

Designation: D3314 - 02 (Reapproved 2021)

# Standard Test Method for Rubber—Chemical Analysis for Polystyrene Blocks In SBR (Styrene-Butadiene Rubber) and Styrene-Reinforced Latices<sup>1</sup>

This standard is issued under the fixed designation D3314; 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 ( $\varepsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method covers the determination of long polystyrene blocks in SBR rubbers and styrene-reinforced latices.

1.2 Percent block styrene content may be determined in the range from 1 to 100 %.

1.3 This test method is intended for use on gel-free polymers, but it may be used on polymers containing gel, if it has been proven that gel does not interfere.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see Section 7.

1.5 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:<sup>2</sup>

- D1076 Specification for Rubber—Concentrated, Ammonia Stabilized, Creamed, and Centrifuged Natural Latex
- D1416 Test Methods for Rubber from Synthetic Sources— Chemical Analysis (Withdrawn 1996)<sup>3</sup>

- D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries
- E145 Specification for Gravity-Convection and Forced-Ventilation Ovens

### 3. Summary of Test Method

3.1 The test method is based upon oxidative cleavage of the ethylenic bonds in the block copolymer by treating a 1,2-dichlorobenzene solution of the polymer with tertiary butyl hydroperoxide (2-methyl-2-hydroperoxypropane) with osmium tetroxide catalyst. The saturated portions of the polymer, which contain no ethylenic bonds, remain unattacked. The small fragments (low molecular weight aldehydes) and the low-molecular weight polystyrene fragments from scissions within the random copolymer block are soluble in methyl alcohol, whereas the detached high-molecular weight polystyrene from the styrene homopolymer block is insoluble in alcohol. It is therefore possible to separate the high-molecular weight polystyrene, which constitutes the homopolymer block, from the polymer solution.

#### 4. Significance and Use

4.1 This test method is suitable for manufacturing control, development, and research studies.

#### 5. Apparatus

5.1 *Erlenmeyer Flask*, or round-bottom flask for use with the heating mantle, of 250-cm<sup>3</sup> capacity with ground-glass joint. An iodine flask is also satisfactory.

- 5.2 Air Condenser, for 5.1.
- 5.3 Beaker, 600-cm<sup>3</sup>.
- 5.4 Graduated Cylinder, 50-cm<sup>3</sup>.
- 5.5 *Pipet*, 1-cm<sup>3</sup>.

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5.6 *Buret*, 100-cm<sup>3</sup>, for dispensing tertiary butyl hydroperoxide.

5.7 Thermometer, to 150°C range.

5.8 *Crucible*, Gooch-type, fritted-glass, medium-porosity, 25 to  $50 \cdot \text{cm}^3$  size.

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<sup>&</sup>lt;sup>1</sup> This test method is under the jurisdiction of ASTM Committee D11 on Rubber and Rubber-like Materials and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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<sup>&</sup>lt;sup>2</sup> 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.

 $<sup>^{3}\,\</sup>text{The}$  last approved version of this historical standard is referenced on www.astm.org.

5.9 *Hot Plate*, capable of operating to provide 120 to 130°C to boiling solution, or heating mantle for round-bottom flasks operating in the same temperature range.

5.10 *Drying Oven*, capable of controlling at 100°C Type 1B oven in accordance with Specification E145.

## 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.<sup>4</sup> 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 1,2-Dichlorobenzene.

6.3 Methanol.

6.4 Osmium Tetroxide (0.004 M Solution in Toluene 1 kg/m<sup>3</sup> (0.1 g/100 cm<sup>3</sup>))—Protect the solution from light. Decomposition is indicated by formation of a black precipitate. The vapors are highly toxic. Therefore, use due precaution in reagent preparation, use, and disposal. One cubic centimetre of this stock solution is needed for each analysis. In view of the toxicity of the reagent, the amount of solution prepared should not greatly exceed the number of determinations to be made over a reasonable period of time, depending on the stability of the solution and the work load.

6.5 Sulfuric Acid (density 1.84 Mg/m<sup>3</sup>)—( $H_2SO_4$ ).

6.6 *Tertiary Butyl Hydroperoxide* (2-*Methyl-2-Hydroperoxypropane*), approximately 70 % purity assay is typical.

6.7 Toluene.

# 7. Use of Osmium Tetroxide

7.1 Precautions:

7.1.1 Store osmium tetroxide ampules (maximum total of 3 g) inside capped pipe or its equivalent.

7.1.2 Persons working with osmium tetroxide or its solutions should wear rubber gloves, a rubber apron, and a face shield or goggles.

7.1.3 Keep solutions of osmium tetroxide (maximum of 0.5 g) in unbreakable containers and store and use in the hood. The volume of air mechanically exhausted should be such that the hood-face velocities are within acceptable limits (a recommended minimum of (0.5 m/s) 100 ft/min).

7.1.4 Mark all containers of osmium tetroxide, whether concentrated or diluted with "DANGER" labels.

7.1.5 Transfer all osmium tetroxide or its solutions to be disposed of, to polyethylene bottles and incinerate. Filtrates are

collected in a dump-can set aside for chlorinated solvents, and the contents are also incinerated. Do not accumulate waste solutions.

## 7.2 Hazards:

7.2.1 Osmium tetroxide is a yellow crystalline mass at room temperature. It can be hazardous in either its crystalline or vapor form. On contact with the skin or eyes, it produces irritation and if not removed immediately, may cause dermatitis and ulceration of the skin and intense conjunctivitis and corneal ulceration to the eye. Inhalation of osmium tetroxide may cause capillary bronchitis and dermatitis. Even small amounts, if inhaled over a considerable period, cause headache, insomnia, pharyngeal and laryngeal distress, and digestive disturbance. (Warning—Analysts must thoroughly familiarize themselves with a current Material safety data Sheet (MSDS) for osmium tetroxide.)

7.2.2 The vapor has a pronounced acrid, chlorine-like odor, which should be taken as a warning of the toxic concentration in the atmosphere, and personnel should immediately remove to an area of fresh air. The minimum perceptible concentration is 0.02 g/m<sup>3</sup> of air. The threshold safety limit is 0.002 mg/m<sup>3</sup> of air. Therefore, it cannot be detected by odor at the threshold safety limit. The melting point of the crystals is 56°C and the boiling point at 100 kPa is 130°C. However, it begins to sublime and distill well below the boiling point.

# 8. Sampling

8.1 If the sample is latex, prepare a dried film in accordance with Specification D1076.

8.2 If the sample is an oil-extended rubber, conduct an ETA extraction in accordance with Test Methods D1416.

8.3 In all cases, use a random unhomogenized sample.

# 9. Procedure

9.1 For a sample containing less than 30 % block styrene, cut approximately 0.5 g of rubber weighed to the nearest 0.1 mg into small pieces. Add the pieces to a  $250 \text{-cm}^3$  Erlenmeyer flask (or round-bottom flask), to which 35 cm<sup>3</sup> of 1,2-dichlorobenzene has been previously added. For rubbers containing more than 30 % block styrene, use a 0.3-g specimen.

9.2 Fit an air condenser to the flask and heat it and its contents to 120  $\pm$  5°C, until the rubber dissolves.

9.3 Remove the flask from the hot plate or heating mantle and cool it just enough to stop refluxing. Separate the air condenser from the flask, add 10 cm<sup>3</sup> of the tertiary butyl hydroperoxide solution (see 6.6) and 1 cm<sup>3</sup> of the osmium tetroxide solution (see 6.4). Replace the air condenser and continue heating the resulting solution at 100 to 120°C for 12 to 15 min. (Polystyrene is itself slowly degraded in this process, therefore digestion time should be constant and not lengthy.)

9.4 Remove the flask from the hot plate or heating mantle. When it has cooled so that it can be held without discomfort, pour the solution slowly and with constant stirring into a 600-cm<sup>3</sup> beaker containing 350 cm<sup>3</sup> of methanol to which 5

<sup>&</sup>lt;sup>4</sup> 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.