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## Standard Test Methods for Polyurethane Raw Materials: Determination of the Isocyanate Content of Aromatic Isocyanates<sup>1</sup>

This standard is issued under the fixed designation D5155; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope \*

1.1 These test methods measure the isocyanate content of aromatic isocyanates used as polyurethane raw materials.

1.1.1 *Test Method A*—Unheated toluene-dibutylamine determines the ~~amount of toluene diisocyanate content, the amine equivalent and the isocyanate content of~~ refined toluene-2,4-diisocyanate and toluene-2,6-diisocyanate, or mixtures of the two. Other isomers, if present, will be included in the determination. This test method may also be applied to other isocyanates of suitable reactivity and solubility.

1.1.2 *Test Method B*—~~Heated toluene-dibutylamine determines the amine equivalent of crude or modified isocyanates derived from toluene diisocyanate, methylenebis-(4-phenylisocyanate), and polymethylene polyphenylisocyanate. —Heated toluene-dibutylamine determines the amine equivalent and the isocyanate content of crude or modified isocyanates derived from toluene diisocyanate, methylene di-(4-phenylisocyanate) and polymeric (methylene phenylisocyanate).~~

1.1.3 *Test Method C*—~~Unheated trichlorobenzene-toluene-dibutylamine determines the isocyanate content of crude or modified isocyanates derived from toluene diisocyanate, methylene-bis-(4-phenylisocyanate), and polymethylene polyphenylisocyanate. This test method can also be used to assay isomer mixtures of toluene diisocyanate and methylene-bis-(phenylisocyanate). —Unheated trichlorobenzene-toluene-dibutylamine determines the amine equivalent and the isocyanate content of crude or modified isocyanates derived from toluene diisocyanate, methylene-di-(4-phenylisocyanate) and polymeric (methylene phenylisocyanate).~~

1.2 *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. For specific warning and precautionary statements, see Note 2.*

NOTE 1—Method C of this test method is equivalent to Method B of ISO 14896.

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

D883 [Terminology Relating to Plastics](#)

D1193 [Specification for Reagent Water](#)

E180 [Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals](#)

[Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals](#)

E691 [Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)

#### 2.2 ISO Standard:

ISO 14896 Polyurethane Raw Materials-Determination of Isocyanate Content

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *polyurethane*—a polymer prepared by the reaction of an organic diisocyanate or polyisocyanate with compounds containing hydroxyl groups:

3.1.1.1 *Discussion*—Polyurethanes or urethanes, as they are sometimes called, may be thermosetting, thermoplastic, rigid or soft and flexible, or cellular or solid (see Terminology)

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D20 on Plastics and are the direct responsibility of Subcommittee D20.22 on Cellular Materials—Plastics and Elastomers. These test methods were recommended to ASTM by the Society of the Plastics Industry Polyurethane Raw Materials Analysis Committee.

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<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.

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

3.1 *Definitions*—For definitions of terms that appear in this test method, refer to Terminology D883).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *amine equivalent*—the weight of sample that will combine with 1.0-g equivalent weight of dibutylamine.

3.2.2 *assay*—the percent by weight of toluene diisocyanate present in the sample.

3.2.3 *isocyanate (NCO) content*—the ~~weight~~ percent of the by weight of NCO groups present in the sample.

#### 4. Summary of Test Methods

4.1 All three test methods react the isocyanate sample with an excess amount of dibutylamine to form the corresponding urea. The NCO content is determined from the amount of dibutylamine consumed in the reaction. ~~Each~~The test method varies solvent or heating times to yield accurate assays of the sample in question. methods differ in the reaction conditions, or solvents used, or both.

4.1.1 *Test Method A*—The sample is added to an excess amount of dibutylamine in toluene and allowed to stand at room temperature for 15 min. The reaction mixture is diluted with isopropyl alcohol, and the excess dibutylamine is back-titrated with hydrochloric acid.

4.1.2 *Test Method B*—The sample is added to an excess amount of dibutylamine in toluene and stirred for 20 min. The resulting solution is then heated rapidly to 100°C, removed from the heat, and allowed to stand for 30 min. The reaction mixture is diluted with isopropyl alcohol, and the excess dibutylamine is back-titrated with hydrochloric acid.

4.1.3 *Test Method C*—The sample is added to ~~a solution~~an excess amount of dibutylamine in toluene and trichlorobenzene. The resulting solution is allowed to stand until it has cooled to room temperature. The reaction mixture is diluted with methanol and back-titrated with hydrochloric acid.

#### 5. Significance and Use

5.1 These test methods can be used for research or for quality control to characterize isocyanates used in polyurethane products.

#### 6. Interferences

6.1 Phosgene, the carbamyl chloride of the isocyanate, hydrogen chloride, and any other acidic or basic compounds will interfere. In refined isocyanates, these impurities are usually present in such low amounts that they do not affect the determination. While some crude or modified isocyanates contain acidities of up to approximately 0.05 %, the NCO content is not normally corrected.

#### 7. Reagents and Materials

7.1 *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>3</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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Types I through IV of Specification D1193.

#### 8. Sampling

~~8.1 Since organic isocyanates react with atmospheric moisture to form ureas, take special precautions in sampling (see Note 2). Usual sampling methods (for example, sampling an open drum with a thief), even when conducted rapidly, can cause contamination of the sample with insoluble urea. Therefore, blanket the sample with dry air or nitrogen at all times.~~

~~NOTE 2—Warning: Organic isocyanates are toxic when absorbed through the skin, or when the vapors are breathed. Precaution: Provide adequate ventilation and wear protective gloves and eyeglasses.~~

8.1 Since organic isocyanates react with atmospheric moisture, take special precautions in sampling. Usual sampling methods, even when conducted rapidly, can cause contamination of the sample with insoluble urea. Therefore, blanket the sample with dry air or nitrogen at all times. (Warning—Many diisocyanates are known or suspected sensitizers. Over-exposure to diisocyanates can lead to adverse health effects, which include the development of occupational asthma and other respiratory, skin, and eye effects. Engineering controls and/or personal protective equipment, including respiratory, skin, and eye protection, are to be used when there is a potential for over-exposure to diisocyanates. The product suppliers' Material Data Safety Sheet (MSDS) provides more detailed information about potential adverse health effects and other important safety and handling information. Always follow the specific instructions provided on the MSDS.)

#### 9. Test Conditions

9.1 Since isocyanates react with moisture, keep the laboratory humidity low, preferably below 50 % relative humidity.

<sup>3</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 *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.

**TEST METHOD A—UNHEATED TOLUENE-DIBUTYLAMINE**
**10. Apparatus**

- 10.1 Any weighing device that can weigh a liquid by difference to the nearest 0.001 g.  
 10.2 *Cooling Bath*—Any container approximately 50 mm deep filled with ice and water.  
 10.3 Pipet capable of reproducibly delivering  $50 \pm .05$  mL.  
 10.4 Buret capable of dispensing 0.05 mL at a time.

**11. Reagents**

- 11.1 *Bromcresol Green Indicator Solution*—Using 1.5 mL of 0.1 *N* sodium hydroxide, extract the bromcresol green from 0.100 g of bromcresol green indicator-grade powder, stirring vigorously until the amount of insoluble residue remains constant. Decant the aqueous portion into a 100-mL volumetric flask and dilute to the mark with water.  
 11.2 *Dibutylamine Solution (260 g/L)*—Dilute 260 g of dry dibutylamine to 1 L with dry toluene. Dry the solution with a drying agent.<sup>4</sup>  
 11.3 *Hydrochloric Acid (1 N)*—Prepare 1 *N* HCl (hydrochloric acid) and standardize frequently enough to detect changes of 0.001 *N*.  
 11.4 *Isopropyl Alcohol*.  
 11.5 *Toluene*, dry with a drying agent.<sup>4</sup>

**12. Procedure**

- 12.1 Run sample and blank determinations side by side. Run the blank determination exactly as described as follows, in 12.2-12.4, but without adding the sample.  
 12.2 Add a magnetic stirring bar and 40 mL of dry toluene to a 500-mL Erlenmeyer flask that has been rinsed successively with water, alcohol, and high-purity acetone, dried at 100°C, and allowed to cool in a desiccator. Accurately add, by pipet or buret,<sup>5</sup> 50 mL of dibutylamine solution and mix carefully.  
 12.3 While stirring the contents of the flask, slowly add 6.5 to 7.0 g of the sample weighed to the nearest 0.001 g (Note 3>Note 2). Wash down the sides of the flask with 10 mL of dry toluene, then stopper the flask loosely and allow it to stand at room temperature for 15 min.

NOTE 3—If 2—If spattering is anticipated, cool the flask and contents in the cooling bath before adding the sample and continue to cool until the heat of reaction is dissipated. Add 10 mL of dry toluene, stopper the flask loosely, and allow the contents to come to room temperature.

- 12.4 Add 225 mL of isopropyl alcohol and 0.8 mL of bromcresol green indicator solution. Titrate with 1 *N* HCl solution in a 50 or 100-mL buret<sup>6</sup> while stirring the flask contents with the magnetic stirring bar. Near the end point, slowly add the HCl dropwise. The end point is reached when the blue color disappears and a yellow color appears that persists for at least 15 s (Note 4>Note 3).

NOTE 4—Alternatively, the end point may be determined using a potentiometer and electrodes. When using this apparatus, it may be necessary to transfer the solution to a 600-mL beaker prior to titration. After transfer, rinse the Erlenmeyer flask with 25 mL of isopropyl alcohol and add the rinse to the 600-mL beaker. To titrate, immerse the calomel and glass electrodes or a combination electrode of the pH meter (standardized with pH 4.0 and pH 7.0 standard buffers) and titrate the sample to the break that occurs at approximately pH 4.2 to 4.5 with 1.0 *N* HCl while stirring the solution with a stirring bar.

**13. Calculation**

13.1 Calculate the assay, %, as follows:

13.1 Calculate the assay as follows:

$$\%TDI = \frac{(B - S)(N)(87.08)(100)1000(W)}{1000}$$

When constants are combined, this equation reduces to:

$$(2) \quad \%TDI = \frac{(B - S)(N)(87.08)(W)}{1000}$$

13.2 Calculate the amine equivalent as follows:

$$Amine\ Equivalent = \frac{1000(W)}{N(B - S)} \quad (3)$$

<sup>4</sup> The 4A Molecular Sieve, or its equivalent, has been found suitable. The 4A Molecular Sieve is available from VWR International, Inc., 1310 Goshen Parkway, West Chester, PA 19380.

<sup>5</sup> Pipets and burets shall conform to National Institute of Standards and Technology tolerances, as given in Pepper, E. L., and Mulligan, G. C., "Testing of Glass Volumetric Apparatus," *NIST Circular C434*, 1941, available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20025.

<sup>6</sup> If an isocyanate other than TDI is used, substitute the equivalent weight of the material being analyzed.

<sup>6</sup> If an isocyanate monomer other than TDI is used, substitute the equivalent weight of the material being analyzed. The calculated assay result will be percent by weight of the monomer used.