Designation: D 5523 – 94 (Reapproved 1999)ε1

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 D 5523; 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.

ε[1] NOTE—ASTM Headquarter's address in 13.1 was corrected editorially in April 2000.

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), 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.* Specific warning and precautionary statements are given in Note 4.

NOTE 1—There is no equivalent ISO standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 883 Terminology Relating to Plastics[2]

D 1193 Specification for Reagent Water[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, see Terminology D 883.

3.1.1 *Discussion*—Polyurethanes or urethanes, as they are sometimes called, may be thermosetting, thermoplastic, rigid or soft and flexible, or cellular or solid (see Terminology D 883).

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.

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

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 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 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 species that does not generate chloride ion 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 not producing chloride ion 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.

[1] This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.22 on Cellular Plastics.

Current edition approved March 15, 1994. Published May 1994.

[2] *Annual Book of ASTM Standards*, Vol 08.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

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 should be stored in 0.01 *N* methanolic silver nitrate solution in order to keep the electrode conditioned properly.

NOTE 3—Monomeric MDI samples may be solid when received in the laboratory. An oven may 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.[4] 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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D 1193.

8.3 *Methanol*.

8.4 2-*Propanol.*

8.5 *Nitric Acid*, concentrated, 70 %.

8.6 *Silver Nitrate*.

8.7 *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*.

8.8 *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

9.1 Take special precautions in sampling since organic isocyanates react with atmospheric moisture (see Note 4). 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.

NOTE 4—**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.

10. Test Conditions

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

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 5).

11.2 Add 100 mL of 2-propanol to the beaker, cover, and stir the sample for 10 min.

11.3 Add 100 mL of methanol, cover, and continue stirring the sample solution for an additional 20 min (Note 6).

11.4 Add ten drops of concentrated nitric acid solution to the sample solution.

11.5 Cool the sample solution to room temperature in an ice bath if necessary.

11.6 Titrate the sample solution potentiometrically with the appropriate methanolic silver nitrate solution (Note 7).

11.7 Record the volume of titrant used to reach the end point to at least the nearest 0.001 mL.

NOTE 5—The beaker must be of such size to accommodate approximately 300 mL of solution, and it must be of a shape to allow the proper coverage for the electrode. For monomeric MDI, the beaker may be warmed on a hot plate to melt the sample prior to the addition of 2-propanol. This will assist in dissolution of the sample in 2-propanol.

NOTE 6—The stir times were chosen to ensure an adequate reaction time for material that has been adjusted with an acid chloride. In monomeric, unadjusted material, the stirring times may be reduced to those required to obtain uniform solutions and stable electrode responses (approximately 2 min).

NOTE 7—For expected acidities or hydrolyzable chlorines below 20 ppm, use the 0.001 *N* methanolic silver nitrate solution as the titrant.

12. Calculation

12.1 Calculate the acidity, as ppm HCl, as follows:

$$\text{acidity} = \frac{S \times N \times 36.465 \times 10^6}{W \times 1000} \quad (1)$$

where:

S = $AgNO_3$ required for titration of the sample, mL,
N = normality of $AgNO_3$ solution, meq/mL,
W = sample weight, g,
36.465 = equivalent weight of HCl, mg/meq,
1000 = factor for converting milligrams to grams, and
10^6 = factor for converting to parts per million.

12.2 Because hydrolyzable chlorine is measured, the ppm hydrolyzable chlorine can be calculated as follows:

$$\text{hydrolyzable chlorine} = \frac{S \times N \times 35.465 \times 10^6}{W \times 10000} \quad (2)$$

where:

S = $AgNO_3$ required for titration of the sample, mL,
N = normality of $AgNO_3$ solution, meq/mL,
W = sample weight, g,
35.465 = equivalent weight of Cl, mg/meq,
1000 = factor for converting milligrams to grams, and
10^6 = factor for converting to parts per million.

13. Precision and Bias [5]

13.1 Attempts to develop a precision and bias statement for this test method have not been successful due to the limited

[4] *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.

[5] Supporting data are available from ASTM Headquarters. Request RR:D-20-1181.

number of laboratories participating in round-robin tests. Data on precision and bias cannot be given for this reason. Anyone wishing to participate in the development of precision and bias data should contact the Chairman, Subcommittee D20.22 (Section D20.22.01), ASTM, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428–2959.

13.2 A limited round robin was conducted with nine laboratories.

13.2.1 It has been estimated that duplicate results for either acidity or hydrolyzable chlorine by the same analyst should be considered suspect if they differ by ±3.9 ppm for results greater than 10 ppm and± 0.6 ppm for results less than 10 ppm.

13.2.2 It has been estimated that results reported by different laboratories for either acidity or hydrolyzable chlorine should be considered suspect if they differ by ±15.5 ppm for results greater than 10 ppm and ±3.5 ppm for results less than 10 ppm.

14. Keywords

14.1 acidity; HC; hydrolyzable chlorine; isocyanates; isocyanates aromatic; MDI; methylene-bis-(4-phenylisocyanate); polyurethane; raw materials; TDI; test method; titration; toluene diisocyanate