Designation: D 5799 – 95

Standard Test Method for Determination of Peroxides in Butadiene[1]

This standard is issued under the fixed designation D 5799; 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 procedure covers the determination of peroxides in butadiene.

1.2 This test method covers the concentrations range of 1 to 10 ppm by mass (ppmw) as available oxygen.

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 Liquefied Petroleum (LP) Gases–Manual Method[2]

D 3700 Practice for Containing Hydrocarbons Fluid Samples Using a Floating Piston Cylinder[3]

3. Summary of Test Method

3.1 A known mass of the butadiene sample is placed in a flask and evaporated. The residue is then refluxed with acetic acid and sodium iodide reagents. The peroxides react to liberate iodine which is titrated with standard sodium thiosulfate solution using visual end-point detection. Interfering traces of iron are complexed with sodium fluoride.

4. Significance and Use

4.1 Due to the inherent danger of peroxides in butadiene, specification limits are usually set for their presence. This test method will provide values that can be used to determine the peroxide content of a sample of commercial butadiene.

4.2 Butadiene polyperoxide is a very dangerous product of the reaction between butadiene and oxygen that can occur. The peroxide has been reported to be the cause of some violent explosions in vessels that are used to store butadiene.

5. Apparatus

5.1 *Condensers*, Liebig, with 24/40 standard-tapered ground-glass joint connections.

5.2 *Cylinders*, graduated, 100-mL capacity.

5.3 *Flask*, Erlenmeyer, 250-mL capacity, with 24/40 standard-tapered ground-glass connections with marking at 100 mL.

5.4 *Heating Mantle*, electric for 250-mL Erlenmeyer flasks.

5.5 *Microburette*, 10-mL capacity, graduated in 0.02-mL divisions.

5.6 *Water Bath*, a thermostatically controlled liquid bath capable of maintaining a water temperature of 60 ± 1°C (140 ± 2°F).

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*—Unless otherwise indicated, references to water shall be understood to mean deionized or distilled water.

6.3 *Acetic Acid*, 94 % by volume. Mix 60 mL of water with 940 mL of glacial acetic acid (CH_3COOH).

NOTE 1—**Warning:** Danger—Poisonous and corrosive. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.

6.4 *Carbon Dioxide*, solid (dry ice).

NOTE 2—**Warning:** Use gloves to avoid frostbite when handling.

6.5 *Potassium Dichromate Solution, Standard (0.1 N)*—Dissolve 2.452 g of potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 500 mL in a volumetric flask.

NOTE 3—**Warning:** Avoid contact with eyes and skin and avoid breathing of dust.

6.6 *Sodium Fluoride*.

6.7 *Sodium Iodide*.

6.8 *Sodium Thiosulfate Solution, Standard (0.1 N)*—Dissolve 12.5 g of sodium thiosulfate ($Na_2S_2O_3 \times 5H_2O$) plus

[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.D on Hydrocarbons for Chemical and Special Uses.

Current edition approved Oct. 10, 1995. Published December 1995.

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

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

[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.