Designation: D8036 – 16

Standard Test Method for Polyurethane Raw Materials: Determination of Dimer Ratio in Pure MDI[1]

This standard is issued under the fixed designation D8036; 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 determines the ratio of the infrared absorbance of uretidinedione (dimer) in methylene-4,4'- di-(phenylisocyanate) to an infrared absorbance at a reference wavelength within the same material. It is applicable to monomeric methylene-di(phenylisocyanate), or "Pure MDI," containing 95 % or greater methylene-4,4'-di(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.*

NOTE 1—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 Terminology in this test method is in accordance with Terminology D883.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *dimer, n*—uretidinedione, with the structure in Fig. 1, is an undesirable reaction product of two or more isocyanate groups.

4. Summary of Test Method

4.1 The infrared spectrum of a dichloromethane solution of the sample is recorded in the 1600 to 2000 cm^{-1} region. The absorbance ratio of the peak maximum at approximately 1778 cm^{-1}, corresponding to the carbonyls present in uretidinedione, to the para-substituted ring combination peak maximum at approximately 1900 cm^{-1} is calculated.

5. Significance and Use

5.1 This test method can be used for research or for quality control to determine the dimer ratio of Pure MDI.

5.2 Uretidinedione begins forming in Pure MDI with the rate of formation increasing with increasing temperature. High levels can affect the appearance of Pure MDI and the quality of products made from it.

6. Apparatus

6.1 *Spectrometer*—A Fourier-Transform infrared spectrometer accurate to 0.2 % transmission and capable of resolving the dimer peak maximum at approximately 1778 cm^{-1} and reference peak maximum at approximately 1900 cm^{-1}.

6.2 *Cell,* sealed sodium chloride (NaCl) liquid absorption cell with 0.5-mm path length.

6.3 *Glassware,* 25-mL, glass-stoppered, volumetric flask and an all-glass syringe.

7. Reagents and Materials

7.1 *Purity of Reagents*—Use reagent grade chemicals in all tests. Unless otherwise noted, all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[3] It is acceptable to use other grades, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Dichloromethane,* reagent grade.

[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.22 on Cellular Materials - Plastics and Elastomers.

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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 *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.

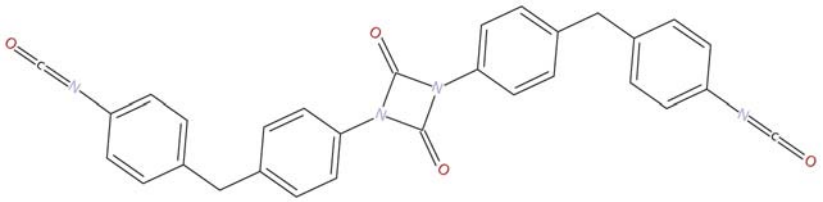

FIG. 1 Dimer Structure

8. Sampling

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—** Diisocyanates are eye, skin and respiratory irritants at concentrations above the occupational exposure limit (TLV or PEL). Diisocyanates can cause skin and respiratory sensitization (asthma) in some people. Once sensitized, it is essential to limit further exposure to diisocyanates. Use a combination of engineering controls and personal protective equipment, including respiratory, skin and eye protection, to prevent overexposure to diisocyanates. Consult the product suppliers' Safety Data Sheet (SDS) for more detailed information about potential health effects and other specific safety and handling instructions for the product.)

9. Test Conditions

9.1 Since isocyanates react with moisture, keep laboratory humidity low, preferably around 50 % relative humidity. See the Warning note in 8.1.

10. Calibration

10.1 Because the result of the analysis is a ratio of absorbances, no calibration standards are necessary. This ratio is independent of the type and brand of infrared instrument used.

11. Procedure

11.1 Scan an open-path background (the light path clear of any cell). Use a resolution of 4 cm^{-1} or better and take at least 16 scans to average. All scans shall be ratioed to this background scan.

11.2 Transfer 4.5 to 5.5 grams of sample into a dry, 25-mL, glass-stoppered, volumetric flask. Dilute to volume with dichloromethane, stopper, and mix thoroughly. Fill the cell with this solution using the glass syringe and record the absorbance spectrum from 1600 to 2000 cm^{-1} using the same resolution and number of scans as the background.

12. Calculation

12.1 Measure the height of the reference peak maximum at approximately 1900 cm^{-1} using baseline points at about 1949 and 1848 cm^{-1}. Measure the height of the dimer peak maximum at approximately 1778 cm^{-1} using baseline points at about 1812 and 1760 cm^{-1}. (see Fig. 2)

12.2 Calculate the 1778/1900-cm^{-1} absorbance height ratio, and express the result to two decimal places.

13. Precision and Bias

13.1 *Precision*—The repeatability standard deviation has been determined to be 0.0024 (see Table 1). The reproducibility of this test method is being determined and will be available on or before January 2021.

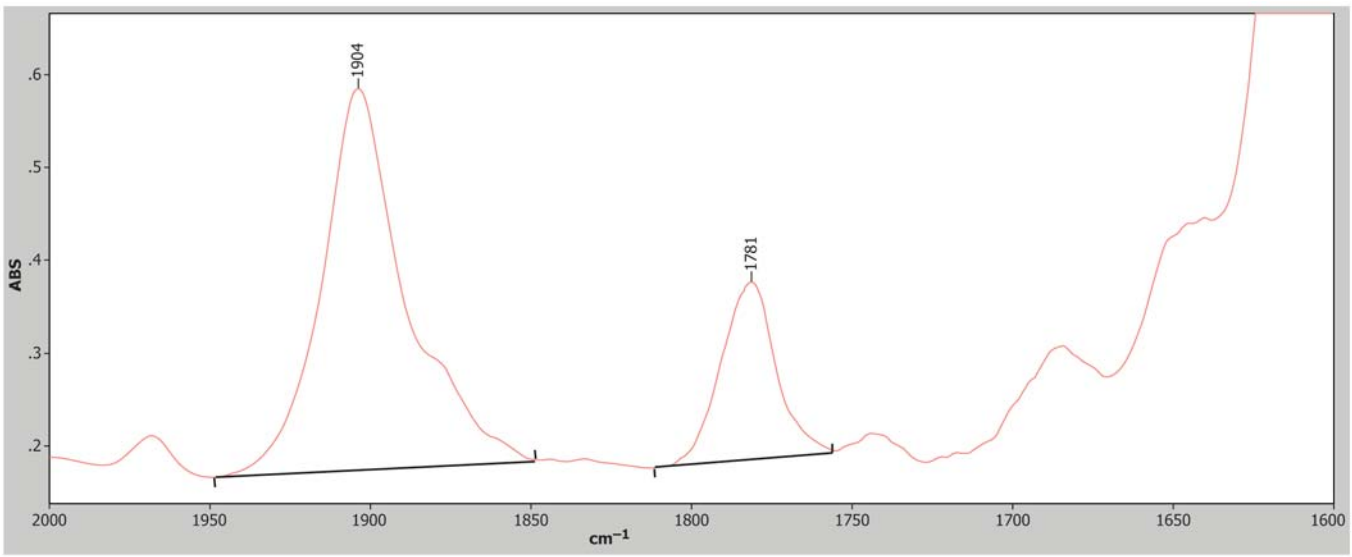

FIG. 2 IR Spectrum of Pure MDI Showing the Uretidinedione Peak at 1781 cm^{-1} and the Reference Peak at 1904 cm^{-1}

TABLE 1 Repeatability Standard Deviation

Analysis #	Dimer Ratio
1	0.4519
2	0.4518
3	0.4529
4	0.4514
5	0.4530
6	0.4477
7	0.4483
8	0.4474
9	0.4504
10	0.4544
Average	0.4509
Standard Deviation	0.0024

13.2 *Bias*—There are no recognized standards by which to estimate the bias of this test method.

14. Keywords

14.1 FTIR; infrared; IR; dimer; polyurethane raw material; Pure MDI; uretidinedione; monomer; methylene-4,4'- di(phenylisocyanate); MDI