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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Phthalic Anhydride Content of Alkyd Resins and Esters Containing Other Dibasic Acids (Gravimetric)[1]

This standard is issued under the fixed designation D 1306; 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.

ε[1] NOTE—Keywords were added editorially in October 1996.

1. Scope

1.1 This test method covers the gravimetric determination of phthalic anhydride in alkyd resins and esters that contain dibasic acids such as maleic, fumaric, adipic, and sebacic, which would interfere if Test Method D 563 was used.

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]

3. Summary of Test Method

3.1 The specimen is saponified with alcoholic potassium hydroxide and benzene to precipitate quantitatively the potassium salt of phthalic acid as $C_6H_4(COOH)_2 \cdot C_2H_5OH$. Interfering substances are eliminated by dissolving the precipitate in water, adjusting the pH of the solution to 2.5 with nitric acid, and filtering. Phthalic acid is then precipitated as nonstoichiometric lead phthalate and calculated to phthalic anhydride, using a factor obtained when compositions of known purity were analyzed similarly.

4. Significance and Use

4.1 The phthalic anhydride content of alkyd resins controls the properties of the final film.

5. Apparatus

5.1 *Flask and Condenser*—A 500-mL Erlenmeyer flask fitted with an air-cooled glass reflux condenser 30 in. (760 mm) in length. The connection between the flask and condenser shall be a standard-taper 24/40 ground-glass joint.

5.2 *Water Bath.*

5.3 *Guard Tube*, filled with soda lime.

5.4 *Fritted-Glass Filter Crucible*, medium porosity, of 30-mL capacity.

5.5 *Filter Flasks*, suction-type.

5.6 *Crucible Holder.*

5.7 *Oven*, of gravity convection type.

5.8 *Desiccator*, containing concentrated H_2SO_4 (sp gr 1.84) as the desiccant.

5.9 *Flash Filtrator.*

5.10 *pH Test Assembly.*

5.11 *Volumetric Flask*, 100-mL.

5.12 *Erlenmeyer Flask*, 250-mL, wide-mouth, with glass stopper not smaller than a No. 27.

5.13 *Delivery Pipet*, 2-mL.

6. Reagents

6.1 *Purity of Reagent*—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.

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

6.3 *Acetic Acid, Glacial.*

6.4 *Alcohol-Benzene Wash Solution*—Mix 1 volume of absolute ethyl alcohol (Note 1) with 3 volumes of benzene.

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[1] This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications, and is 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

NOTE 1—The alcohol may be denatured Formula 2-B, but must be anhydrous.

6.5 *Benzene* (anhydrous).

6.6 *Ether* (anhydrous).

6.7 *Lead Acetate Solution*—Dissolve 25 g of lead acetate trihydrate in glacial acetic acid and dilute to 100-mL volume with acetic acid.

6.8 *Methanol* (anhydrous).

6.9 *Nitric Acid* (1 + 3)—Mix 1 volume of concentrated nitric acid (HNO_3) (sp gr 1.42) with 3 volumes of water.

6.10 *Potassium Hydroxide Alcoholic, Solution* (66 g/L)—Dissolve 66 g of potassium hydroxide (KOH) in 1 L of absolute ethyl alcohol (Note 1). Allow the solution to stand overnight protected against carbon dioxide (CO_2) absorption. Filter just before use.

7. Procedure

7.1 Weigh by difference, from a closed container into the 500-mL Erlenmeyer flask, a sample of resin or resin solution sufficient to yield from 0.8 to 1.2 g of potassium alcohol phthalate. Add 150 mL of benzene, warming slightly on the steam bath if necessary, to effect solution. Add 60 mL of alcoholic KOH solution, and attach the condenser. Place the flask in a water bath to a depth approximately equal to that of the contents of the flask. Warm the bath, maintaining a temperature of 40°C for 1 h, then gradually raise the temperature until the alcoholic solution boils gently. Reflux for 1½ h.

7.2 Remove the flask from the bath and wash down the inside of the condenser with a few millilitres of alcohol-benzene wash solution. Remove the condenser, cap the flask with the soda-lime guard tube, and cool by means of running water or an ice bath.

7.3 When cool, filter immediately and as rapidly as possible, through a fritted-glass crucible that previously has been tared, using the alcohol-benzene wash solution for transferring the precipitate and washing the reaction flask. Wash the precipitate with successive portions of alcohol-benzene wash solution until a few millilitres of washings collected in a second suction flask are no longer alkaline to phenolphthalein. (Normally about 75 mL of wash solution are sufficient.) Do not allow air to be drawn through the crystals as they are hygroscopic. Finally, pour 25 mL of ether into the crucible and draw through the precipitate with the aid of suction.

7.4 Wipe the outer surface of the crucible with a clean cloth and place in a gravity convection oven at 60°C for 1 h. Cool to room temperature in a desiccator, and weigh.

NOTE 2—The crucible weighings are for determining aliquot size and need be weighed to the nearest 10 mg only.

7.5 Dissolve the contents of the crucible in 70 mL of water, using a filtrator so as to collect the washings in a 250-mL beaker. Adjust the pH of the specimen to 2.5, using HNO_3 (1 + 3) and a pH test assembly. After the specimen has stood 30 min or longer, filter through double thicknesses of the finest paper directly into a 100-mL volumetric flask (Note 3). Dilute to volume with water, simultaneously using the water to wash the beaker and filter paper; mix thoroughly.

NOTE 3—If the solution does not cloud when acidified, it may be diluted to volume at once and the filtering omitted.

7.6 Withdraw an aliquot containing not less than 60 nor more than 90 mg of the dissolved salts. Transfer this aliquot into the 250-mL Erlenmeyer flask. Dry the contents of the flask in the oven at 60°C. Add 5 mL of glacial acetic acid, vent the stopper by inserting a paper strip under one side, and heat in the oven at 60°C for 1 h. Add 100 mL of anhydrous methanol and continue heating in the oven with occasional agitation until the material is completely dissolved. To the hot solution, add slowly, by pipet, 2.0 mL of lead acetate solution. Agitate the solution during the addition of this reagent. Return the flask to the 60°C oven for 1 h. Remove and stopper tightly after 30 min. Allow to stand 12 h or longer. Filter the solution through a dry tared fritted-glass crucible of medium porosity, to which additional mats of coarse and fine asbestos have been added. Agitate the solution just before filtering. Wash the flask thoroughly, using anhydrous methanol. Examine the filtrate carefully before discarding and, if cloudy, filter again through the same crucible. Dry the crucible for 1 h at 105°C, cool in a desiccator, and weigh.

8. Calculation

8.1 Calculate the percent of phthalic anhydride A in the specimen as follows:

$$A = [(P \times 0.323)/S] \times 100 \quad (1)$$

where:

P = lead precipitate, g, and

S = specimen represented in the aliquot used, g.

9. Precision

9.1 Two results obtained by operators should be considered suspect if they differ by more than 1 % absolute.

10. Keywords

10.1 alkyd resins; dibasic acids; esters; gravimetric; phthalic anhydride