Designation: D 1157 – 91 (Reapproved 2000)ε1

An American National Standard

Standard Test Method for Total Inhibitor Content (TBC) of Light Hydrocarbons[1]

This standard is issued under the fixed designation D 1157; 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.

ε[1] NOTE—Warning notes were placed in the text in November 2000.

1. Scope

1.1 This test method[2] covers the determination of total *p*-tertiary-butylcatechol inhibitor added to polymerization and recycle grades of butadiene or to other C_4 hydrocarbon mixtures containing no phenolic material other than catechol or no oxidized phenolic material other than that derived from oxidation of catechol. In general, all phenols and their quinone oxidation products are included in the calculated catechol content. Small amounts of polymer do not interfere. This test method is applicable over the range of TBC from 50 to 500 mg/kg.

1.2 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are 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. Referenced Documents

2.1 *ASTM Standards:*

D 1265 Practice for Sampling Liquified Petroleum (LP) Gases[3]

3. Summary of Test Method

3.1 The catechol is separated from the butadiene by evaporation. The residue is dissolved in water and an excess of ferric chloride is added. The intensity of the yellow-colored complex is compared in a photoelectric colorimeter with that produced by known concentrations of the catechol.

4. Significance and Use

4.1 *p*-tertiary-butyl catechol is commonly added to commercial butadiene in amounts of 50 to 250 mg/kg as an oxidation inhibitor. This test method is suitable for use by both producers and users of butadiene within the limitations described in the scope.

5. Apparatus

5.1 *Photometer*—A sensitive photoelectric photometer capable of producing light of narrow spectral range that is predominantly blue (425 nm).

5.2 *Graduates*, 100-mL.

5.3 *Volumetric Flasks*, 100-mL; or stoppered graduated mixing cylinder, 100-mL.

5.4 *Erlenmeyer Flasks*, 250-mL.

5.5 *Funnels*, 75-mm diameter.

5.6 *Pipet*, 5-mL.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] 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.

6.2 *Purity of Water*—References to water shall be understood to mean distilled water.

6.3 *Ferric Chloride, Standard Solution*— Dissolve 20.0 g of ferric chloride ($FeCl_3 \cdot 6H_2O$) in ethanol (95 %). Add 9.2 mL of HCl (sp gr 1.19), and then dilute with ethanol (95 %) to 1000 mL in a volumetric flask.

6.4 *p-Tertiary-Butylcatechol, Standard*— (**Warning**—Potentially hazardous. May cause skin irritation or burns; can

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricantsand is the direct responsibility of Subcommittee D02.04 on C_4 Hydrocarbons.

Current edition approved March 15, 1991. Published May 1991. Originally published as D 1157 – 51. Last previous edition D 1157 – 84.

[2] This method was derived from the method developed and cooperatively tested by the Butadiene Producers' Committee on Specifications and Methods of Analysis of the Office of Rubber Reserve, which appears in the Butadiene Laboratory Manual as Method 2.1.9.1.

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

[4] *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 *Analar 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.

be absorbed through the skin. May be harmful or fatal if swallowed. Avoid contact with eyes; may burn and impair vision. May be harmful to respiratory system. May produce quinones and flammable butylenes on decomposition. Use with adequate ventilation. Store in flammable liquids storage area.) Dissolve 0.63 g of *p*-tertiary-butylcatechol (95 % minimum purity) in 10 mL of ethanol (95 %) and dilute with water to 100 mL in a volumetric flask. When used in place of 100 mL (63 g) of sample, consider 1.00 mL of this solution to be equivalent to 100 ppm of catechol. This solution is not stable and should be prepared as needed.

7. Sampling

7.1 Supply samples to the laboratory in high-pressure sample cylinders. Use the procedures described in Practice D 1265, or similar methods.

8. Calibration and Standardization

8.1 *Preparation of Standard Solutions*— Prepare a standardization curve showing the relation between the absorbance and the catechol content as follows: Make up solutions of known catechol content by pipetting 0, 1, 2, 3, 4, and 5-mL portions of the standard catechol solution (1.00 mL = 100 mg/kg) into separate 100-mL volumetric flasks, or stoppered, graduated mixing cylinders. Then add enough water to each flask or cylinder to make a total volume of approximately 90 mL. Add 5.0 ± 0.1 mL of standard $FeCl_3$ solution, bring the total volume to 100 mL and mix well.

8.2 *Measurement of Standards*—Five to fifteen minutes after the addition of the $FeCl_3$ reagent, measure the absorbance of the solution by means of a photoelectric photometer, using water as a reference standard and using light that is predominantly blue (425 nm).

8.3 *Preparation of Calibration Curve*— Subtract the reading obtained for the zero catechol standard from each of the above readings, using the same volumes of $FeCl_3$ solution and water and observing the same time limits. Record the difference as the respective" net" absorbance. Assuming 1.0 mL of the standard catechol solution to be equal to 100 mg/kg of catechol in the butadiene, plot the net absorbance against the amount of added catechol in mg/kg.

NOTE 1—While this test method of plotting a curve is the recognized method, it has been found that the blank or zero reading using the $FeCl_3$ reagent described in 6.3 does not change, thus enabling, for control work, the plotting of a curve that can be read directly.

9. Procedure

9.1 *Preparation of Sample*—Measure 100± 1 mL of liquid sample (**Warning**—Extremely flammable gas under pressure. May form explosive peroxides upon exposure to air. Harmful if inhaled. Irritating to eyes, skin, and mucous membranes.) into a graduate that has been cooled to below − 20°C. Pour the sample into a 250-mL Erlenmeyer flask and allow the liquid to evaporate at room temperature behind a shield in a well-ventilated hood. A steam bath may be used to complete the evaporation. Add 30 mL of water to the flask, stopper, shake, and filter through a rapid, hardened, low-ash paper that has previously been moistened. Repeat with two more 30-mL portions of water. Combine all filtrates, add from a pipet 5.0 ± 0.1 mL of standard $FeCl_3$ solution, dilute to 100 mL, and mix well.

9.2 *Measurement of Sample*—After the addition of the $FeCl_3$ reagent, allow the solution to stand for from 5 to 15 min; then measure the absorbance of the solution by means of a photoelectric photometer, using water as a reference standard.

NOTE 2—Care must be taken to have the comparison tubes clean and free from fingerprints and spilled solution. From time to time, the two tubes should be checked against each other with blank solution in both.

9.3 *Measurement of Sample*—Make a "blank" determination, following the same procedure, but omitting the addition of the sample. Subtract the absorbance of the "blank" from that of the sample and record the difference as the "net" absorbance.

NOTE 3—A "blank" determination need be made only when first using a bottle of freshly prepared $FeCl_3$ solution to ascertain that the reagent was made properly.

10. Calculation

10.1 By use of the calibration curve, convert the net absorbance obtained to milligrams per kilograms of *p*-tertiary-butylcatechol.

11. Precision and Bias

11.1 *Precision*—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

11.2 *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:

p-tertiary butyl catechol range, mg/kg	Repeatability
50 to 500	10

11.3 *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, in the normal and correct operation of the test method exceed the following values only one case in twenty:

p-tertiary butyl catechol range, mg/kg	Reproducibility
50 to 500	20

11.4 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method for measuring TBC in hydrocarbons, no statement on bias is being made.

12. Keywords

12.1 light hydrocarbons; oxidation inhibitor; *p*-tertiary butylcatechol; photometer