Designation: D1157 – 23

Standard Test Method for Total Inhibitor Content (TBC) of Light Hydrocarbons[1,2]

This standard is issued under the fixed designation D1157; 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 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 mg/kg to 500 mg/kg.

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

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

1.3.1 *The user is advised to obtain LPG safety training for the safe operation of this test method procedure and related activities.*

1.4 *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:*[3]

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

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-butylcatechol is commonly added to commercial butadiene in amounts of 50 mg/kg 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 Section 1.

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

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricantsand is the direct responsibility of Subcommittee D02.D0.04 on C4 and C5 Hydrocarbons.

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[2] This test 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] 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.

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

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 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 D1265 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 mL, 1 mL, 2 mL, 3 mL, 4 mL, 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 mL ± 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 mL ± 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 mL ± 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 min to 15 min, then measure the absorbance of the solution by means of a photoelectric photometer, using water as a reference standard.

NOTE 2—Take care 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:

[4] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.