Designation: D 5376 – 06

Standard Test Method for Rubber Compounding Materials—Determination of the Basic Nitrogen Content in Rubber Antioxidant: Polymerized TMQ[1]

This standard is issued under the fixed designation D 5376; 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 the nitrogen content of polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ). It is based on a potentiometric titration of an acetone solution of TMQ with perchloric acid in acetic acid.

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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *lot sample*—a production sample representative of a standard production unit, normally referred to as "the sample."

4. Summary of Test Method

4.1 A sample of 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) is dissolved in acetone and the nitrogen in TMQ is determined by a potentiometric titration with perchloric acid in acetic acid.

5. Significance and Use

5.1 This test method is designed to determine the nitrogen content of oligomeric 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) antioxidant. TMQ is used for heat protection of vulcanized rubber.

5.2 This test method is suitable for assessing product specifications since nitrogen content is related to product performance, that is, antioxidant efficiency and heat protection. For comparison of product quality at different production facilities sufficient interlaboratory accuracy and precision are required.

6. Interferences

6.1 Based on past experience, one significant source of error in this test method is the titration end point assessment. Problems can be avoided by closely following the procedure.

6.2 Theoretically, any material containing basic nitrogen, capable of forming HCl-salt, will be measured by this test method. Extensive high performance liquid chromatograph (HPLC) analyses of the product indicates that the most significant interfering impurities are products formed by side reactions between aniline and acetone, such as those given in Fig. 1.

6.3 Other possible interfering impurities may include the anilino end groups attached to TMQ oligomers, such as those given in Fig. 2.

7. Apparatus

7.1 *Standard Laboratory Glassware and Equipment.*

7.2 *Potentiometer.*

7.3 *Reference Electrode,* platinum electrode in an electrolytic glass cell with a frit of porosity 4, filled with a saturated solution of lithium perchlorate in acetic acid (see Fig. 3).

7.4 *Glass Electrode.*

7.5 *Weighing Pipet*, 5 cm^3.

7.6 *Buret*, 25 cm^3, Class A, graduated in 0.1 cm^3 increments.

7.7 *Buret*, 50 cm^3, Class A, graduated in 0.1 cm^3 increments.

7.8 *Magnetic Stirrer.*

7.9 *Erlenmeyer Flask*, 300 cm^3 narrow-neck.

[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

Current edition approved Oct. 1, 2006. Published November 2006. Originally approved in 1993. Last previous edition approved in 2002 as D 5376 – 93 (2002).

[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.

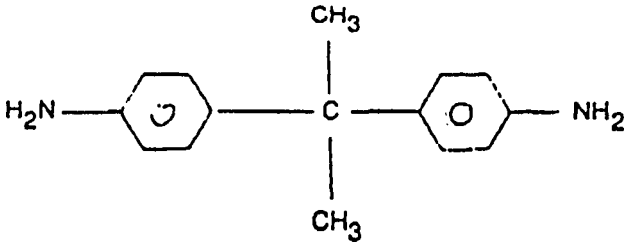
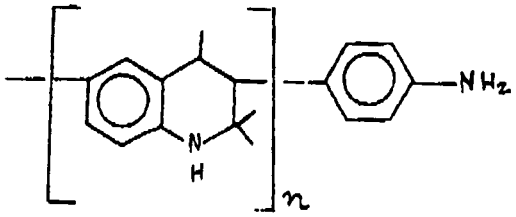


FIG. 1 1(*a*) 2,2-bis (4′-amino-phenyl)-propane



and/or

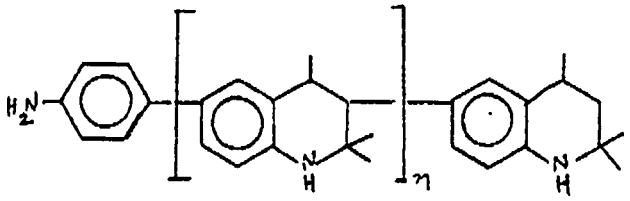


FIG. 2 1(*b*) (Top)—3–(4′-amino-phenyl)-terminated oligomeric 2,2,4-trimethyl-1,2-dihydroquinoline; (Bottom)—6-(4′-amino-phenyl)-terminated oligomeric 2,2,4-trimethyl-1,2-dihydroquinoline

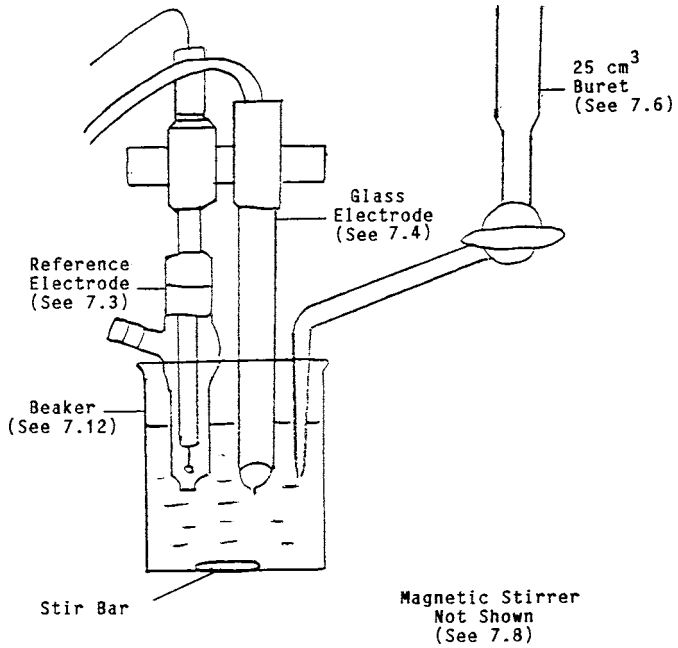


FIG. 3 Titration Vessel

7.10 *Measuring Cylinder*, 50 cm^3.
7.11 *Beaker*, 150 cm^3.
7.12 *Beaker*, 400 cm^3.
7.13 *Dropping Funnel*, 50 cm^3.
7.14 *Thermometer*, range −20 to +60°C.
7.15 *Pipet*, 5 cm^3.
7.16 *Volumetric Flask*, 2 dm^3.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents 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.

8.2 *Acetic Acid*, p.a.
8.3 *Acetic Anhydride*, p.a.
8.4 *Acetone*, p.a.
8.5 *Lithium Perchlorate*, 3 H_2O p.a.
8.6 *Perchloric acid*, p.a. approx. 70 %.
8.7 *Phenolphthalein*, 1 % dissolved in ethanol.
8.8 *Potassium Hydrogen Phthalate*, p.a.
8.9 *Sodium Hydroxide (1 N)*—Aqueous sodium hydroxide.

9. Hazards

9.1 Perchloric acid (70 to 72 %) is a strong oxidant. Care must be exercised to keep it from contacting organic matter. Seventy to 72 % perchloric acid must be kept at or below room temperature. When hot and concentrated it is known to be explosive.

9.2 Acetic anhydride is a noxious chemical and corrosive to the skin. Avoid breathing vapors and use gloves and goggles for protection. Acetone is flammable and vapors form explosive mixtures. Consult appropriate texts for further information on the use and disposal of these chemicals.

10. Sampling

10.1 To ensure sample homogeneity, grind a minimum of 10 g of a "lot" sample with a mortar and pestle. Take test unit (0.4 g) from this composite.

11. Reagent Preparation and Standardization

11.1 As is the case with any titration method, it is extremely important that the titrants are accurately standardized.

11.2 Prepare the primary titrant (0.1 *N* perchloric acid) by diluting 70 % perchloric acid with acetic acid, having first eliminated the water content by reaction with acetic anhydride.

[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 *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.