Designation: D4274 – 16

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 and health 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.

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]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

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

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 Terminology D883.

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

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[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**

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.

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.

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:

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[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."

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

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.

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 ($KHC_8 H_4 O_4$) 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:

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

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.

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

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:

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

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:

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

where the terms are as defined as in 18.10.

19. Calculation

19.1 See Section 12.

20. Report

20.1 See Section 13.

21. Precision and Bias

21.1 See Section 14.

TEST METHOD C—REFLUX PHTHALATION

22. Interferences

22.1 Excessive amounts of water in the sample will interfere by destruction of the esterification reagents. If the water content of the sample exceeds 0.2 %, it is recommended that the sample be dried.

22.2 Primary and secondary amines and higher fatty acids react with the reagent to form stable compounds and would be included in the analysis.

23. Apparatus

23.1 *Soil Digestion Flasks,* 250-mL capacity, with standard-taper 24/40 joints and 24-in. air condensers.

23.2 *Oil Bath,* maintained at 115 ± 2°C.

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

24. Reagents

24.1 *Pyridine*—See 17.1.

24.2 *Phthalic Anhydride (Pyridine Reagent)*—See 17.2.

24.3 *Phenolphthalein* (10 g/L)—See 17.3.

24.4 *Potassium Acid Phthalate*—See 17.4.

24.5 *Sodium Hydroxide, Standard Solution* (0.5 *N*)—See 17.5.

25. Procedure

25.1 Weigh into the flasks, by means of a hypodermic syringe or other suitable equipment, the amount of sample, g, calculated as follows, and weigh to the nearest 0.1 mg. No material must be allowed to touch the neck of the flask:

$$\text{Sample size} = 561/\text{estimated hydroxyl number} \qquad (13)$$

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

25.2 Accurately pipet 25 mL of the phthalic anhydride-pyridine reagent into each flask. Swirl the flask to effect solution of the sample. Put the air condensers in place, and place the flasks in an oil bath, maintained at 115 ± 2°C, for 1 h. Keep sufficient oil in the bath to cover approximately one half of the flask.

25.3 After the heating period, remove the assembly from the bath and cool to room temperature. Wash down the condenser with 50 mL of redistilled pyridine, and remove the condenser. Add 0.5 mL of phenolphthalein indicator solution and titrate with 0.5 *N* NaOH solution to a pink end point that persists for at least 15 s.

25.4 Run a blank in the same manner, omitting the sample. 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.

25.5 *Acidity or Alkalinity Correction*—See 18.9.

26. Calculation

26.1 See Section 12.

27. Report

27.1 See Section 13.

28. Precision and Bias

28.1 See Section 14.

TEST METHOD D—IMIDAZOLE-CATALYZED PHTHALIC ANHYDRIDE PRESSURE BOTTLE

29. Interferences

29.1 Primary and secondary amines and mercaptans usually will react quantitatively along with the hydroxyl group. Tertiary aliphatic amines are sufficiently basic to produce end-point errors in the titration if present in sufficient concentration.

29.2 Tertiary alcohols, higher fatty acids, and easily saponified esters interfere.

29.3 Saturated aldehydes or compounds that produce a free carbonyl group under the conditions of the reaction do not interfere. Secondary hydroxyl compounds containing a beta-carbonyl group do not esterify but are dehydrated.

29.4 If the water content of the sample exceeds 0.1 %, it is recommended that the sample be dried.

29.5 Free acids interfere by consuming the standard alkali solution, and strong bases interfere by consuming an equivalent amount of phthalic acid; provisions for determining and applying corrections for these interferences are included in the test method. Some of the higher fatty acids are converted to anhydrides, releasing water which will consume phthalation reagent.

29.6 The indicator solution is prepared with pyridine because the usual solvent, alcohol, reacts with the phthalation reagent even at room temperature.

30. Apparatus

30.1 *Bottles,* pressure, borosilicate glass, approximately 350 mL.

30.2 *Pressure Bottle Bags,* heavy fabric, with a draw string to contain bottle.

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

30.4 *Hot Water Bath,* heated by steam to 98 ± 2°C, containing enough water to cover the liquid in the sample bottles. The temperature is to be uniform throughout the bath.

31. Reagents

31.1 *Pyridine*—Distill from phthalic anhydride, discarding the fraction boiling below 114 to 115°C.[7] Store in brown glass bottles.

31.2 *Imidazole*—Reagent grade or equivalent.

31.3 *Esterification Reagent*—Weigh 111 to 116 g of phthalic anhydride into a 1-qt brown bottle. Add 700 mL of pyridine and shake the bottle vigorously until solution is complete. Add 16 to 18 g of imidazole and swirl carefully to dissolve. The reagent must stand overnight before it is used. Avoid prolonged exposure of the reagent to moisture in the air. In the blank titration as described below, exactly 25 mL of this reagent must consume between 95 and 100 mL of 0.500 *N* sodium hydroxide.

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

31.5 *Potassium Acid Phthalate*—National Institute of Standards and Technology standard sample.

31.6 *Sodium Hydroxide, Standard Solution* (0.5 *N*)— Standardize a 0.5 *N* solution of sodium hydroxide as follows:

31.6.1 Crush, do not grind, about 10 g of potassium acid phthalate to about 100 mesh and dry for 1 to 2 h at 100°C. Place in a glass-stoppered container and cool in a desiccator. Accurately weigh 4 to 4.5 g of the dried potassium acid phthalate and transfer to a 500-mL flask that has been swept free of carbon dioxide. Add 200 mL of carbon-dioxide-free water, stopper the flask, and shake it gently until the sample is dissolved. Add phenolphthalein indicator and titrate with a 50-mL buret to a pink end point with the 0.5 *N* NaOH solution.

31.6.2 Calculate the normality of the NaOH as follows:

$$\text{Normality} = W/(V \times 0.2042) \quad (14)$$

where:

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

32. Procedure

32.1 Clean and dry the pressure bottles. Make sure that the rubber gaskets are in good condition and that the caps can be fastened securely. Prepare two bottles for duplicate blank determination and two bottles for a duplicate analysis of each sample.

32.2 Accurately pipet 25 mL of the esterification reagent into each of the bottles. Use the same pipet for all bottles. Do not allow reagent to contact the gaskets.

32.3 Weigh samples to the nearest 0.1 mg directly into the sample bottles. Calculate the amount required for each sample, g, as follows:

$$\text{Sample size} = \frac{561}{\text{approximate hydroxyl number}} \quad (15)$$

If the approximate molecular weight is known, calculate the sample weight, g, as follows:

$$\text{Sample size} = \frac{\text{approximate molecular weight}}{100 \times \text{number of OH groups per molecule}} \quad (16)$$

NOTE 5—**Caution:** Since the calculated weight will be near the maximum permitted by the test method, adhere closely to the calculated weight. Use a hypodermic syringe or similar apparatus to contain the sample and weigh before and after addition.

32.4 Cap the bottles and swirl them until the samples are completely dissolved. If necessary, warm the bottles in a steam bath for several minutes. Enclose samples and blanks securely in fabric bags, and place them in a water bath maintained at 98 ± 2°C for 15 min. Maintain sufficient water in the bath to just cover the liquid in the bottles.

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

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

32.7 To each bottle add 50 mL of redistilled pyridine and 10 mL of distilled water and swirl thoroughly. For polyols that have good solubility in water, the addition of pyridine is deleted. Wait 2 min, and then add about 0.5 mL of phenolphthalein indicator solution. Titrate with standard 0.5 *N* sodium hydroxide to a pink end point that persists for at least 15 s. The net titration (blank minus sample) must be 18 to 22 mL. If it is not, repeat the determination, adjusting the sample size accordingly.

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[7] Reagent-grade pyridine has been used successfully without redistillation.

32.8 *Acidity or Alkalinity Correction*—If the sample contains more than 0.05 milliequivalents of acidity or alkalinity, the result must be corrected as follows:

32.8.1 Add 60 mL of redistilled pyridine and 10 mL of distilled water to each of two 250-mL Erlenmeyer flasks.

32.8.2 Add 0.5 mL of the phenolphthalein solution.

32.8.3 Neutralize the solution to a phenolphthalein end point with either sodium hydroxide (about 0.1 *N*) or sulfuric acid (about 0.1 *N*).

32.8.4 Add the amount of sample calculated in 32.3 by weighing to the nearest 0.1 mg and mix well.

32.8.5 If the solution is colorless, titrate with standard 0.5 *N* sodium hydroxide to a pink end point that persists for at least 15 s.

32.8.6 If the solution is pink, titrate with standard 0.5 *N* sulfuric acid to a colorless end point.

32.8.7 Calculate correction, *D*, as follows:

$$D = \frac{E \times N \times 56.1}{\text{g of sample}} \tag{17}$$

where:

E = standard acid or alkali used, mL, and
N = normality of the acid or alkali.

33. Calculation

33.1 Calculate hydroxyl number, mg KOH per g sample, as follows:

$$\text{Hydroxyl number} = \frac{(B - A)N \times 56.1}{\text{g sample}} \tag{18}$$

where:

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

33.2 If correction for acidity was required, apply it as follows:

$$\text{Hydroxyl number (corrected)} = \text{hydroxyl number } (\textit{from} \;\; 33.1) + D. \tag{19}$$

33.3 If correction for alkalinity was required, apply as follows:

$$\text{Hydroxyl number (corrected)} = \text{hydroxyl number } (\textit{from} \;\; 33.1) - D. \tag{20}$$

34. Report

34.1 Report the hydroxyl number to the nearest 0.1 unit if the value is below 100 and to the nearest unit if the value is above 100. Duplicate runs which agree to within 1.3 % are acceptable for averaging (95 % confidence interval).

35. Precision and Bias[8]

35.1 *Precision*—Table 1 is based on a round robin conducted in 1980 per Practice E691, involving six polyol samples with hydroxyl numbers from 35 to 528 tested by twelve laboratories. For each polyol, all of the samples were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. Each laboratory obtained two test results for each material on each of two separate days. The results were then calculated in accordance with Practice E180.

TABLE 1 Test Method D, Catalyzed Phthalic Anhydride Method: Hydroxl Number Results From Twelve Laboratories, Six Polyols

Sample	Mean	S_r	S_R	I_r	I_R
A	34.666	0.102	0.476	0.29	1.33
B	57.154	0.171	0.714	0.48	2.00
C	468.160	1.530	5.680	4.28	15.90
D	528.430	2.020	5.720	5.66	16.02
E	39.950	0.204	1.031	0.57	2.89
F	54.128	0.677	0.804	1.90	2.25

35.2 In Table 1, for the polyols indicated and the test results that are derived from testing two specimens of each polyol on each of two separate days:

35.2.1 S_r is the within-laboratory standard deviation of the average: $I_r = 2.83\ S_r$. (See 35.2.3 for application of I_r.)

35.2.2 S_R is the between-laboratory standard deviation of the average: $I_R = 2.83\ S_R$. (See 35.2.4 for application of I_R.)

35.2.3 *Repeatability*—In comparing two test results for the same polyol, obtained by the same operator using the same equipment on the same day, those test results are to be judged not equivalent if they differ by more than the I_r value for that polyol and condition.

35.2.4 *Reproducibility*—In comparing two test results for the same polyol, obtained by different operators using different equipment on different days, those test results are to be judged not equivalent if they differ by more than the I_R value for that polyol and condition. (This applies between different laboratories or between equipment within the same laboratory.)

35.2.5 Any judgement in accordance with 35.2.3 and 35.2.4 will have an approximate 95 % (0.95) probability of being correct.

35.2.6 Other polyols can yield somewhat different results.

35.3 For further information on the methodology used in this section, see Practice E691.

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

TEST METHOD E—IMIDAZOLE-CATALYZED PYROMELLITIC DIANHYDRIDE METHOD

36. Interferences

36.1 Excessive amounts of water in the sample will interfere by destruction of the esterification reagent. If the water content of the sample exceeds 0.2 %, it is recommended that the sample be dried.

36.2 Primary and secondary amines and higher fatty acids react with the reagent to form stable compounds and would be included in the analysis.

36.3 Aldehydes and phenols do not react under the conditions of Test Method E. Tertiary alcohols and alkoxysilanes interfere by reacting 50 to 60 %.

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[8] Supporting data are available from ASTM Headquarters. Request RR: D20-1113.

37. Apparatus

37.1 *Flasks,* iodine, 250-mL.

37.2 *Cylinders,* graduated, 100-mL.

37.3 *Flasks,* volumetric, 1000-mL.

37.4 *Repipets,*[9] 50-mL and 10-mL.

37.5 *Buret,* 50-mL.

37.6 *Stirrer,* magnetic with stirring bars.

37.7 *Water bath,* maintained at 70 to 80°C.

38. Reagents

38.1 *Dimethylformamide (DMF), Technical Grade*—The DMF must not contain more than approximately 300 ppm water. It is dried by contacting with 4A molecular sieves, either batchwise or, preferably, by passage through a column packed with sieves.

38.2 *Pyromellitic Dianhydride (PMDA) Reagent*—Weigh 51 g of PMDA into a 1000-mL volumetric flask. While swirling, add approximately 900 mL of dry DMF. Place a stirring bar in the flask and stir until the PMDA is completely dissolved (the solution can remain hazy). Dilute to volume with DMF and mix. Transfer, under a nitrogen atmosphere, to the reservoir of the 50-mL repipet. Allow this solution to stand overnight before use. This amount of reagent is sufficient for approximately eight samples and blanks, each in duplicate. Larger amounts of reagents are prepared and stored under a nitrogen atmosphere for as long as one week.

38.3 *Imidazole Reagent*—Weigh 105 g of IMDA into a 1000-mL volumetric flask. Add approximately 900 mL of dry DMF. Place a stirring bar in the flask and stir until the IMDA is completely dissolved. Allow the solution to come to room temperature, dilute to volume with DMF, and mix. Transfer, under a nitrogen atmosphere, to the reservoir of the 10-mL repipet. This amount of reagent is sufficient for approximately eight samples and blanks, each in duplicate. Larger amounts of reagents are prepared and stored under a nitrogen atmosphere for as long as one week.

38.4 *Thymolphthalein Indicator Solution (10 g/L)*—Prepare a solution of 1 g of thymolphthalein in 100 mL of alcohol.

38.5 *Potassium Acid Phthalate*—National Institute of Standards and Technology standard sample.

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

38.6.1 Crush (do not grind) about 12 g of potassium acid phthalate ($KHC_8H_4O_4$) to a fineness of approximately 100 mesh and dry for 1 to 2 h at 100°C. Place in a glass-stoppered container and cool in a desiccator. Accurately weigh 4.5 to 5 g of the dried potassium acid phthalate and transfer it to a 500-mL flask which has been swept free of carbon dioxide. Add 200 mL of water that is free of carbon dioxide, stopper the flask, and shake gently until the sample is dissolved. Add thymolphthalein indicator solution and titrate to a blue end point with the 0.5 *N* NaOH solution using a 50-mL buret.

38.6.2 Calculate the normality of the NaOH as follows:

$$\text{Normality} = \frac{W}{(V \times 0.2042)} \tag{21}$$

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)

38.7 *Water,* distilled or deionized, or equivalent.

38.8 *Nitrogen,* available at low-pressure delivery.

39. Procedure

39.1 Into 250-mL iodine flasks, weigh duplicate sample amounts calculated below:

$$\text{g of sample} = \frac{\text{molecular wt of sample} \times 0.0075}{\text{number of hydroxyl groups per mole}} \tag{22}$$

39.2 By means of a repipet, add 40 mL of PMDA reagent to each flask including duplicate blanks.

39.3 By means of a repipet, add 10 mL of IMDA reagent to each flask.

39.4 Stopper the flasks, swirl to mix, add 2 drops of DMF to each stopper-well, and place the flasks in a 70 to 80°C water bath for 10 to 15 min.

39.5 Remove the flasks, add 75 mL of water to each, and swirl to mix.

39.6 For samples that tend to foam during titration, add a stirring bar and stir vigorously on a magnetic stirrer.

39.7 Add 10 drops of thymolphthalein indicator solution and titrate the contents of each flask with 0.5 *N* sodium hydroxide to a faint blue end point which persists for 15 seconds.

39.8 If a corrected hydroxyl number is desired, proceed as follows:

39.8.1 Weigh a third sample into a 250-mL iodine flask.

39.8.2 Add a neutralized mixture consisting of 50 mL of isopropanol, 75 mL of water, and 10 drops of thymolphthalein indicator solution. Swirl to dissolve the sample.

39.8.3 If the solution is blue, titrate with standard acid solution; if the solution is colorless, titrate with standard alkali solution.

39.8.4 The acidity or alkalinity correction to be applied is calculated in 40.2.

40. Calculation

40.1 Calculate hydroxyl number, mg KOH/g, as follows:

$$\text{Hydroxyl number} = \frac{(B - A) \times N \times 56.1}{\text{g sample}} \tag{23}$$

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[9] The sole source of supply of the apparatus known to the committee at this time is Lab Industries, Inc., 620 Hearst Avenue, Berkeley, CA 94710. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

where:

B = average mL of NaOH solution consumed by the blanks,

A = NaOH solution consumed by the sample, mL, and

N = normality of NaOH solution.

56.1 = Eq weight of KOH, mg/meq.

40.2 Calculate correction, mg KOH/g, as follows:

$$\text{Correction} = \frac{C \times N \times 56.1}{\text{g sample}} \quad (24)$$

where:

C = acid or alkali solution used in 39.8.3, mL, and

N = normality of acid or alkali solution.

40.3 Hydroxyl number, mg KOH/g, corrected, for samples that are originally alkaline (titrated with acid) is obtained by subtracting the correction from the uncorrected hydroxyl number.

$$\text{Hydroxyl number (corrected)} = \text{hydroxyl number} - \text{Correction} \quad (25)$$

40.4 Hydroxyl number, mg KOH/g, corrected, for samples that are originally acidic (titrated with alkali) is obtained by adding the correction to the uncorrected hydroxyl number.

$$\text{Hydroxyl number (corrected)} = \text{hydroxyl number} + \text{Correction} \quad (26)$$

41. Report

41.1 Report the hydroxyl number to the nearest 0.1 unit if the value is below 100 and to the nearest 1 unit if the value is above 100. Duplicate runs which agree within 1.8 % relative are acceptable for averaging (95 % confidence interval).

42. Precision and Bias[10]

42.1 *Precision*—Table 2 is based on a round robin conducted in 1980 per Practice E691, involving four polyol samples with hydroxyl numbers from 33 to 539 tested by six laboratories. For each polyol, all of the samples were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. Each laboratory obtained two test results for each material on each of two separate days. The results were then calculated in accordance with Practice E180.

TABLE 2 Test Method E, Pyromellitic Dianhydride Method: Hydroxl Number Results From Six Laboratories, Four Polyols

Sample	Mean	S_r	S_R	I_r	I_R
A	33.251	0.283	1.627	0.79	4.56
B	57.107	0.476	0.903	1.33	2.53
C	475.420	1.830	6.760	5.12	18.93
D	539.530	5.950	7.890	16.66	22.09

42.2 In Table 2, for the polyols indicated and the test results that are derived from testing two specimens of each polyol on each two separate days:

42.2.1 S_r is the within-laboratory standard deviation of the average: $I_r = 2.83\ S_r$. (See 42.2.3 for application of I_r.)

42.2.2 S_R is the between-laboratory standard deviation of the average: $I_R = 2.83\ S_R$. (See 42.2.4 for application of I_R.)

42.2.3 *Repeatability*—In comparing two test results for the same polyol, obtained by the same operation using the same equipment on the same day, those test results are to be judged not equivalent if they differ by more than the I_r value for that polyol and condition.

42.2.4 *Reproducibility*—In comparing two test results for the same polyol, obtained by different operators using different equipment on different days, those test results are to be judged not equivalent if they differ by more than the I_R value for that polyol and condition. (This applies between different laboratories or between equipment within the same laboratory.)

42.2.5 Any judgement in accordance with 42.2.3 and 42.2.4 will have an approximate 95 % (0.95) probability of being correct.

42.2.6 Other polyols can yield somewhat different results.

42.3 For further information on the methodology used in this section, see Practice E691.

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

43. Keywords

43.1 acetic anhydride; esterification; hydroxyl number; phthalic anhydride; polyester; polyether; polyol; pyromellitic dianhydride; titration

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue, D4274 - 11, that may impact the use of this standard. (April 1, 2016)

(1) Sections 4.2, 4.3, 4.5: Summary of Test Methods—Added that water is added to hydrolyze excess reagent, to be consistent with the other methods.

(2) Section 2.2: ISO Standards—Added ISO 14900.

(3) Various edits throughout the method to remove non-mandatory language.

(4) Section 12.2: Calculation—Changed equations in 12.2 for clarification

(5) Section 33.3: Calculation—Corrected reference in equation and changed to be consistent with the other methods.

(6) Sections 40.3 and 40.4 – Corrected equations for clarification and consistency with the other methods.

(7) Added Note 2.

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[10] Data supporting the precision estimates are available in the Research Reports file at ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428–2959.

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