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Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols[1]

This standard is issued under the fixed designation D4274; 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 measure the hydroxyl groups in polyester and polyether polyols containing primary and secondary hydroxyl groups. They also apply to many other hydroxyl-containing substances.

1.1.1 *Test Method A—Acetic Anhydride Pressure Bottle,* recommended for polyesters.

1.1.2 *Test Method B—Phthalic Anhydride Pressure Bottle,* recommended for polyethers and polyesters.

1.1.3 *Test Method C—Phthalic Anhydride Reflux,* recommended for polyethers and polyesters.

1.1.4 *Test Method D—Imidazole–Catalyzed Phthalic Anhydride Pressure Bottle,* recommended for polyethers, polyesters, polymer polyols, and amine-initiated polyols.

1.1.5 *Test Method E—Imidazole-Catalyzed Pyromellitic Dianhydride Esterification*, recommended for polyols used for flexible and rigid polyurethane foams and urethane elastomers. It is recommended for polyester polyols, polyether polyols, amine-started polyols, and polymer polyols (polyacrylonitrile/copolystyrene-based).

1.2 Another ASTM test method for measuring hydroxyl groups is Test Method E222.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—This standard, ISO 14900 and ISO 6796 address the same subject matter, but differ in technical content.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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 (Withdrawn 2009)[3]

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E203 Test Method for Water Using Volumetric Karl Fischer Titration

E222 Test Methods for Hydroxyl Groups Using Acetic Anhydride Acetylation

E456 Terminology Relating to Quality and Statistics

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

E2935 Practice for Evaluating Equivalence of Two Testing Processes

2.2 *ISO Standard:*[4]

ISO 6796 Polyglycols for Industrial Use—Determination of Hydroxyl Number—Phthalic Anhydride Esterification Method

ISO 14900 Plastics—Polyols for Use in the Production of Polyurethane—Determination of Hydroxyl Number

3. Terminology

3.1 *Definitions*—Terms used in this standard are defined in accordance with Terminology D883, unless otherwise specified. For terms relating to precision and bias and associated issues, the terms used in this standard are defined in accordance with Terminology E456.

[1] These test methods are 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] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

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

3.2 *Definitions of Terms Specific to This Standard*—There are no terms in these test methods that require new or other than dictionary definitions.

4. Summary of Test Methods

4.1 *Test Method A*—The sample is acetylated with a solution of acetic anhydride in pyridine in a pressure bottle at 98°C. The excess reagent is hydrolyzed with water and the acetic acid is titrated with standard sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the blank and sample solutions. (**Warning—**Acetic anhydride and pyridine are toxic and flammable. In addition, acetic anhydride is corrosive. Proper precautions must be taken in handling these reagents.).

4.2 *Test Method B*—The hydroxyl group is esterified with a solution of phthalic anhydride in pyridine in a pressure bottle at 98°C. The excess reagent is hydrolyzed with water and the acidic species are titrated with standard sodium hydroxide solution.

4.3 *Test Method C*—The hydroxyl group is esterified with a solution of phthalic anhydride in pyridine under reflux conditions at 115°C. The excess reagent is hydrolyzed with water and the acidic species are titrated with standard sodium hydroxide solution.

4.4 *Test Method D*—The hydroxyl group is esterified by reaction with phthalic anhydride in a pyridine medium at approximately 100°C. The esterification reaction is catalyzed by imidazole. The excess anhydride is hydrolyzed with water, and the phthalic acid formed is titrated to the phenolphthalein end point with standard sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the blank and the sample solution.

4.5 *Test Method E*—The hydroxyl group is esterified with a solution of imidazole (IMDA) and pyromellitic dianhydride (PMDA) in dimethylformamide in an iodine flask at 70 to 80°C. The excess reagent is hydrolyzed with water and the acidic species are titrated with standard sodium hydroxide solution.

4.6 For the methods above, automatic titrators are acceptable to use for the titration portion of the test provided the method is tested to obtain equivalent or better results than the manual titration.

5. Significance and Use

5.1 These test methods are suitable for research and as quality control and specification tests. It is necessary to know the hydroxyl contents of polyols in order to formulate polyurethane systems.

6. Reagents

NOTE 2—Test methods A through D use pyridine as a solvent, which is a suspected teratogen. Avoid contact with skin and inhalation of vapors. Use only in a well-ventilated area, such as a fume hood. Use a combination of engineering controls and personal protective equipment, including respiratory, skin and eye protection, to prevent over-exposure to pyridine. In the event a non-pyridine method is required, use test method E.

6.1 *Purity of Reagents*—Use reagent-grade chemicals in all tests. Unless otherwise indicated, all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades are allowed, provided they are pure enough to be used without lowering accuracy.

6.2 *Purity of Water*—Unless otherwise indicated, use Type II water conforming to Specification D1193.

7. Sampling

7.1 Polyesters and polyethers usually contain molecules covering an appreciable range of molecular weights. These have a tendency to fractionate during solidification. Unless the material is a finely-ground solid it is necessary to melt (using no higher temperature than necessary) and mix the resin well before removing a sample for analysis. Many polyols are hygroscopic, and care is to be taken to provide minimum exposure to atmospheric moisture during the sampling.

TEST METHOD A—ACETYLATION

8. Interferences

8.1 Dry the sample if it contains more than 0.2 % water. More than that will interfere by destroying the esterification reagents.

8.2 Primary and secondary amines and long-chain fatty acids react with the reagent to form stable compounds that would be included in the analysis.

9. Apparatus

9.1 *Bottle,* pressure, heat-resistant, approximately 350 mL.

9.2 *Bag,* heavy fabric with draw string to hold bottle. As an alternative, a stainless steel mesh jacket fitted to cover the bottle is used.

9.3 *Buret,* 100-mL total capacity, range of graduated portion 50 mL, 0.1-mL graduations.

NOTE 3—As a substitute, if the 100-mL buret is not available, the first 50 mL of titrant is added by pipet (uniform drainage time for all aliquots) and the titration completed with a 50-mL buret.

9.4 *Water Bath,* 98 ± 2°C, containing enough water to cover the liquid in the sample bottles. The water level must be as prescribed, and the temperature must be within the prescribed range and uniform throughout the bath.

10. Reagents

10.1 *Acetic Anhydride.*

10.2 *Acetylation Reagent*—Mix 127 mL of acetic anhydride with 1000 mL of pyridine (10.5). Prepare the reagent fresh daily and keep it in a dark bottle. Do not use it if it is darker than pale yellow.

[5] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."