~~Designation:D5523–04~~ Designation: D5523 – 10

Standard Test Method for Polyurethane Raw Materials: Acidity by Argentometric Determination of Hydrolyzable Chlorine in Monomeric, Aromatic Isocyanates[1]

This standard is issued under the fixed designation D5523; 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 measures the hydrolyzable chlorine content of monomeric, aromatic isocyanates used as polyurethane raw materials and expresses it as HCl acidity. The test method is applicable to toluene diisocyanate (TDI) and monomeric ~~methylene-bis-(4-phenylisocyanate),~~methylene di(phenylisocyanate), known as MDI. The main sources of hydrolyzable chlorine and, therefore, acidity in monomeric aromatic isocyanates are carbamyl chlorides, acid chlorides, and dissolved phosgene. All of these compounds react with alcohols and water to form hydrochloric acid.

1.2 This test method applies only to monomeric isocyanates in which all of the acidity is derived from species that generate HCl on solvolysis.

1.3 The values stated in SI units are to be regarded as the 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.*

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

3. Terminology

3.1 *Definitions:* ~~—For~~ For definitions of terms used in this test method, see Terminology D883.

~~3.1.1 *Discussion*—Polyurethanes or urethanes, as they are sometimes called, can be thermosetting, thermoplastic, rigid or soft and flexible, or cellular or solid (see Terminology D883).~~

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *acidity*—the acid strength of a sample expressed as parts per million hydrochloric acid (HCl) ~~present in the sample.~~ present.

3.2.2 *hydrolyzable chlorine*—the amount of chlorine released as chloride ion under the conditions of the test, expressed ~~in~~as parts per million ~~of chlorine in the sample.~~ chlorine.

4. Summary of Test Method

4.1 The sample reacts with 2-propanol to form urethanes and hydrochloric acid, which is liberated from the labile carbamyl chlorides, acid chlorides, and dissolved phosgene. The chlorides of the liberated acid are then determined potentiometrically using standard methanolic silver nitrate solution and calculated as parts per million HCl.

5. Significance and Use

5.1 This test method ~~can be used~~is suitable for research or for quality control to characterize TDI and MDI.

5.2 This test method was developed to overcome problems with low-level acidity determinations that use glass electrodes in the

[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 Plastics.~~

~~Current edition approved October 1, 2004. Published October 2004. Originally approved in 1994. Last previous edition approved in 1999 as D5523-94(1999)~~on Cellular Materials - Plastics and Elastomers.

Current edition approved Aug. 1, 2010. Published September 2010. Originally approved in 1994. Last previous edition approved in 2004 as D5523 - 04 $^{\varepsilon 1}$. ~~DOI: 10.1520/D5523-04.~~ DOI: 10.1520/D5523-10.

[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.

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

presence of reagent alcohol solvents. Reagent alcohols contain acidic and basic species, which complicate the glass electrode methods at low levels of acidity.

6. Interferences

6.1~~Any acidic~~ 6.1 Acidic species that ~~does~~do not generate chloride ions under the conditions of this test method will not be determined because acidity is determined indirectly from the chloride ion concentration.

6.2 Acidic species that do not ~~producing~~produce chloride ions are expected to be negligible at low levels of acidity and for the monomeric isocyanates in this test method.

6.3 Care must be taken to avoid chloride contamination of glassware and sample containers.

7. Apparatus

7.1 *Potentiometric Titrator*.

7.2 *Combination Silver Billet Electrode* (Note 2).

7.3 *Oven*, 70°C (Note 3).

7.4 *Magnetic Stirrer*.

NOTE 2—The combination silver billet electrode is to be stored in 0.01 *N* ~~methanolic silver nitrate solution in order to keep the electrode conditioned properly.~~ methanolic silver nitrate solution in order to keep the electrode conditioned properly. The use of chloride containing solutions must be avoided during storage and maintenance of the apparatus.

NOTE 3—Monomeric MDI samples can be solid when received in the laboratory. An oven is to be used to melt the sample prior to beginning the test procedure.

8. Reagents and Materials

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 can 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 *Methanol*.

8.3 2-*Propanol.*

8.4 *Nitric Acid*, concentrated, 70 %.

8.5 *Silver Nitrate*.

8.6 *Methanolic Silver Nitrate Solution* (0.01 *N*)—Prepare by dissolving 1.70 g $AgNO_3$/L of solution. Potentiometrically standardize with titration-grade sodium chloride frequently enough to detect changes of 0.00005 *N*.

8.7 *Methanolic Silver Nitrate Solution* (0.001 *N*)—Prepare by dissolving 0.170 g $AgNO_3$/L of solution. Potentiometrically standardize with titration-grade sodium chloride frequently enough to detect changes of 0.000005 *N*.

9. Sampling

~~9.1Take special precautions in sampling since organic isocyanates react with atmospheric moisture. Even when conducted rapidly, usual sampling methods (for example, sampling an open drum with a thief) can cause contamination of the sample with moisture that results in the formation of insoluble ureas. Therefore, blanket the sample with dry air or nitrogen at all times.~~

9.1 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—** ~~Organic isocyanates are toxic when absorbed through the skin, or when the vapors are breathed. Provide adequate ventilation and wear protective gloves and eyeglasses.~~ 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.)

10. Test Conditions

~~10.1Since isocyanates react with moisture, keep the laboratory humidity low, preferably below 50% relative humidity.~~

10.1 Samples are to remain sealed against moisture until immediately before testing.

11. Procedure

11.1 Weigh 10.0 g of the sample into a beaker and record the weight to the nearest 0.0001 g (Note 4).

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[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.