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AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428

Standard Test Methods for Glycerol, Ethylene Glycol, and Pentaerythritol in Alkyd Resins[1]

This standard is issued under the fixed designation D 1615; 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—Keywords were added editorially and editorial changes made throughout in May 1995.

1. Scope

1.1 These test methods cover the determination of glycerol, ethylene glycol, and pentaerythritol in alkyd resins and resin solutions. Other polyhydric alcohols that can be oxidized by periodic acid to formaldehyde or formic acid, or both, will interfere with the determination of glycerol and ethylene glycol (see Test Methods D 2456 or D 2998). Urea, melamine, or phenolic resins interfere and render this procedure inapplicable.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 563 Test Method for Phthalic Anhydride Content of Alkyd Resins and Resin Solutions[2]

D 1193 Specification for Reagent Water[3]

D 1398 Test Method for Fatty Acid Content of Alkyd Resins and Alkyd Resin Solutions[2]

D 2456 Test Method for Identification of Polyhydric Alcohols in Alkyd Resins[2]

D 2998 Test Method for Polyhydric Alcohols in Alkyd Resins[2]

3. Purity of Reagents

3.1 Reagent grade chemicals shall be used 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.[4] 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.

3.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.[3]

NOTE 1—The reagents and samples used in these methods may, under some conditions, be hazardous. Refer to the manufacturer's Material Safety Data Sheets for specific handling and safety precautions. Safe laboratory handling procedures and all applicable OSHA regulations are to be followed.

GLYCEROL AND ETHYLENE GLYCOL

4. Summary of Test Method

4.1 The primary hydroxyl groups of ethylene glycol and glycerol are oxidized to formaldehyde by periodic acid; the secondary hydroxyl group of glycerol is oxidized to formic acid. By acidimetric and iodometric titration, the proportions of formic acid and formaldehyde can be determined respectively, and calculated to glycerol and ethylene glycol by algebraic equations. The equations for the oxidation of the polyhydric alcohols are as follows:

[1] These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.33 on Polymers and Resins.

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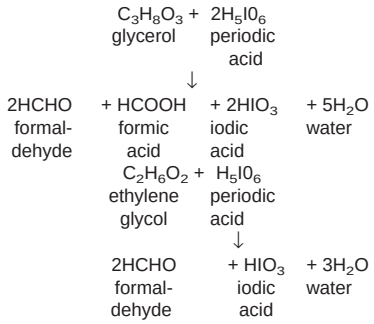
[2] *Annual Book of ASTM Standards*, Vol 06.03.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.



With pentaerythritol, there is no reaction.

5. Apparatus

5.1 *Burets*, 50 and 100-mL capacity.

5.2 *Pipets*, 20 and 50-mL capacity.

5.3 *Beakers*, two of 400-mL capacity.

5.4 *Erlenmeyer Flasks*, four of 1000-mL capacity, glass-stoppered.

5.5 *Volumetric Flasks*, two of 100-mL capacity.

5.6 *Graduated Cylinder*, 10-mL capacity.

5.7 *Filter Paper*, fast, qualitative grade.

5.8 *Watch Glass*.

6. Reagents

6.1 *Methyl Purple Indicator Solution.* [5]

6.2 *Periodic Acid* (11 g/L)—Dissolve 11 g of periodic acid (HIO_4) in water and dilute to 1 L. Prepare fresh daily and store in a brown bottle.

6.3 *Potassium Iodide Solution* (200 g/L)—Dissolve 200 g of potassium iodide (KI) in water and dilute to 1 L.

6.4 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Prepare and standardize a 0.1 *N* aqueous sodium hydroxide (NaOH) solution.

6.5 *Sodium Thiosulfate, Standard Solution* (0.2 *N*)—Prepare and standardize a 0.2 *N* aqueous sodium thiosulfate ($Na_2S_2O_3$) solution.

6.6 *Starch Indicator Solution*—Dissolve 5 g of soluble starch in water and dilute to 1 L. Preserve the solution with 1 g of salicyclic acid.

6.7 *Sulfuric Acid* (1+5)—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with 5 volumes of water.

7. Procedure

7.1 Determine the phthalic anhydride in accordance with Test Method D 563. Following this, extract the fatty acids in accordance with 5.6 through 7 of Test Method D 1398, except *do not* discard the aqueous phase.

7.2 Test the remaining water solution containing the polyalcohols for glycerol and ethylene glycol in the following manner:

7.2.1 Transfer the solution to a 400-mL beaker and evaporate to about 60-mL volume, using an electric hot plate as source of heat. Keep the beaker covered with a watch glass[6] during boiling.

7.2.2 Cool to room temperature, and filter through a rapid paper into a 100-mL volumetric flask. (Take the sample for pentaerythritol determination from this same volumetric flask.) Fill to the mark and agitate.

7.2.3 Pipet 20 mL (⅕ aliquot) (Note 2) into a 1-L Erlenmeyer, glass-stoppered flask. Add 2 drops of methyl purple indicator solution and neutralize with NaOH. Pipet into the 1-L flask also 50 mL of HIO_4 solution, stopper, and swirl to mix thoroughly.

NOTE 2—The aliquot should be so chosen, if possible, that 15 to 20 % of the periodic acid is consumed during the oxidation. Considerable excess of periodic acid is required to complete the oxidation, and in case more than 20 % is consumed the results should be disregarded and a smaller aliquot taken. On the other hand, too small an aliquot is not advisable, for in such a situation the difference between titration and blank is small and any titration errors are magnified.

7.3 Simultaneously prepare two blanks containing 20 mL of water. Allow to stand 50 to 70 min at room temperature.

7.4 To the aliquot of the sample (7.2.3) and the blank, add 100 mL of water and 3 drops of methyl purple indicator and titrate with 0.1 *N* NaOH solution to neutrality. Use the 50-mL buret and record the volume to the nearest 0.01 mL.

7.5 To the solution that has just been titrated, add 150 mL of water, 30 mL of KI solution, and 25 mL of H_2SO_4 (1+5). Titrate with 0.2 *N* $Na_2S_2O_3$ solution to faint iodine color, add 10 mL of starch indicator and titrate to the disappearance of the blue color.

NOTE 3—If the end point is not stable, as indicated by return of the blue color in the stoppered flask in 5 min, add water and titrate to a stable end point. Use the 100-mL buret and record the volume to the nearest estimated 0.05 mL.

8. Calculations

8.1 Calculate the percentage of glycerol, *G*, as follows:

$$G = [(A - B)N \times 0.09206)/WF] \times 100$$

where:

A	=	millilitres of NaOH solution required for titration of the sample,
B	=	millilitres of NaOH solution required for titration of the blank,
N	=	normality of the NaOH solution,
0.09206	=	grams of glycerol equivalent to 1 mL of 1 *N* NaOH solution (acidimetric),
W	=	grams of sample used, and
F	=	aliquot fraction = ⅕.

8.2 Calculate the percentage of glycerol and ethylene glycol, *T*, as a percentage of glycerol as follows:

$$(T = [(B' - A')N \times 0.023015)/WF] \times 100$$

where:

A′	=	millilitres of $Na_2S_2O_3$ solution required for titration of the sample,

[5] Methyl purple indicator manufactured by the Fleisher Chemical Co., Benjamin Franklin Station, Washington 4, D.C., U.S. Patent No. 2,416,619, has been found satisfactory for this purpose.

[6] The Speedyvap watch glass has been found satisfactory for this purpose.