**Designation: E 335 – 96**

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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# Standard Test Method for Hydroxyl Groups by Pyromellitic Dianhydride Esterification[1]

This standard is issued under the fixed designation E 335; 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.

*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope

1.1 This test method covers the determination of hydroxyl groups attached to primary and secondary carbon atoms in aliphatic and alicyclic compounds. It is not suitable for the determination of hydroxyl groups attached to tertiary carbon atoms. Phenolic hydroxyl groups do not react.

NOTE 1—Other methods for determination of hydroxyl groups are given in ASTM Test Method D 1957, Test Method for Hydroxyl Value of Fatty Oils and Acids,[2] ASTM Methods D 2849, Methods of Testing Urethane Foam Polyol Raw Materials,[3] ASTM Test Methods E 222, Test Methods for Hydroxyl Groups by Acetic Anhydride Acetylation,[4] ASTM Test Method E 326, Test Method for Hydroxyl Groups by Phthalic Anhydride Esterification,[4] ASTM Test Method E 567, Test Method for Tertiary Hydroxyl Groups with Hydrogen Bromide,[4] and Test Methods D 2195, Test Methods for Pentaerythritol.[2]

1.2 *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.* Specific precautionary statements are given in Section 9.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[5]
E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[4]
E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[4]
E 203 Test Method for Water Using Karl Fischer Reagent[4]
E 287 Specification for Burets[6]
E 300 Practice for Sampling Industrial Chemicals[4]

## 3. Terminology

3.1 *Definition:*

3.1.1 *hydroxyl number*—the milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of material. In the case of pure compound, the hydroxyl number is inversely proportional to the hydroxyl equivalent weight:

$$\text{Equivalent weight (g/equivalent)} = \frac{56100}{\text{hydroxyl number}} \quad (1)$$

## 4. Summary of Test Method

4.1 The hydroxyl group is esterified by reaction with pyromellitic dianhydride in a dimethyl sulfoxide-pyridine medium at approximately 100°C. The excess anhydride is hydrolyzed with water and the pyromellitic 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.

## 5. Significance and Use

5.1 Hydroxyl is an important functional group and knowledge of its content is required in many intermediate and end-use applications. This test method is for the determination of primary and secondary hydroxyl groups and can be used for the assay of compounds containing them.

## 6. Interferences

6.1 Primary and secondary amines and mercaptans usually will react quantitatively along with the hydroxyl group. Tertiary aliphatic amines may be sufficiently basic to cause end-point errors in the titration. In this case, potentiometric determination of the end point may improve the precision of this test method.

6.2 Tertiary alcohols will interfere with the accuracy of this test method. Easily saponified esters will interfere during the titration. This interference, usually indicated by a fading end point, can be minimized by cooling the solution before titration.

6.3 Ethers other than epoxides-saturated aldehydes or compounds that produce a free carbonyl group under the conditions of the reaction do not interfere.

6.4 Excessive amounts of water in the sample will interfere by consuming the reagent. A small amount of water can be accommodated by adjustment of the sample size used for analysis (Note 4).

6.5 Free acids interfere by consuming the standard alkali solution and strong bases interfere by consuming an equivalent

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[1] This test method is under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E15.22 on Functional Groups.

Current edition approved March 10, 1996. Published May 1996. Originally published as E 335 – 67 T. Last previous edition E 335 – 90.

[2] *Annual Book of ASTM Standards*, Vol 06.03.
[3] *Annual Book of ASTM Standards*, Vol 08.02.
[4] *Annual Book of ASTM Standards*, Vol 15.05.
[5] *Annual Book of ASTM Standards*, Vol 11.01.
[6] *Annual Book of ASTM Standards*, Vol 14.02.

amount of pyromellitic acid. Provisions for determining and applying corrections for these interferences are included in this test method. Some of the higher fatty acids may be converted to anhydrides, releasing water which will consume the esterification reagent.

6.6 Due to reaction of alcohol, even at room temperature, the indicator solution must not be prepared in this solvent.

## 7. Apparatus

7.1 *Buret,* 100-mL total capacity, range of graduated portion 50 mL, 0.1-mL graduation, preferably equipped with a PTFE stopcock (Note 7). Complete specifications are given in Specification E 287.

7.2 *Flasks*, Erlenmeyer, 300 mL with glass stoppers.

7.3 *Pipet,* 50-mL transfer.

7.4 *Steam Bath,* 100°C.

## 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.[7] 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water as defined in Specification D 1193.

8.3 *Dimethylsulfoxide*—**Caution**—See 9.1.

8.4 *Pyridine*—**Caution**—See 9.2.

8.5 *Pyromellitic Dianhydride*, [8] 90 % minimum assay. A method for assaying the material is given in the Appendix X1.

NOTE 2—Pyromellitic dianhydride that is low in anhydride content due to pickup of water, may be regenerated by drying at 170°C for 48 h.

8.6 *Esterification Reagent* (0.5 *M*)—Dissolve a weight of reagent containing 109 g of pyromellitic dianhydride (gram reagent × 100/percent of pyromellitic dianhydride) in 525 mL of dimethylsulfoxide, then add 425 mL of pyridine. The solution should be clear. If necessary filter through a sintered glass funnel (do not use filter paper).

8.7 *Hydrochloric Acid, Standard* (0.5 *N*)—Prepare and standardize hydrochloric acid (HCl) in accordance with the appropriate sections of Practice E 200. 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 using the Eq 2 given in 8.9. 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 presence of strong base in the sample being analyzed.

8.8 *Phenolphthalein Solution in Pyridine* (10 g/L)—Dissolve 1 g of phenolphthalein in pyridine and dilute with pyridine to 100 mL[9].

8.9 *Sodium Hydroxide, Standard Solution* (1.0 *N*)—Prepare and standardize sodium hydroxide (NaOH) solution in accordance with the appropriate sections of Practice E 200. Determine and record the temperature at which the standardization was performed. The factor for thermal expansion of this solution is 0.00035. For calculation of the hydroxyl content, the normality of the solution shall be corrected to the temperature at which the determination is performed using the following Eq 2:

$$N_{t2} = N_{t1} + (t_1 - t_2)(\ 0.00035) \quad (2)$$

where:

$N_{t1}$ = normality when standardized,
$N_{t2}$ = normality during analysis of samples,
$t_1$ = temperature of solution during standardization, °C, and
$t_2$ = temperature of solution during analysis of samples, °C.

## 9. Precautions

9.1 *Dimethylsulfoxide* — Dimethylsulfoxide is recognized as an experimental teratogen by the National Institute of Occupational Safety and Health. Precautions should be taken, especially by women of childbearing capability, to avoid exposure by skin contact or inhalation of vapors.

9.1.1 Also, dimethylsulfoxide penetrates the skin rapidly and could act as a carrier for other substances dissolved in it or present on the skin. It has analgesic properties.

9.1.2 If solutions containing dimethylsulfoxide contact the skin, the affected area should immediately be washed thoroughly with water.

9.2 *Pyridine*—Pyridine is mildly irritating to the skin. Inhalation of vapors can cause damage to the central nervous system. Kidney and liver damage have been reported in experimental animals. Avoid unnecessary exposure to vapors of pyridine. If solutions containing pyridine contact the skin, the affected area should be washed immediately with water.

## 10. Sampling

10.1 Special precautions may be necessary to ensure that the sample taken for analysis is representative of the whole. Refer to Practice E 300 for a detailed discussion of sampling procedures.

## 11. Procedure

11.1 To each of a sufficient number of flasks to make all blank and sample determinations in duplicate, pipet 50.0 mL of the esterification reagent. A uniform drainage time must be used for all aliquots.

11.2 Reserve two of the flasks for the blank determination. Into the other flasks add an appropriate weight of sample (Note 3, Note 4, and Note 7).

NOTE 3—Determine the sample weight as follows:

[7] *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.

[8] The practical grade available from E. I. DuPont de Nemours or from Distillation Products is suitable.

[9] This reagent is also described in Practice E 200.

$$\text{Sample weight, g} = \frac{(824)}{\text{approximate hydroxyl number}} \quad (3)$$

Since the calculated weight will be near the optimum for the method (15 meq), adhere closely to the indicated weight. The sample weight should not exceed 10 g.

NOTE 4—If the sample contains an appreciable amount of water, the sample weight must be adjusted to accommodate this interference. In this case, determine the sample weight by using one of the following (Eq 4 or Eq 5):

$$\text{Sample weight, g} = \frac{824}{(\text{approximate hydroxyl number} \pm 31.2R)} \quad (4)$$

$$\text{Sample weight, g} = \frac{0.250}{[0.0094\,R + (0.1701 \times n \times S/MW)]} \quad (5)$$

where:

$R$ = percent water in sample as determined by Test Method E 203 or other equivalent procedure,
$S$ = purity of sample, %
$MW$ = molecular weight of compound, and
$n$ = number of hydroxyl groups present in the molecule.

Precision and accuracy are decreased when appreciable amounts of water are present, because of the required decrease in sample size.

NOTE 5—Where the hydroxyl content is low or only a small amount of sample is available, use a 0.1 *M* pyromellitic dianhydride solution for esterification, 0.2 *N* NaOH solution for titration, and increase the reaction time by 50 %. In this case the sample size will be only one fifth that calculated in Note 3.

11.3 Wet the stopper with a few drops of pyridine, insert it loosely in the flask and swirl the flask. The sample must be completely dissolved before heating to ensure complete reaction. Then place the flask on the steam bath for 20 min.

NOTE 6—For some compounds a shorter or longer period may be required. The optimum time should be determined for each compound.

11.4 Carefully rinse the stopper and walls of the flask with 20 mL of water and swirl to mix. Then, loosely stopper and again heat on the steam bath for an additional 2 min.

11.5 Cool to room temperature.

11.6 Remove the stopper, rinsing it with a small amount of water, collecting the water in the flask. Add 0.5 to 1 mL of the phenolphthalein indicator solution, and, while swirling the flask, titrate (Note 7) with the 1.0 *N* NaOH solution to the first faint end point permanent for 15 s. Record the volume of titrant to 0.02 mL (Note 8). Record the temperature of the NaOH solution.

NOTE 7—As a substitute, if a 100-mL buret is not available, the first 50 mL of titrant may be added by pipet using a uniform drainage time for all aliquots and the titration completed with a 50-mL buret.

NOTE 8—If the volume of 1.0 *N* NaOH solution required for the sample is less than 85 % of that required for the blank, the sample was too large, and the analysis should be repeated with a smaller weight of sample. In some cases a smaller excess of esterification reagent may be adequate, but this must be validated for the particular type of compound. In no case should the sample titration be less than 70 % of that required for the blank.

## 12. Calculation

12.1 Calculate the hydroxyl content in terms of either hydroxyl number or percentage of hydroxyl-containing compound as follows (Note 9):

$$\text{Hydroxyl number} = \frac{[(A - B) \times N_t \times 56.1]}{W} \quad (6)$$

$$\text{Hydroxyl-containing compound, \%} = \frac{[(A - B) \times N_t \times MW \times 100]}{(W \times n \times 1000)} \quad (7)$$

where:

$A$ = NaOH solution required for titration of the blank, mL,
$B$ = NaOH solution required for titration of the sample, mL,
$N_t$ = normality of the solution at the temperature during analysis (see 8.9),
$n$ = number of hydroxl groups in the compound,
$MW$ = molecular weight of the hydroxyl-containing compound, and,
$W$ = sample used, g

NOTE 9—If the sample contains free acid or strong base, a correction should be applied. This correction may be determined as follows: To 26 mL of dimethyl sulfoxide, 21 mL of pyridine, and 120 mL of water in a flask add 0.5 to 1 mL of phenolphthalein indicator solution and titrate with the 1.0 *N* NaOH solution to the first faint pink color that persists for 15 s. To the solution add an accurately weighed sample of approximately the same weight as that used in 11.2, mix by swirling, and titrate to the original end point using 1.0 *N* NaOH solution or 0.5 *N* HCl as required. Use the volume, normality of the titrant, and the weight of sample as $(A - B)$, $N_t$, and $W$, respectively, to calculate the correction for hydroxyl number or percent hydroxyl-containing compound in accordance with 12.1. If NaOH was required to neutralize the sample, add the correction. If HCl was required to neutralize the sample, subtract the correction.

## 13. Report

13.1 Report the percentage of the hydroxyl-containing compound to the nearest 0.1 unit. Report the hydroxyl number to the nearest 0.1 unit if the value is below 100 and the nearest 1 unit if the value is above 100.

## 14. Precision and Bias

14.1 The following criteria should be used for judging the acceptability of results (Note 10):

14.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 0.31 % relative at 42 df. The 95 % limit for the difference between two such runs is 0.9 % relative.

14.1.2 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts on different days, has been estimated to be 0.57 % relative at 20 df. The 95 % limit for the difference between two such averages is 1.6 % relative.

14.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 1.48 % relative at 6 df. The 95 % limit for the difference between two such averages is 4.1 % relative.

NOTE 10—The precision statements are based on an interlaboratory study performed in 1966 on one sample each of dodecanol, pentanol, and 1,6-hexanediol. The precision of results for a sample of pentaerythritol included in this study was not as good as for the other compounds evaluated. For this sample the coefficients of variation were approximately twice as large as shown above. Eight laboratories analyzed each sample in duplicate and replicated the analysis on another day. Practice E 180 was used in developing these precision statements. The statements were recalculated from previous precision statements to conform with current precision definitions.

14.2 The bias of this test method has not been determined due to the unavailability of suitable reference materials.

## 15. Keywords

15.1 determination; esterification; hydroxyl group; hydroxyl number; pyromellitic dianhydride

## APPENDIX

**(Nonmandatory Information)**

### X1. DETERMINATION OF ANHYDRIDE CONTENT OF PYROMELLITIC DIANHYDRIDE

X1.1 The following procedure shall be used to assay the pyromellitic dianhydride to determine that it complies with the requirement in 8.5.

X1.1.1 **Reagents**

X1.1.1.1 *Aniline*.

X1.1.1.2 *Dimethylsulfoxide*. (**Caution**—See 9.1).

X1.1.1.3 *Ethylene Glycol*.

X1.1.1.4 *Isopropyl Alcohol*.

X1.1.1.5 *Solvent Solution*—Mix ethylene glycol and isopropanol 1 to 1 by volume.

X1.1.1.6 *Hydrochloric Acid, Standard* (0.2 *N Alcoholic*)—Dilute 16.6 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1 L with the ethylene glycol-isopropanol solvent solution. Standardize the solution by the procedure described in the appropriate sections of Practice E 200. Alternatively the solution may be standardized by titrating 50 mL against the 1.0 *N* NaOH solution (see 8.9) using phenolphthalein indicator solution. The solution should be standardized at the temperature and on the day it is used for analysis.

X1.1.2 **Procedure**

X1.1.2.1 Accurately weigh approximately 0.5 g of pyromellitic dianhydride in a 20 by 150-mm test tube. Add aniline drop by drop until about 0.9 g has been added and accurately weigh the amount of aniline added. As a blank, accurately weigh approximately 0.4 g of aniline in a separate test tube.

X1.1.2.2 Allow the tubes to stand at room temperature for 5 min.

X1.1.2.3 To each tube add 5 mL of dimethylsulfoxide. Break up and dissolve the solids in the sample mixture using a glass rod and allow to stand at least another 10 min.

X1.1.2.4 Quantitatively transfer the contents of each tube to a separate 150-mL beaker using the solvent solution (see X1.1.1.5) to effect the transfer. Bring the total volume in each beaker to approximately 50 mL with the solvent solution.

X1.1.2.5 Titrate each solution potentiometrically with the 0.2 *N* HCl. Plot the meter readings versus millilitres of acid on coordinate graph paper. Select as the endpoint, the volume of acid (to 0.02 mL) required to titrate to the midpoint of the break in the curve. An automatic recording potentiometric titrator may be used.

X1.1.3 **Calculation**

X1.1.3.1 Calculate the pyromellitic dianhydride content of the sample as follows:

$$\frac{(V_a \times W_a)}{W_b} = V_b \tag{X1.1}$$

$$\text{Pyromellitic dianhydride, \%} = \frac{[(V_b - V_c) \times N \times 10.91]}{W_c} \tag{X1.2}$$

where:

$V_a$ = standard acid for the blank, mL,
$V_b$ = standard acid calculated for the aniline used in the sample, mL,
$V_c$ = standard acid for the sample, mL,
$W_a$ = aniline added to sample, g,
$W_b$ = aniline used in blank, g, and
$W_c$ = sample used for determination, g.

X1.1.4 **Report**

X1.1.4.1 Report pyromellitic dianhydride content to 0.1 %.