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

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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~~ safety, health, and ~~health~~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.*

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

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*—~~The terminology in these test methods follows the standard terminology defined in~~ 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.

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.

[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.

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.*

[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."

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.

10.3 *Hydrochloric Acid, Standard* (0.5 *N*)—Prepare and standardize in accordance with Sections 20 to 24 of Practice E200. Determine and record the temperature at which the standardization was performed. The concentration of the solution shall be corrected to the temperature at which the determination is performed as described in 10.6. The factor for the thermal expansion of this solution is 0.00014. This solution is required only if a correction is to be applied for the presence of strong base in the sample being analyzed.

10.4 *Phenolphthalein Indicator Solution*—Dissolve 1 g of phenolphthalein in 100 mL of pyridine.

10.5 *Pyridine,* containing from 0.30 to 0.45 % water. Determine the water content of the pyridine using Test Method E203. Add the required amount of water. The volume of water to add, mL per litre of pyridine is calculated as follows:

$$\text{Water to add} = 4.0 - 9A \tag{1}$$

where A = percent of water in pyridine.

10.6 *Sodium Hydroxide, Standard Solution* (0.5 *N*)—Prepare and standardize in accordance with Sections 14 to 19 of Practice E200. Determine and record the temperature at which the standardization was performed. The factor for thermal expansion of this solution is 0.00014. For calculation of the hydroxyl content, the normality of the solution shall be corrected to the temperature at which the determination is performed by the following:

$$Nt_2 = Nt_1 + (t_1 - t_2)(F) \tag{2}$$

where:

Nt_1 = normality when standardized,
Nt_2 = normality during analysis of samples,
t_1 = temperature of solution during standardization,° C,
t_2 = temperature of solution during analysis of samples, °C, and
F = factor to correct for thermal expansion of the solution (see each solution for appropriate factor).

11. Procedure

11.1 Pipet 20.0 mL of the acetylation reagent to each pressure bottle for the blank and sample determinations (in duplicate). Use the same drainage time for each aliquot.

11.2 Reserve two of the bottles for the blank determinations; weigh samples to the nearest 0.1 mg into the other bottles. Determine the sample weight, g, as follows:

$$\text{Sample weight} = (561 \times 0.98)/\text{approximate hydroxyl number} \tag{3}$$

Since the calculated weight will be near the maximum permitted by the test method, adhere closely to the indicated weight.

11.3 Stopper the bottle and swirl it until the sample is completely dissolved. Enclose each bottle in a fabric bag and place all bottles as close together as possible in the water bath at 98 ± 2°C for 2 h. Keep enough water in the bath to cover the level of liquid in the bottles.

11.4 Remove the bottles from the bath and allow them to cool to room temperature. Untie the bags, uncap the bottles to release any pressure, and then remove the bags.

11.5 Carefully rinse any liquid on the stopper into the bottle and rinse the walls of the flask with 20 to 30 mL of water. Add clean crushed ice to each of the bottles until about half full.

11.6 Add 1 mL of the phenolphthalein indicator solution and titrate immediately with the 0.5 *N* NaOH solution to the first faint pink end point that persists for 15 s. The solution is to be swirled during the titration, with vigorous swirling as the end point is reached. Record the volume of titrant to 0.02 mL (Note 4). Record the temperature of the NaOH solution.

NOTE 4—If the volume of 0.5 *N* NaOH solution required for the sample is less than 80 % of that required for the blank, the sample was too large and the analysis must be repeated with a smaller sample.

11.7 *Acidity or Alkalinity Correction*—If the sample contains significant acidity or alkalinity, correct the result as follows. Weigh into a 400-mL Erlenmeyer flask the same amount of sample used before for the hydroxyl determination. Add to the flask 75 mL of redistilled pyridine, 75 mL of distilled water, and 0.5 mL of phenolphthalein indicator solution.

11.8 *Acidity Correction*—If the solution is colorless, titrate with standard 0.1 *N* NaOH to a pink end point that persists for at least 15 s. Make a blank titration on the reagent mixture described in 11.7, omitting the sample. The acidity correction, mg KOH/g, is calculated as follows:

$$\text{Acidity correction} = [(A - B)N \times 56.1]/W \tag{4}$$

where:

A = NaOH solution required for titration of the sample, mL,
B = NaOH solution required for titration of the blank, mL,
N = normality of the NaOH solution, and
W = sample used, g.
56.1 = Eq weight of KOH, mg/meq

11.9 *Alkalinity Correction*—If the solution in 11.7 is pink, titrate to the disappearance of the pink color with 0.1 *N* HCl, and then add 1.0 mL excess. Back-titrate with standard 0.1 *N* NaOH to a pink end point that persists for at least 15 s. Titrate with standard 0.1 *N* NaOH a blank containing exactly the same amount of added 0.1 *N* HCl and the reagent mixture described in 11.7 omitting the sample. The alkalinity correction, mg KOH/g, is calculated as follows:

$$\text{Alkalinity correction} = [(B - A)N \times 56.1]/W \tag{5}$$

where the terms are as defined as in 11.8.

12. Calculation

12.1 Calculate the hydroxyl number, mg KOH/g, of sample as follows:

$$\text{Hydroxyl number} = [(B - A)N \times 56.1]/W \tag{6}$$

where:

A = NaOH required for titration of the sample, mL,
B = NaOH required for titration of the blank, mL,
N = normality of the NaOH, and
W = sample used, g.

12.2 If the sample contains free acidity or alkalinity as measured in 11.7 – 11.9, the result in 12.1 must be corrected as follows:

$$\text{Hydroxyl number (corrected)} = \text{hydroxyl number} + \text{acidity correction, or} \tag{7}$$

$$\text{Hydroxyl number (corrected)} = \text{hydroxyl number} - \text{alkalinity correction} \tag{8}$$

13. Report

13.1 Report the corrected hydroxyl number to the nearest 0.1.

14. Precision and Bias[6]

14.1 *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. Contact the Chairman, Subcommittee D20.22, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428–2959 to participate in the development of precision and bias data.

[6] Supporting data are available from ASTM Headquarters. Request RR:D20-1089.

14.2 It is estimated that duplicate results by the same analyst are to be considered suspect if they differ by more than 1 unit (where the measured hydroxyl number <120) or by more than 1 % relative (measured hydroxyl Number >120).

14.3 *Bias*—There are no recognized standards on which to base an estimate of bias for this test method.

TEST METHOD B—PRESSURE-BOTTLE PHTHALATION

15. Interferences

15.1 Excessive amounts of water in the sample will interfere by destruction of the esterification reagent. Dry the sample if it contains more than 0.2 % water.

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

16. Apparatus

16.1 *Bottles,* pressure or storage, borosilicate glass.

16.2 *Pressure Bottle Bags.*

16.3 *Buret,* Normax, bulb, 100-mL capacity.

17. Reagents

17.1 *Pyridine*—Distill from phthalic anhydride, discarding the fraction boiling below 114 to 115°C. Store in brown glass bottles.

17.2 *Phthalic Anhydride (Pyridine Reagent)*—Weigh 111 to 116 g of phthalic anhydride into a 1-qt brown bottle. Add 700 mL of pyridine, which has been distilled from phthalic anhydride (see 17.1), and shake vigorously until dissolved. The reagent must stand overnight before use. Reagent that develops a color is to be discarded. In the blank titration as described in the following procedure, exactly 25 mL of this reagent must consume between 95 and 100 mL of 0.500 *N* sodium hydroxide.

17.3 *Phenolphthalein Indicator Solution* (10 g/L)—Prepare a solution of 1 g of phenolphthalein in 100 mL of pyridine.

17.4 *Potassium Acid Phthalate*—Use material that is traceable to the National Institute of Standards and Technology.

17.5 *Sodium Hydroxide, Standard Solution* (0.5 *N*)— Prepare a 0.5 *N* solution of sodium hydroxide (NaOH) and standardize as follows:

17.5.1 Crush (do not grind) about 10 g of potassium acid phthalate ($KHC_8H_4O_4$) to approximately 100 mesh and dry it for 1 to 2 h at 100°C. Place in a glass-stoppered container and cool in a desiccator. Accurately weigh 4 to 5 g of the dried potassium acid phthalate and transfer it to a 500-mL flask that has been swept free of carbon dioxide. Add 200 mL of water that is free of carbon dioxide, stopper the flask, and swirl it gently until the sample is dissolved. Add phenolphthalein indicator and titrate to a pink end point with the 0.5 *N* NaOH solution using a 50-mL buret.

17.5.2 Calculate the normality of the NaOH as follows:

$$\text{Normality} = W/(V \times 0.2042) \quad (9)$$

where:

W = $KHC_8H_4O_4$, g, and
V = NaOH required for titration of the $KHC_8H_4O_4$, mL.
0.2042 = Eq/L potassium acid phthalate (204.2 g/eq divided by 1000 to convert mL to L).

18. Procedure

18.1 Prepare a sufficient number of clean, dry pressure bottles to make all blank and sample determinations in duplicate. Replace the rubber gaskets, if necessary, and make certain the caps can be fastened securely.

18.2 Accurately pipet 25 mL of the phthalic anhydride reagent into each of the bottles. Use the same pipet for both sample and blank determinations. Do not allow the reagent to contact the rubber gasket.

18.3 Reserve two of the bottles for the blank determination.

18.4 Introduce into each of the other bottles the amount of sample, g, calculated as follows, as weighed to the nearest 0.1 mg:

$$\text{Sample size} = 561/\text{estimated hydroxyl number} \tag{10}$$

Since the calculated weight will be near the maximum permitted by the method, adhere closely to the indicated weight. Weigh the sample from a hypodermic syringe. Swirl to dissolve completely.

18.5 Cap the bottles and enclose them in the pressure bottle bags. Keep the samples and blanks as close together as possible in a water bath, maintained at 98 ± 2°C, for 2 h. Maintain sufficient water in the bath to just cover the liquid in the bottles.

18.6 Remove the bottles from the bath and allow them to cool to room temperature.

18.7 When the bottles have cooled, open the bags, uncap them carefully to release any pressure, and then remove the bags.

18.8 To each bottle, add 50 mL of redistilled pyridine and 0.5 mL of the phenolphthalein indicator solution, and titrate with standard 0.5 *N* NaOH solution to a pink end point that persists for at least 15 s. It is essential that the net titration (blank minus sample) be between 18 and 22 mL. If it is not, repeat the determination, adjusting the sample size accordingly.

18.9 *Acidity or Alkalinity Correction*—If the sample contains significant acidity or alkalinity, the result must be corrected as follows.

18.9.1 Weigh into a 400-mL Erlenmeyer flask an amount of sample equal to that taken previously for the hydroxyl determination. Add to the flask 75 mL of redistilled pyridine, 75 mL of distilled water, and 0.5 mL of phenolphthalein indicator solution.

18.10 *Acidity Correction*—If the solution is colorless, titrate with standard 0.1 *N* NaOH solution to a pink end point that persists for at least 15 s. Make a blank titration on the reagent mixture described in 18.9.1, omitting the sample. The acidity correction, mg KOH/g, is calculated as follows:

$$\text{Acidity correction} = [(A - B)N \times 56.1]/W \tag{11}$$

where:

A = NaOH solution required for titration of the sample, mL,
B = NaOH solution required for titration of the blank, mL,
N = normality of the NaOH solution, and
W = sample used, g.
56.1 = Eq weight of KOH, mg/meq.

18.11 *Alkalinity Correction*—If the solution in 18.9.1 is pink, titrate to the disappearance of the pink color with 0.1 *N* HCl, and then add 1.0 mL in excess. Back titrate with standard 0.1 *N* NaOH solution to a pink end point that persists for at least 15 s. Titrate with 0.1-*N* NaOH solution a blank containing exactly the same amount of added 0.1 *N* HCl and the reagent mixture described in 18.9.1, omitting the sample. The alkalinity correction, mg KOH/g, is calculated as follows:

$$\text{Alkalinity correction} = [(B - A)N \times 56.1]/W \tag{12}$$

where the terms are as defined as in 18.10.