Designation: D5799 – 95 (Reapproved 2014)

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

1. Scope

1.1 This test method 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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]

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

D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder

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.

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.[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.

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). (**Warning—**

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

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[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.

[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.

Poisonous and corrosive. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.)

6.4 *Carbon Dioxide,* solid (dry ice). (**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. (**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 0.1 g of sodium carbonate (Na_2CO_3) in 500 mL of water (the Na_2CO_3 is added to stabilize the $Na_2S_2O_3$ solution). Let this solution stand a week or more before using. Standardize against 0.1 N $K_2Cr_2O_7$ solution. Restandardize at frequencies to detect changes of 0.0005 in normality.

7. Sampling

7.1 Butadiene should be sampled in a metal container of a type which ensures maximum safety and which is resistant to butadiene corrosion. The size of the container is dependent upon the number of times the test is to be performed according to this test method. Refer to Practice D1265 or Practice D3700 for instructions on sampling.

8. Procedure

8.1 Remove the oxygen from a 250-mL Erlenmeyer flask by adding several pellets (approximately 1 cm in size) of dry ice and allowing the CO_2 to displace the air. This will take approximately 5 min.

8.2 Record the weight to one decimal place of the sample cylinder, and then transfer approximately 100 mLs of butadiene sample from the cylinder to the 250 mL Erlenmeyer flask containing several pellets of dry ice. Reweigh the sample cylinder and record the weight of the sample as the difference of the two weights. (**Warning—**Butadiene is a flammable gas under pressure.)

8.3 Place the flask in a water bath at 60°C in a well ventilated hood. Allow the butadiene to evaporate while keeping an inert atmosphere above the liquid butadiene by continuing to add pellets of dry ice at intervals until all the butadiene has evaporated. (**Warning—**Peroxides are unstable and react violently when taken to dryness. Peroxides at the levels experienced during the test method evaluation have not caused a problem, but caution needs to be exhibited in handling by the use of personal protective equipment.)

8.4 Remove the flask from the water bath and allow to cool to ambient temperature. Add 50 mL of 94 % acetic acid and 0.20 ± 0.02 g of sodium fluoride. Add several more pellets of dry ice to the flask and allow to stand for 5 min.

8.5 Add 6.0 ± 0.2 g of sodium iodide to the flask and immediately connect to the Liebig condenser. Turn on the heating mantle and reflux the solution for 25 ± 5 min. Keep the equipment away from strong light during refluxing.

8.6 At the end of the reaction period, turn off the heating mantle and remove the flask with condenser from the mantle. Immediately add 100 mL of water through the top of the condenser followed by several pellets of dry ice.

8.7 Maintaining an inert atmosphere with CO_2 pellets, remove the flask from the condenser and allow to cool to ambient temperature. Cold water may be used to assist in this step. Titrate the liberated iodine with 0.1 N sodium thiosulfate until a clear endpoint is reached.

8.8 Repeat 8.4 through 8.7 for the reagent blank.

9. Calculation

9.1 Calculate the peroxide content as follows:

$$\text{peroxide, as } O_2\text{, ppmw} = \frac{(A - B) \times N \times 16\,000}{W} \quad (1)$$

where:

A = $Na_2S_2O_3$ solution required for titration of the sample, mL,
B = $Na_2S_2O_3$ solution required for titration of the blank, mL,
N = normality of the $Na_2S_2O_3$ solution,
W = sample weight, g, and
16 000 = milliequivalents of oxygen.

10. Precision and Bias[4]

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

10.1.1 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case of twenty:

$$R = 1.4 \text{ ppmw}$$

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

$$R = 3.4 \text{ ppmw}$$

10.2 *Bias*—As no reliable source of butadiene polyperoxide is available, the actual bias of the test method is unknown; but published data reports that this test method determines 90 % of the polyperoxide.[5]

11. Keywords

11.1 butadiene; butadiene polyperoxide; peroxide

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1372.

[5] For a discussion of the background for this test method, see Mayo, Hendry, Jones, and Scheatzle, Industrial and Engineering Chemical , *Product Research*, Vol 7, 1968, p. 145.

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