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An American National Standard

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Standard Test Method for Middle Distillate Fuel Storage Stability at 43°C (110°F)[1]

This standard is issued under the fixed designation D 4625; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers a method for evaluating the inherent storage stability of distillate fuels having flash points above 38°C (100°F) and 90 % distilled points below 340°C (644°F).

NOTE 1—ASTM specification fuels falling within the scope of this test method are Specification D 396, Grade Nos. 1 and 2; Specification D 975, Grades 1-D and 2-D; and Specification D 2880, Grades 1-GT and 2-GT.

1.2 This test method is not suitable for quality control testing but, rather it is intended for research use to shorten storage time relative to that required at ambient storage temperatures.

1.3 Appendix X1 presents additional information about storage stability and the correlation of Test Method D 4625 results with sediment formation in actual field storage.

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:* [2]

D 381 Test Method for Existent Gum in Fuels by Jet Evaporation

D 396 Specification for Fuel Oils

D 975 Specification for Diesel Fuel Oils

D 2880 Specification for Gas Turbine Fuel Oils

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *adherent insolubles*, *n*—gums formed during storage which remain tightly attached to the walls of the vessel.

3.1.2 *filterable insolubles*, *n*—solids formed during storage which can be removed from the fuel by filtration.

3.1.3 *inherent storage stability*, *n—of middle distillate fuel*—the resistance to change in storage in contact with air, but in the absence of other environmental factors such as water, or reactive metallic surfaces and dirt.

3.1.4 *total insolubles*, *n*—sum of the filterable insolubles plus the adherent insolubles.

4. Summary of Test Method

4.1 Four-hundred millilitre volumes of filtered fuel are aged by storage in borosilicate glass containers at 43°C (110°F) for periods of 0, 4, 8, 12, 18, and 24 weeks. After aging for a selected time period, a sample is removed from storage, cooled to room temperature, and analyzed for filterable insolubles and for adherent insolubles.

5. Significance and Use

5.1 Fuel oxidation and other degradative reactions leading to formation of sediment (and color) are mildly accelerated by the test conditions, compared to typical storage conditions. Test results have been shown to predict storage stability more reliably than other more accelerated tests. See Appendix X1 for information on the correlation of test results with actual field storage.

5.2 Because the storage periods are long (4 to 24 weeks), the test method is not suitable for quality control testing, but does provide a tool for research on storage properties of fuels.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.14 on Stability and Cleanliness of Liquid Fuels.

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This test method was adopted as a joint ASTM/IP standard in 1986.

[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.

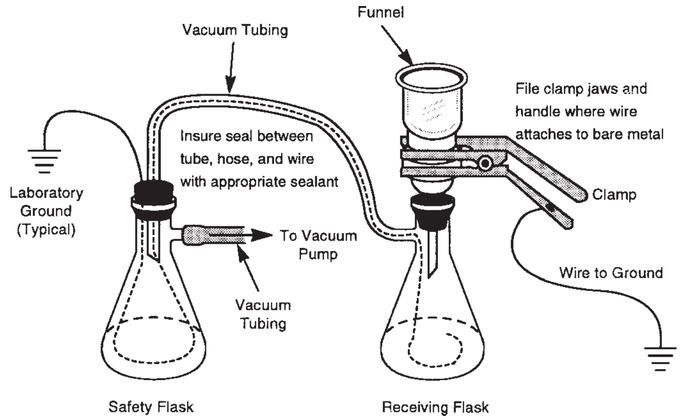

FIG. 1 Schematic of Filtration System

5.3 Because environmental effects and the materials and nature of tank construction affect storage stability, the results obtained by this test are not necessarily the same as those obtained during storage in a specific field storage situation.

6. Apparatus

6.1 *Sample Containers*, borosilicate glass bottles. The containers must have a lid or cover, preferably with a polytetrafluoroethylene (PTFE) insert and a hole for a borosilicate glass vent. The total capacity of the containers is 500 mL.

6.2 *Storage Oven*, large enough to contain all of the sample bottles. The oven shall be thermostatically controlled to maintain a temperature of 43 ± 1°C (110 ± 2°F). It shall be as dark as possible to prevent degradation due to photolytic reactions and shall also be *explosion proof*.

6.3 *Filter Drying Oven*, shall be capable of safely evaporating the solvent at 90 ± 5°C for the drying of filter materials.

6.4 *Filtration System*—Arrange the following components as shown in Fig. 1.

6.4.1 *Funnel and Funnel Base*, with filter support for a 47–mm diameter membrane and a locking ring or spring action clip.

6.4.2 *Ground/Bond Wire*, 0.912–2.59 mm (No. 10–No. 19) bare-stranded, flexible stainless steel or copper installed in the flasks and grounded as shown in Fig. 1.

6.4.3 *Receiving Flask*, 1.5 L or larger borosilicate glass vacuum filter flask, which the filtration apparatus fits into, equipped with a sidearm to connect to the safety flask.

6.4.4 *Safety Flask*, 1.5 L or larger borosilicate glass vacuum filter flask equipped with a sidearm to connect the vacuum system. A fuel and solvent resistance rubber hose, through which the grounding wire passes, shall connect the sidearm of the receiving flask to the tube passing through the rubber stopper in the top of the safety flask.

6.4.5 *Vacuum System*, either a water-aspirated or a mechanical vacuum pump may be used if capable of producing a vacuum of 1 to 100 kPa below atmospheric pressure when measured at the receiving flask.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Nylon Test and Control Membrane Filters*—plain, 47-mm diameter, nominal pore size 0.8-μm. (Membrane filters with a grid imprinted on their surface may be used as control membrane filters for identification.)

7.3 *Hydrocarbon Solvent, 2,2,4-trimethylpentane (isooctane)*—ASTM knock test reference fuel grade, prefiltered through two glass-fiber filters. (**Warning—**Extremely flammable. Harmful if inhaled. Vapors may cause flash fire.)

7.4 *Adherent Insolubles Solvent* (**Warning—**Extremely flammable. Vapors harmful. May cause flash fire)—Mix equal volumes of reagent grade acetone (**Warning—**Extremely flammable. Vapors may cause flash fire), methyl alcohol (**Warning—**Flammable. Vapor harmful. May be fatal or cause blindness if swallowed or inhaled. Cannot be made nonpoisonous), and toluene (**Warning—**Flammable. Vapor harmful.).

8. Sampling Procedure

8.1 Samples for testing shall be obtained by an appropriate method outlined in Practice D 4057. Sample containers should be 1 gal (3.78 L) or larger, epoxy-lined cans. Fill sample cans almost to the top to avoid a significant air space. Purge the void space with nitrogen. Store the samples at reduced temperature, −7 to 4°C (20 to 40°F), prior to use, where possible.

9. Preparation of Apparatus and Sample Bottles

9.1 *Sample Storage Bottles*—Scrub each bottle with a detergent solution and rinse it with water. Soak the bottle overnight in a mildly alkaline laboratory glassware cleaning solution. Rinse the bottle with tap-water, then invert it and flush it with a stream of distilled water. Allow the bottles to dry and rinse the bottles with 50 mL of the fuel sample. Vent the

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

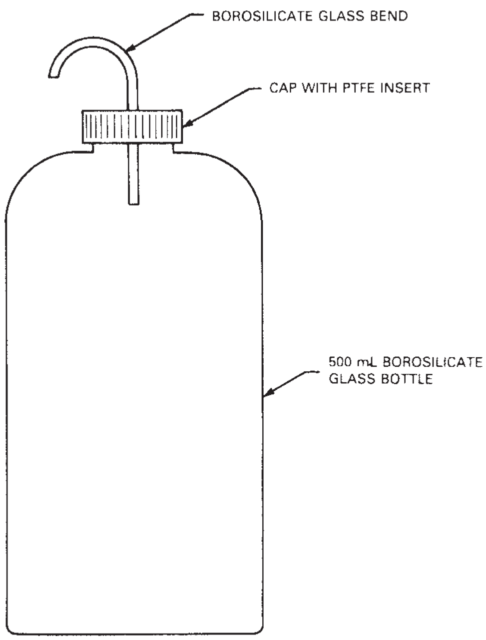

FIG. 2 Sample Storage Container

bottles during storage, using a glass tube bent in an upside down "U," (see Fig. 2), to prevent contamination of the sample from airborne particulates. Insert the glass tube through a cover, preferably equipped with a polytetrafluoroethylene (PTFE) insert (see Fig. 2).

9.2 Clean all components of the filtration apparatus as described in 9.2.1–9.2.7.

9.2.1 Remove any labels, tags, and so forth.

9.2.2 Wash with warm tap water containing detergent.

9.2.3 Rinse thoroughly with warm tap water.

9.2.4 Rinse thoroughly with deionized water. Container caps should be handled only externally with clean laboratory crucible tongs during this and subsequent washings.

9.2.5 Rinse thoroughly with propan-2-ol that has been filtered through a 0.45 µm membrane filter.

9.2.6 Rinse thoroughly with filtered flushing fluid and dry.

9.2.7 Keep a clean protective cover (the cover may be rinsed with filtered flushing fluid) over the top of the sample container until the cap is installed. Similarly, protect the funnel opening of the assembled filtration apparatus with a clean protective cover until ready for use.

9.3 *Preparation of Membrane Filters*:

9.3.1 Each set of test filters consists of one test membrane filter and one control membrane filter. For fuels containing little particulate materials, only one set of filters is required. If the fuel is highly contaminated, more than one set of filters may be required. The two membrane filters used for each individual test shall be identified by marking the petri dishes used to hold and transport the filters. Clean all glassware used in preparation of membrane filters as described in 9.2.

9.3.1.1 Using forceps, place the test and control membrane filters side by side in a clean petri dish. To facilitate handling, the membrane filters should rest on clean glass support rods, or watch glasses, in the petri dish.

9.3.1.2 Place the petri dish, with its lid slightly ajar, in a drying oven at 90 ± 5°C and leave it for 30 min.

9.3.1.3 Remove the petri dish from the drying oven, and place it near the balance. Keep the petri dish cover ajar, but keep it such that the membrane filters are still protected from contamination from the atmosphere. Allow 30 min for the membrane filters to come to equilibrium with room air temperature and humidity.

9.3.1.4 Remove the control membrane filter from the petri dish with forceps, handling by the edge only, and place it centrally on the weighing pan of the balance. Weigh it, record the initial mass to the nearest 0.0001 g, and return it to the petri dish.

9.3.1.5 Repeat 9.3.1.4 for the test membrane filter.

9.3.1.6 Using clean forceps, place the weighed control membrane filter centrally on the membrane filter support of the filtration apparatus (see Fig. 1). Place the weighed test membrane filter on top of the control membrane filter. Install the funnel and secure with locking ring or spring clip. Do not remove the plastic film from the funnel opening until ready to start filtration.

10. Preparation of Sample

10.1 If the fuel has been stored at reduced temperature, allow the sample to come to ambient temperature. To dissolve any separated wax, be certain that the entire fuel sample is at least 5°C above its cloud point before proceeding.

10.2 Assemble a filtration system, as shown in Fig. 1, to filter the fuel. Clean the receiving flask, separatory funnel, and glass funnel in the same manner as the storage bottles (9.1). Rinse these items with filtered *iso*octane and then air.

11. Procedure

11.1 *Sample Aging*:

11.1.1 Adjust the storage oven for sample storage to a temperature of 43 ± 1°C (110 ± 2°F).

11.1.2 Place 400 mL of filtered fuel into each bottle. Use two bottles for each sampling period. (Commonly used sampling periods are 0, or any of the following: 4, 8, 12, and 24 weeks). Fill three extra bottles with fuel to be used in case of accidents, for further tests at other times of storage, or to extend the overall test duration.

11.1.3 Label each storage bottle with the time and date the test is started, sample identification, and the time and date when the bottle is to be removed from storage. Place the bottles in the oven in random order.

11.1.4 Perform zero-week analyses on the same day as the other samples are placed in storage. Zero-week data are necessary to provide base data and assure satisfactory technique.

11.2 *Determination of Filterable Insolubles*:

11.2.1 At the end of each prescribed period of time, remove two bottles from the storage oven and allow them to cool to 21 to 27°C (70 to 80°F) in a dark environment. This may take from 4 to 24 h.

11.2.2 After cooling, pour fuel from the sample container to the graduated cylinder, start the vacuum, and then transfer 100 mL of fuel to the filter funnel.

11.2.2.1 Continue transferring 100 mL increments of fuel to the filter funnel. When all the fuel from the sample container has been filtered, or if filtration slows so that 100 mL of sample requires greater than 10 min for complete filtration, then remove the filter support/filter funnel from the receiving flask, pour the filtered fuel into a clean graduated cylinder, and record the volume of fuel that was filtered in millilitres. Keep the fuel sample filtrate separate from the solvent washings filtrate. This allows the fuel to be used for additional analyses. If all the fuel has been filtered, thoroughly rinse the sample container and the graduated cylinder with one or more portions of filtered flushing fluid, pour the rinses into the funnel, and proceed to 11.2.2.2. If all the fuel has not been filtered, proceed to 11.2.2.2 and 11.2.2.3, and then repeat from 11.2.2.1.

11.2.2.2 Wash down the inside of the funnel and the outside of the joint between the funnel and filter base filtered with flushing fluid. With the vacuum applied, carefully separate the funnel from the filter base. Wash the periphery of the membrane filter by directing a gentle stream of filtered flushing fluid from the edge to the center, exercising care not to wash any of the particulate from the surface of the membrane filter. Maintain vacuum after the final washing for 10 to 15 s to remove excess filtered flushing fluid from the membrane filter.

11.2.2.3 Using clean forceps, carefully remove the test and control membrane filters from the filter base and place them side by side on clean glass support rods or watch glasses in a clean, covered petri dish. Dry and reweigh the membrane filters as described in 9.3, taking care not to disturb the particulate on the surface of the test membrane filter. Record the final control membrane filter mass and the final test membrane filter mass to the nearest 0.0001 g for each filtration.

NOTE 2—Do not mix rinsings and filtrate if filtrate color changes are being measured.

NOTE 3—If severe filter plugging is encountered so that filtration is not complete in 3 h, discontinue the test with the notation that filter plugging occurred.

11.2.3 Repeat the procedure in 11.2.2 through 11.2.2.3 for the second bottle.

11.3 *Determination of Adherent Insolubles on Sample Bottle*—After the final washing with the hydrocarbon solvent, dissolve any adherent gum on the sample container walls with two washings of 30 to 35 mL of the adherent insolubles solvent. Pour each washing into previously weighed 100-mL beakers. Evaporate the solvent at 160°C (320°F) by the air jet method described in Test Method D 381. After the solvent is completely evaporated place the beakers in a desiccator without desiccant and allow to cool to room temperature. Weigh the beakers to the nearest 0.1 mg. Use a tare beaker (moisture blank) also as outlined in Test Method D 381.

12. Calculation

12.1 Calculate the total insolubles (T_i) in milligrams per 100 mL of fuel after aging, as follows:

$$T_i = (F_i + A_i)/4 \tag{1}$$

where:

T_i = total insolubles, mg/100 mL,

F_i = mass of filterable insolubles, mg, as determined in 11.2, and

A_i = moisture corrected mass of adherent insolubles, mg, as determined in 11.3.

13. Report

13.1 Report T_i, F_i, and A_i from 12.1 for both bottles to show repeatability of tests at each aging period.

14. Precision and Bias [4]

14.1 The precision of this test method as determined by the statistical examination of the interlaboratory test results is as follows.

14.2 *Repeatability*—The difference between successive 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 in one case in twenty (see Fig. 3).

$$\text{Repeatability} = 0.62\sqrt{X} \tag{2}$$

where:

X = the average of two results, mg/100 mL.

14.3 *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, exceed the following values only in one case in twenty (see Fig. 3).

$$\text{Reproducibility} = 2.20\sqrt{X} \tag{3}$$

where:

X = the average value of two results, mg/100 mL.

14.4 *Bias*—The nature of this test and the parameters being measured are such that a true bias statement cannot be written.

14.5 These precision data were obtained by statistical examination in interlaboratory tests.

15. Keywords

15.1 accelerated test; adherent insolubles; distillate fuel; filterable insolubles; prediction; storage stability

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1203.

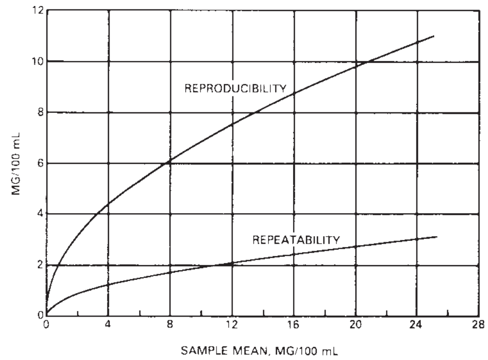

FIG. 3 Repeatability and Reproducibility for Total Insolubles Measurements

APPENDIX

(Nonmandatory Information)

X1. CORRELATION OF 43°C STABILITY TEST RESULTS WITH ACTUAL FIELD STORAGE

X1.1 *Introduction*—The storage stability properties of distillate fuels depend on complex oxidative and non-oxidative interactions of olefins, dienes, nitrogen-containing compounds, sulfur-containing compounds, and oxygen-containing compounds which are present in fuel. These reactions may be promoted by other contaminants such as dissolved metal salts. Storage stability varies enormously due to refinery feedstock source (crude oil or otherwise) and the type of processing used to produce components in the finished fuel. Because the chemical reactions leading to formation of sediment (and color) vary depending on the type and amount of unstable materials present, the effects of degradation-accelerating conditions will also vary.

X1.2 *Effect of Aging Temperature*—Fuel degradation is accelerated in the 43°C test by aging at a higher than ambient temperature. The rate of degradation for various fuel types does not change uniformly as temperature is increased. The relationship between temperature and rate depends on the activation energies of the rate-controlling steps in the chemical degradation reactions. These will vary from fuel to fuel; indeed, the chemical reactions may change under accelerated conditions to give a sediment with a different composition. This effect is minimized in the 43°C test.

X1.3 *Correlation Effects*—The consequence of variation in the chemical reactions leading to degradation during storage is that some fuels show consistent effects from temperature acceleration; others do not. The reliability of correlations of accelerated test results with actual storage stability is enhanced when fuels tested are from the same feedstock source, or are similarly processed.

X1.4 *Correlation of Ambient and 43°C Storage*—For most practical purposes, it has been shown that aging fuel at 43°C results in an approximately fourfold acceleration of the degradation for an ambient temperature of 21°C, that is, a week of 43°C storage is roughly equivalent to a month of storage at normal (environmental) ambient temperatures.[5,6] Depending on fuel composition and actual storage conditions, this correlation may vary substantially in either direction.

[5] "Navy-CRC Barge Storage Program," Report No. 341, Project CG-1-58, Coordination Research Council, Inc., September 1959.

[6] Stavinoha, L. L. and Westbrook, S. R., "Accelerated Stability Test Techniques for Middle Distillate Fuels," and Garner, M. Q. and White, E. W., "Correlation of Long-Term Storage and Accelerated Stability Tests," *Distillate Fuel Stability and Cleanliness, ASTM STP 751,* L. L. Stavinoha and C. P. Henry, Eds., American Society for Testing and Materials, Philadelphia, 1981, pp. 3 and 34 respectively.