.1.3 *cloud point*, *n—in petroleum products and biodiesel fuels*, the temperature of a liquid specimen when a wax crystal structure that is similar in appearance to a cloud is formed upon cooling under prescribed conditions.

3.1.3.1 *Discussion*—The cloud point appears 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. This is typically at the lower portion of the test jar when using the apparatus described in Test Method D 2500.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

Current edition approved July 10, 2003. Published August 2003. Originally approved in 1995. Last previous edition approved in 2002 as D 5773–02.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

[4] Available from the Institute of Petroleum, 61 New Cavendish Street, London, England WIM 8AR.

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *automatic cloud point, n*—the temperature of a specimen, when the appearance of the cloud is determined under the conditions of this test method.

3.2.1.1 *Discussion*—The cloud point in this test method is determined by an automatic instrument using an optical device for detection of the crystal formation. The apparatus and the conditions are different from those established for Test Method D 2500, although according to interlaboratory examination, the results have been determined to be equivalent to Test Method D 2500.

3.2.2 *D 2500/IP219 equivalent cloud point, n*—the temperature of a specimen, in integers, calculated by rounding the results of this test method to the next lower integer.

3.2.2.1 *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 D 2500, then this calculation can be performed. Some apparatus can perform this calculation automatically.

3.2.3 *Peltier device, n*—a solid state thermoelectric device constructed with dissimilar semiconductor materials and configured in such a way that it will transfer heat to or away from a test specimen dependent on the direction of electric current applied to the device.

4. Summary of Test Method

4.1 A specimen is cooled by a Peltier device at a constant rate of 1.5 ± 0.1°C/min while continuously being illuminated by a light source. The specimen is continuously monitored by an array of optical detectors for the first appearance of a cloud of wax crystals. The detectors are sufficient in number to ensure that any solid phase hydrocarbon crystals that may form are detected. The temperature at which the appearance of a cloud of wax crystals is first detected in the specimen is recorded to 0.1°C resolution. When the recorded temperature is rounded to the next lower integer temperature, it is designated as the D 2500/IP 219 equivalent cloud point per Test Method D 5773.

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 a 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 are equivalent to Test Method D 2500.

NOTE 1—This is based on the Test Method D 2500 equivalent cloud point in which the 0.1°C result is rounded to the next lower integer.

5.5 This test method determines the cloud point in a shorter period of time than Test Method D 2500.

NOTE 2—In cases of samples with cloud points near ambient temperatures, time savings may not be realized.

5.6 This test method eliminates most of the operator time required of Test Method D 2500.

5.7 This test method does not require the use of a mechanical refrigeration apparatus.

NOTE 3—In certain cases of high ambient temperature, a source of cooling water may be required to measure low temperature cloud points (see 7.1).

6. Apparatus

6.1 *Automatic Apparatus*[5]—The automatic cloud point apparatus described in this test method consists of a test chamber controlled by a microprocessor that is capable of controlling the heating and cooling of the test specimen, optically observing the first appearance of a cloud of wax crystals and recording the temperature of the specimen described in detail in Annex A1.

6.2 The apparatus shall be equipped with a specimen cup, optical detector array, light source, digital display, Peltier device, and a specimen temperature measuring device.

6.3 The Peltier device shall be capable of heating or cooling the test specimen at a constant rate of 1.5 ± 0.1°C/min.

6.4 The temperature measuring device in the specimen cup shall be capable of measuring the temperature of the test specimen from −40 to +70°C at a resolution of 0.1°C.

6.5 The apparatus shall be equipped with fittings to permit the circulation of a liquid cooling medium, if required, to remove heat generated by the Peltier device and other electronic components of the apparatus.

NOTE 4—Some apparatus are designed to use ambient air as a cooling medium. In such cases, a built-in fan is available to provide circulation of air and there is no need for fittings as described for a liquid cooling medium. The function of the cooling medium is to remove heat from the electronic components. The choice of the cooling medium has no impact whatsoever on the test results.

6.6 The apparatus shall be equipped with fittings to permit the circulation of purge gas to purge the test chamber containing the specimen cup of any atmospheric moisture.

7. Reagents and Materials

7.1 *Cooling Medium*—Air, tap water, or other liquid heat exchange medium sufficient to remove heat generated by the Peltier device and other electronic components from the apparatus. To achieve specimen cooling to −40°C, supply circulation of liquid cooling medium at +25°C or lower to the apparatus. For an apparatus which relies on air as cooling medium, the ambient air temperature has to be below +30°C to achieve specimen cooling to −40°C.

7.2 *Purge Gas*—A gas such as air, nitrogen, helium, or argon with a dew point below the lowest operating temperature

[5] The sole source of supply of the Phase Technology Cloud Point Analyzer model series 10, 30, and 70 known to the committee at this time is Phase Technology, #135-11960 Hammersmith Way, Richmond, B.C. Canada V7A 5C9. The various model series mentioned above are differentiated by their cooling capacities; however, all of them are capable of covering the entire temperature range specified in the scope. 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.

of the analyzer. (**Warning—**Compressed gas under high pressure.) (**Warning—**Inert gas can be an asphyxiant when inhaled.)

7.3 *Adjustable Volume Pipette*, capable of dispensing 0.15 ± 0.01 mL of sample.

7.4 *Cotton Swabs*—Plastic or paper shaft cotton swabs used to clean the sample cup. (**Warning—**The use of swabs with wooden shafts may damage the mirrored surface of the specimen cup.)

8. Sampling

8.1 Obtain a sample in accordance with Practices D 4057 or D 4177.

8.2 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 absolutely necessary.

8.3 The sample shall not be heated above 70°C. When the sample is heated above 70°C, allow the sample to cool below 70°C before filtering or inserting into the apparatus.

8.4 When moisture is present in the sample, 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.

NOTE 5—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.

9.2 Make liquid cooling medium connections if required (see Note 4) and ensure that they do not leak.

9.3 Make purge gas connections and ensure that they do not leak.

9.4 Turn on the liquid cooling medium if required (see Note 4).

9.5 Turn on the purge gas.

9.6 Turn on the main power switch of the analyzer. After the automatic self diagnostics startup sequence is completed, the instrument will display a **READY** message.

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 mutually agreed upon cloud point can be used to verify performance of the apparatus.

11. Procedure

11.1 Open the test chamber lid and clean the specimen cup inside the test chamber with a cotton swab.

11.2 Use a pipet to deliver 0.15 ± 0.01 mL of specimen into the specimen cup. Clean the specimen out of the cup by using a cotton swab. The cup must be cleaned to the point where no visible droplets of specimen remain in the cup.

11.3 Repeat step 11.2.

11.4 Carefully measure 0.15 ± 0.01 mL of specimen into the specimen cup.

11.5 Close and lock the test chamber lid.

11.6 Select the **PRE-HEAT** menu on the apparatus if the expected cloud point is less than 14°C below the specimen ambient temperature. The specimen ambient temperature is displayed on the front panel of the apparatus. With this selection, the apparatus will automatically heat the specimen to a starting temperature of 50°C prior to cooling. If the **PRE-HEAT** menu is not selected, the apparatus will cool the specimen from ambient temperature without any initial heating. When the cloud point is expected to be higher than 35°C, select a higher starting temperature according to manufacturer's instructions. The highest starting temperature that can be programmed is 70°C.

11.7 Push the **RUN** button located on the front panel of the apparatus. With the push of this button, the apparatus will allow the flow of liquid cooling medium, if required, (see Note 4) and the flow of purge gas through the apparatus. (**Warning—**The apparatus will display appropriate warning signals if any of these flows are not properly established. Refer to manufacturer's operating manual for corrective procedures.)

11.8 The specimen is heated if specified as described in 11.6. It is then cooled by the Peltier device while the optical detectors continuously monitor the specimen for the appearance of a cloud of wax crystals. The measurement is automatically terminated once the cloud point is detected.

11.9 When the measurement is complete, the automatic cloud point value per Test Method D 5773 will be displayed on the front panel of the apparatus.

11.10 Unlock and open the test chamber lid and clean the specimen out of the specimen cup with a cotton swab.

12. Report

12.1 Report the temperature recorded in 11.9 as the automatic cloud point Test Method D 5773.

12.2 When specified, round the temperature recorded in 11.9 to the next lower integer and report as the Test Method D 2500 equivalent cloud point per Test Method D 5773.

13. Precision and Bias

13.1 *Precision*—The precision of this test method as determined by the statistical examination of the interlaboratory test results[6,7] 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 1.3°C only in one case in twenty.

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,

[6] Supporting data (the results of the 1990 interlaboratory cooperative test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1373.

[7] Supporting data (the results of the 1997 interlaboratory cooperative test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02–1510.

would in the long run, in normal and correct operation of this test method, exceed 2.5°C only in one case in twenty.

13.1.3 The precision statements were derived from a 1997 interlaboratory cooperative test program.[6] Participants analyzed eleven sample sets as blind duplicates, comprised of various distillate fuels and lubricating oils, and with a cloud point range of +34 to −56°C. Ten laboratories participated with the automatic apparatus and eight laboratories participated with the manual Test Method D 2500/IP219 test method. The precision statistics were compiled and calculated based on the 0.1°C resolution offered by this automatic apparatus. Information on the type of samples and their average cloud points are in the research report.

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 results of the interlaboratory program were examined for bias relative to Test Method D 2500/IP219. A statistically insignificant bias of −0.03°C was observed.

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

13.4.1 *Repeatability for Blends of Biodiesel in Diesel*—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 0.7°C only in one case in twenty.

13.4.2 *Reproducibility for Blends of Biodiesel in Diesel*—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 the normal and correct operation of this test method, exceed 0.9°C only in one case in twenty.

NOTE 6—The precision for blends of biodiesel in diesel samples comprised cloud points from about −2 to +10°C.

13.4.3 The precision statements were derived from a 2001 interlaboratory cooperative test program.[8] Participants analyzed eleven sample sets comprised of two petroleum distillate fuels, diesel and kerosene, with various biodiesel fuels with a temperature range from +10 to −45°C. Fourteen laboratories participated with the automatic machines and ten laboratories participated with the manual Test Method D 2500/IP219. Information on the type of samples and their average cloud points are in the research report.[8]

NOTE 7—One of the outcomes of the interlaboratory study was the selection of the sample types used in the study contributed to a difficulty in determining the precision statement. Kerosene is a sufficiently different fuel type from biodiesel to cause some slight separation of phases upon cooling when in B20 blends. Also, the particular kerosene sample used was atypical, which complicated the study further. Therefore data from the blends of kerosene in biodiesel were not used in the precision statement. In addition, the diesel fuel used in the round-robin was high cloud point material. Due to the cloud point of the base diesel material, this temperature range in the precision statement was limited.

NOTE 8—A future interlaboratory cloud study will be done including a wider range of base biodiesel fuels with various distillate blend stocks.

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

13.6 *Relative Bias*—The statistical analysis for the interlaboratory test program for bias relative to Test Method D 2500/IP219 has been determined for blends of biodiesel in diesel samples.

14. Keywords

14.1 automatic cloud point; cloud point; constant cooling rate; Peltier; petroleum products; thermoelectric; wax crystals

[8] Supporting data (the results of the 2001 interlaboratory cooperative test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02–1524.

ANNEX

(Mandatory Information)

A1. DETAILED DESCRIPTION OF APPARATUS

A1.1 *Test Chamber*, comprised of optical detectors, lens, light source, specimen cup, temperature sensor, Peltier device, and heat sink arranged in a configuration as shown in Fig. A1.1. The lid of the test chamber can be opened to allow cleaning of specimen cup and introduction of new specimen. Once closed and locked, the chamber becomes airtight. An O-ring is used to seal the mating surfaces between the lid and the rest of the chamber. The air trapped in the closed chamber is purged by dry gas. The dry gas inlet and outlet are shown in Fig. A1.1. The test chamber wall is made of black colored metal and plastic components to minimize light reflection.

A1.1.1 *Specimen Cup*, comprised of black plastic wall and a highly polished metal bottom. The polished surface of the bottom serves as a reflective surface for light. The transfer of heat to and away from the specimen through the metal bottom is controlled by the Peltier device.

A1.1.2 *Temperature Sensor*, reading to 0.1°C, permanently embedded into the bottom of the specimen cup and positioned less than 0.1 mm below the top surface of the cup bottom. This temperature sensor, which is made of a single strand platinum, provides accurate measurement of the specimen temperature.

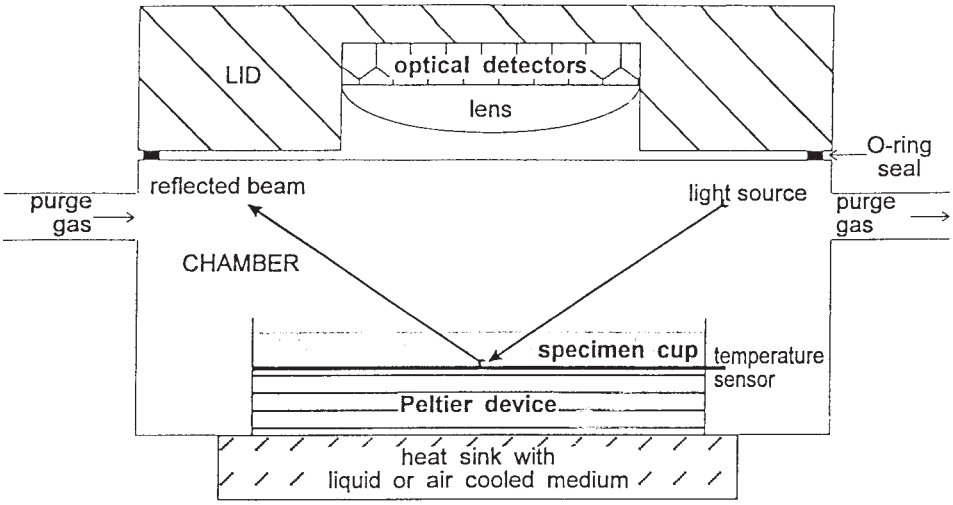

FIG. A1.1 Schematic of Test Chamber

A1.1.3 *Peltier Device*, capable of controlling the specimen temperature over a wide range. The range varies depending on the model series. During specimen cooling, heat is transferred from the top of the device to the bottom. Since the top is in thermal contact with the bottom of the specimen cup, the specimen will be chilled. The bottom of the Peltier device is in thermal contact with the heat sink where heat is dissipated to the cooling medium. During specimen warming, the reverse process will take place.

A1.1.4 *Light Source*, to provide a beam of light with a wavelength of 660 ± 10 nm. The light source is positioned such that it provides an incident beam (Fig. A1.1) impinging onto the specimen at an acute angle. The light is reflected from the polished bottom of the specimen cup. When the specimen is a homogeneous liquid, the reflected beam impinges onto the chamber lid, which is black in color. The reflected light is then absorbed by the black surface. When wax crystals appear in the specimen, the reflected beam is scattered by the solid-liquid phase boundaries. A significant amount of scattered light impinges onto the lens (Fig. A1.2).

A1.1.5 *Optical Detectors*, positioned above the lens to monitor the clarity of the specimen. The distance between the optical detectors and the lens is adjusted such that the image of the specimen is projected onto the light sensitive surface of the optical detectors. Sufficient optical detectors are used to cover the image area.

A1.2 *Apparatus Exterior Interface*, composed of several displays and buttons as shown in Fig. A1.3 (the exact layout of the displays and buttons may vary depending on the model series).

A1.2.1 *Message Display*, provides information on the status of the apparatus. It displays a **READY** message when the apparatus is idle and no fault is found. At the end of a test, the result is displayed. It displays a diagnostic message if a fault is detected in any of the major components of the apparatus. Detailed explanation of the diagnostic messages is available in the manufacturer's service manual.

A1.2.2 *Specimen Temperature Display*, gives an update of the specimen temperature, recorded to 0.1°C, every 2 s.

A1.2.3 *Light Signal Display*, gives an update of the scattered light level received by the optical detectors every 2 s. This information is used by service personnel for troubleshooting purposes.

A1.2.4 *Menu Buttons*, allow the operator to specify the pre-heat requirement for the specimen.

A1.2.5 *Run Button*, allows the operator to start the measurement sequence once the specimen is put inside the test chamber.

A1.2.6 *Reset Button*, allows the operator to stop the measurement sequence. Upon pressing this button, the apparatus will immediately stop the measurement sequence and warm the specimen to about 20°C.

NOTE A1.1—A full description, installation, setup instructions, and maintenance instructions are contained within the manufacturer's manual supplied with each instrument.

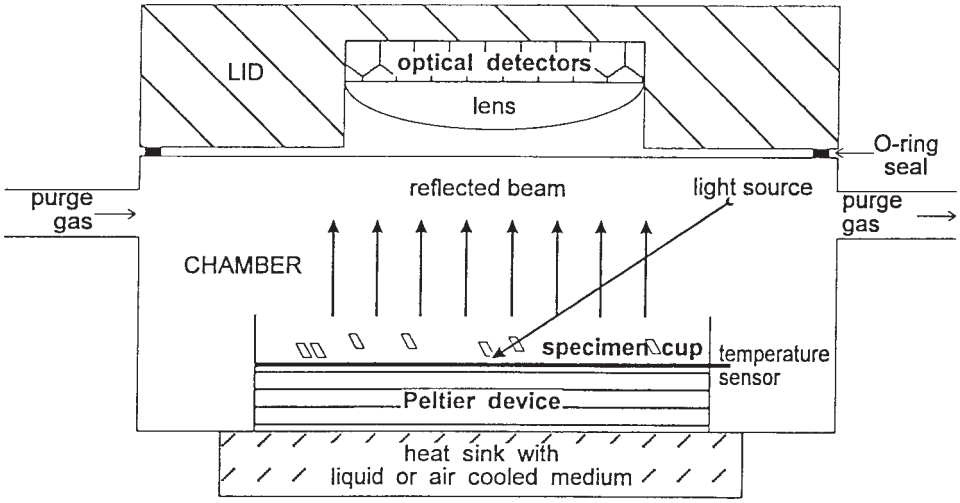

FIG. A1.2 Detection of Crystal Formation

FIG. A1.3 Apparatus Exterior

SUMMARY OF CHANGES

Subcommittee D02.07 has identified the location of selected changes to this standard since the last issue (D 5773–02) that may impact the use of this standard.

(1) Revised Scope to incorporate the 1997 round robin sample temperature range.
(2) Incorporated the 1997 round robin repeatability.
(3) Incorporated the 1997 round robin reproducibility.
(4) Revised 13.1.3 to reflect wording pertaining to the 1997 interlaboratory test program.
(5) Deleted Note 6, because it was redundant with the completion of the 1997 cloud round robin.