Designation: D4661 – 13

Standard Test Methods for Polyurethane Raw Materials: Determination of Total Chlorine in Isocyanates[1]

This standard is issued under the fixed designation D4661; 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 These test methods determine the total chlorine content of aromatic isocyanates used as polyurethane raw materials. The difference between the total chlorine content and the hydrolyzable chlorine content (see Test Method D4663) is a measure of the amount of *o*-dichlorobenzene and other ring-substituted chlorinated products that are present. Both procedures are applicable to a variety of organic compounds but the amount of sample used may have to be varied. (See Note 1.)

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.*

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

D1193 Specification for Reagent Water

D4663 Test Method for Polyurethane Raw Materials: Determination of Hydrolyzable Chlorine of Isocyanates

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods see Terminology D883.

4. Summary of Test Method

4.1 In each test method, the organic matter in the sample is destroyed by combustion with oxygen, the organically combined chlorine being converted to ionic chloride. The chloride is determined potentiometrically by titration with silver nitrate ($AgNO_3$) solution.

4.1.1 *Test Method A*—The sample is combusted in a pressurized oxygen bomb.

4.1.2 *Test Method B*—The sample is combusted at atmospheric pressure in a Schöniger oxygen flask.[3]

5. Significance and Use

5.1 These test methods can be used for research or for quality control to determine the total chlorine content of aromatic isocyanates. In some instances total chlorine content may correlate with performance in polyurethane systems.

6. Interferences

6.1 Bromine and iodine, if present, will react with the silver nitrate ($AgNO_3$) solution leading to an erroneously high total chlorine value.

7. Reagents and Materials

7.1 *Purity of Reagents*—Use reagent-grade chemicals 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.

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

8. Sampling

8.1 Since organic isocyanates react with atmospheric moisture, take special precautions in sampling. Usual sampling

[1] 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.

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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] For information on the Schöniger flask, refer to *Microchemie,* Springer Publishers, Vienna, Austria, Vol 42, 1955, p. 123, or Vol 43, 1956, p. 869.

[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.

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

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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' Safety Data Sheet (SDS) provides more detailed information about potential adverse health effects and other important safety and handling information. Always follow the specific instructions provided on the SDS.)

9. Test Conditions

9.1 Since isocyanates react with moisture, it is highly recommended that moisture be excluded from the sample.

TEST METHOD A—TOTAL CHLORINE BY OXYGEN BOMB

10. Apparatus

10.1 *Weighing Bottle and Balance,* suitable for weighing a liquid sample by difference to the nearest 0.5 milligram.

10.2 *Oxygen Bomb Apparatus.*[5]

10.3 *Fuse Wire,* iron-nickel-chromium, No. 34 B & S gauge.

10.4 *Potentiometric Titrator.*

10.5 *Silver-Silver Chloride Electrode.*

10.6 *Silver Electrode.*

10.7 *Bubble Counter,* a 100-mL graduate and delivery tube or a bent "L" glass tube connected to a piece of rubber tubing. The graduate is filled to the 50-mL mark with water to which 3 mL of 0.1 *N* $AgNO_3$ solution and 1 drop of concentrated nitric acid (HNO_3, sp gr 1.42) have been added. Any turbidity that develops indicates the HCl gas is being lost when venting the bomb.

10.8 *Microburet,* 10-mL capacity, 0.05-mL graduations.

11. Reagents

11.1 *Ethyl Alcohol,* conforming to Formula No. 2 B of the U.S. Treasury Department Bureau of Alcohol, Tobacco, and Firearms.

11.2 *Nitric Acid*—To 100 mL of water cooled in an ice bath, add 100 mL of nitric acid (HNO_3, sp gr 1.42) while stirring vigorously.

11.3 *Oxygen*—Free of combustible materials and halogen compounds.[6]

11.4 *Silver Nitrate, Standard Solution* (0.01 *N*)—Prepare a 0.01 *N* silver nitrate ($AgNO_3$) solution, and standardize frequently enough to detect changes of 0.0005 *N,* either gravimetrically or potentiometrically, using standard hydrochloric acid (HCl).

11.5 *Sodium Carbonate Solution* (50 g/L)—Dissolve 135 g of sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$) in water and dilute to 1 litre.

12. Procedure

12.1 Make certain that the bomb (Note 2), oxygen lines, and fittings are free of oil and grease. (**Warning—**Small quantities of either may cause a violent explosion.)

NOTE 2—When the bomb is used repeatedly, a film may form on its inner surface. Remove this film periodically by rotating the bomb on a lathe at about 300 rpm and polishing the inside surface with Grit No. 2/0 or equivalent paper coated with a light machine oil to prevent cutting and then with a paste made from grit-free chromic oxide and water. This procedure will remove all but very deep pits while polishing the surface well. Before using the bomb, wash it with soap and water to remove residual cutting oil or paste. Bombs with pitted surfaces are not to be used because they will retain chlorine from sample to sample.

12.2 Weigh a 0.9-g sample by difference to ±0.0005 g into the combustion capsule. (**Warning—**A severe safety hazard exists if more than 1 g of sample is used.)

12.3 Fit a 100-mm, iron-nickel fuse wire onto the two electrodes. Place the combustion capsule on the loop electrode and adjust the fuse wire in the capsule so that it is under the surface of the sample but does not touch the capsule. Place about 5 mL of Na_2CO_3 solution in the bomb and, with a rubber policeman, wet the interior surface of the bomb, including the head, as thoroughly as possible. Put the bomb head in the bomb cylinder and the contact ring on top of the bomb head, screwing the cap down finger-tight. Close the outlet valve securely with the special wrench provided and open the main oxygen cylinder slightly. Place the bomb in its bench-mounted holder and tighten the holder bolt with an Allen wrench. Attach the union on the oxygen-filling connection to the inlet valve of the bomb. Admit oxygen slowly (to prevent blowing the sample from the cup) to 20 to 25 atmospheres (2.03 to 2.53 MPa). Close the operating valve of the oxygen cylinder and observe the pressure on the bomb gauge. If a leak is indicated by a gradual pressure drop, check and tighten all connections. Do not continue with the test until the leak is stopped and the bomb holds pressure. Release the pressure from the oxygen tank and disconnect the bomb. Place the valve thumb nut on the oxygen inlet valve and tighten finger tight. (**Warning—**Exercise extreme caution from this point on until the bomb has been fired, cooled, and bled free of oxygen.)

12.4 Pull the plug to the bomb ignition unit. Fill the bomb ignition receptacle ¾-full with water. Submerge the bomb in the center of the ignition receptacle and visually inspect it for oxygen leaks. If the needle valve is not gas tight, tighten the packing gland slightly. Do not fire the bomb until all leaks are repaired. Allow cooling water to circulate around the bomb the entire time the bomb is in the receptacle. (**Warning—**A serious shock hazard exists around the bomb ignition receptacle should the ignition unit be shorted. Always pull the electrical plug before touching this receptacle.)

[5] These test methods as written are based on the use of Parr Bomb No. 1108 which has been found to be satisfactory for this purpose. The Parr Bomb No. 1108 is available from the Fisher Scientific Co., 585 Alpha Dr., Pittsburgh, PA. Equivalent apparatus may be substituted with appropriate changes in the procedure.

[6] Zero grade oxygen is suitable for this analysis. Any grade of oxygen that gives a suitable blank is to be used.

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