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Standard Test Methods for Polyurethane Raw Materials: Determination of Unsaturation of Polyols[1]

This standard is issued under the fixed designation D4671; 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—Reapproved with editorial changes in July 2010.

1. Scope

1.1 These test methods measure unsaturation in polyether polyols. (See Note 1.)

1.1.1 *Test Method A, High-Volume Reagent Method*—Uses about 50 mL of 0.1 *M* mercuric acetate reagent in methanol and 15 g or more of sample. These test methods use an indicator for colorimetric determination of an end point. It is recommended for polyols with low values (below 0.01 millequivalents per gram (meq/g)) of unsaturation where large sample sizes are required.

1.1.2 *Test Method B, Low-Volume Reagent Method*—Uses 2 mL of ca. 0.05 *M* mercuric acetate reagent in methanol and about 1 g of sample or less. These test methods use a potentiometric determination of an end point.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

3. Terminology

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

4. Summary of Test Method

4.1 Carbon-to-carbon unsaturated compounds in the sample are reacted with mercuric acetate and methanol in a methanolic solution to produce acetoxymercuricmethoxy compounds and acetic acid.[4] The amount of acetic acid released in this equimolar reaction, which is determined by titration with standard alcoholic potassium hydroxide, is a measure of the unsaturation originally present. Because the acid cannot be titrated in the presence of excess mercuric acetate, due to the formation of insoluble mercuric oxide, sodium bromide is added to convert the mercuric acetate to the bromide, which does not interfere. Inasmuch as these test methods are based on an acidimetric titration, a suitable correction must be applied if the sample is not neutral to phenolphthalein indicator. Take care to exclude carbon dioxide, which titrates as an acid and gives erroneous results.

5. Significance and Use

5.1 These test methods are suitable for quality control, as specification tests, and for research.

5.2 Side reactions that form unsaturated compounds in polypropylene oxides produce small amounts of polymers with only one hydroxyl group per chain. These unsaturated polymers lower functionality and molecular weight, while broadening the overall molecular-weight distribution.

6. Interferences

6.1 These test methods do not apply to compounds in which the unsaturation is conjugated with carbonyl, carboxyl, or

[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. Test Method A was recommended to ASTM by the Society of the Plastics Industry Polyurethane Raw Materials Analysis Committee.

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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] Sigia, S. and Hanna, J.G., "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, New York, 1979.

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

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nitrile groups. Because water presumably hydrolyzes the reaction products to form basic mercuric salts, quantitative results are obtained only when the system is essentially anhydrous. Acetone in low concentrations does not interfere significantly, although its presence can be detrimental to the end point. Inorganic salts, especially halides, must be absent from the sample because even small amounts of salts can nullify the reaction of the mercuric acetate with the unsaturated compound.

TEST METHOD A—HIGH-VOLUME REAGENT METHOD

7. Apparatus

7.1 *Pipet,* 50-mL capacity.

7.2 *Erlenmeyer Flask,* 250-mL glass-stoppered.

7.3 *Balance,* 1000-g capacity, 0.1-g sensitivity.

7.4 *Buret,* 50-mL capacity.

8. Reagents

8.1 *Purity of Reagents*—Use reagent-grade chemicals in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades are acceptable, 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 *Mercuric Acetate, Methanol Solution (40 g/L)*—Dissolve 40 g of mercuric acetate ($Hg(C_2H_3O_2)_2$ in sufficient methanol to make 1 L of solution and add sufficient glacial acetic acid to require a blank titration of 1 to 10 mL of 0.1 *N* alcoholic KOH solution/50 mL of reagent. Usually 3 or 4 drops of acid are sufficient. Prepare the reagent fresh weekly and filter before using.

8.3 *Sodium Bromide (NaBr).*

9. Procedure

9.1 Add 50 mL of methanol to a sufficient number of 250-mL Erlenmeyer flasks to determine the acidity of each sample in duplicate. Neutralize to a faint pink end point, using a few drops of phenolphthalein indicator solution and 0.1 *N* alcoholic KOH solution. Add 30 g of the sample weighed to the nearest 0.1 g to each flask and swirl to effect complete solution. Titrate with 0.1 *N* alcoholic KOH solution to a pink end point that persists for at least 15 s and record the volume of titrant as *A*.

9.2 Pipet 50 mL of the $Hg(C_2H_3O_2)_2$ solution into each of a sufficient number of 250-mL Erlenmeyer flasks to make all blank and sample determinations in duplicate. Reserve two of the flasks for the blank determination. Into each of the other flasks, introduce 30 g of the sample weighed to the nearest 0.1 g and swirl to effect complete solution. Allow the samples to stand together with the blanks at room temperature for 30 min. Swirl the flasks occasionally. Add 8 to 10 g of NaBr crystals to each flask and swirl to mix thoroughly. Add approximately 1 mL of phenolphthalein indicator solution and titrate immediately with 0.1 *N* alcoholic KOH solution to a pink end point that persists for at least 15 s. Record the volume of titrant used for the samples as *D* and that used for the blank as *E*. The sample titration must not exceed 50 mL of 0.1 *N* alcoholic KOH solution.

10. Calculation

10.1 Calculate the acidity, meq/g, of the sample as follows:

$$C = (A \times N)/W \tag{1}$$

where:

A = 0.1 N alcoholic KOH solution required to neutralize the sample, mL,
N = normality of the alcoholic KOH solution, and
W = sample used, g.

10.2 Calculate the unsaturation, meq/g, of the sample as follows:

$$\text{Total unsaturation} = [(D - E)N/W] - C \tag{2}$$

where:

D = alcoholic KOH solution required for titration of the sample, mL
E = alcoholic KOH solution required for titration of the blank, average mL, and
C = average of results from Eq 1, meq of acidity/g of sample.

11. Precision and Bias

11.1 *Precision*—Attempts to develop a precision and bias statement for this test method have not been successful. For this reason, data on precision and bias cannot be given. Because this test method does not contain a numerical precision and bias statement, it shall not be used as a referee test method in case of dispute. Anyone wishing to participate in the development of precision and bias data can contact the Chairman, Subcommittee D20.22 (Section D20.22.01), ASTM, 100 Barr Harbor Dr., PO Box C700, West Conshohocken, PA 19428.

11.1.1 It is estimated that duplicate results by the same analyst can be considered suspect if they differ by more than 0.002.

11.2 *Bias*—The bias for this test method has not yet been determined.

TEST METHOD B—LOW-VOLUME REAGENT METHOD

12. Apparatus

12.1 *Pipet,* 2-mL capacity.

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[5] *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.