Designation: E1090 – 08

Standard Test Method for Dicumyl Peroxide and Dicumyl Peroxide Decomposition Products in Resins[1]

This standard is issued under the fixed designation E1090; 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 This test method covers and is applicable to the determination of dicumyl peroxide[2] and the decomposition products dimethylbenzyl alcohol and acetophenone in cured and uncured polyethylene (PE) and ethylene vinyl acetate (EVA) resins. These uncured polymers normally contain from 1 to 2 % dicumyl peroxide, whereas the residual peroxide level in the cured polymers is usually less than 0.1 %.

1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.3 Review the current Material Safety Data Sheets (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

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.* Specific hazards are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[4]

E300 Practice for Sampling Industrial Chemicals

E682 Practice for Liquid Chromatography Terms and Relationships

E685 Practice for Testing Fixed-Wavelength Photometric Detectors Used in Liquid Chromatography

E755 Test Method for Dicumyl Peroxide, Assay (Liquid Chromatography)

3. Summary of Test Method

3.1 Dicumyl peroxide and dimethylbenzyl alcohol are extracted from a cryogenically ground sample with methylene chloride. The extract is concentrated, redissolved in methanol, and analyzed by high performance liquid chromatography (HPLC). Acetophenone is extracted from a separate sample with methanol and analyzed directly by HPLC. The analyses are performed on a reversed phase octadecylsilane (ODS) column using acetonitrile/water as the mobile phase and an ultraviolet detector at 254 nm. The concentration of each component is determined by the internal standard technique, using peak height ratios of the sample and standard chromatograms.

4. Significance and Use

4.1 Knowledge of the peroxide content of uncured PE and EVA samples is required to regulate the degree of crosslinking in the cured product. As end use applications of the cured product can be affected by residual amounts of the peroxide or its decomposition products—dimethylbenzyl alcohol and acetophenone—knowledge of these levels is also important. This test method provides a procedure for determining the concentration of these compounds. A method for the HPLC assay of dicumyl peroxide is described in Test Method E755.

5. Apparatus

5.1 *Liquid Chromatograph,* equipped with a 254-nm UV detector, injection valve, and an isocratic-solvent delivery system capable of operating to a gage pressure of 3000 psi. The detector should be equipped with an attenuator switch to change the sensitivity range as required. (See Practices E682 and E685.)

5.2 *Recorder,* 0 to 1 mv range, 1 s or less full-scale deflection, with a chart speed of 0.1 in./min or other convenient

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.15 on Industrial and Specialty General Standards.

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[2] Dicumyl peroxide; peroxide, bis(1-methyl-1-phenylethyl) $C_{18}H_{22}O_2$; CAS Registry No. 80-43-3.

[3] 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.

[4] The last approved version of this historical standard is referenced on www.astm.org.

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

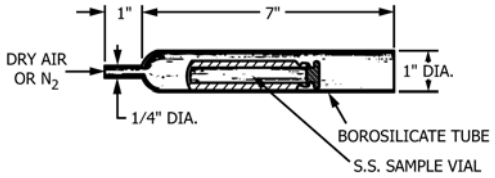

FIG. 1 Tube for Warming Cryogenically Ground Resin Samples to Ambient Temperature

speed that will produce a satisfactory chromatogram. As an alternative, an electronic data system can be used.

5.3 *Chromatographic Column,* reversed phase C-18, from 250 to 300-mm by 3.9-mm inside diameter, containing octadecylsilane chemically bonded to microparticulate silica.[5]

NOTE 1—Commercial HPLC columns may vary in physical dimensions, degree of substrate loading, and size and type of support material. For these reasons, some modification in the operating parameters may be required to achieve optimum separation.

5.4 *Guard Column,* reversed phase C-18, containing octadecylsilane chemically bonded to microparticulate silica.

5.5 *Filter Funnel,* Buchner, 60-mL capacity, with medium porosity glass frit.

5.6 *Vials,* screw cap, 4-dram and 1-dram capacities, with PTFE-lined caps.

5.7 *Freezer Mill,* for pulverizing samples at liquid nitrogen temperature.[6,7]

5.8 *Bottles,* screw cap, wide-mouth, 2-oz capacity, with PTFE-lined caps.

5.9 *Sample Filter,* consisting of a syringe and 0.45-µm filter assembly to remove microparticulate matter from the prepared sample solution.[7,8]

5.10 *Tube,* borosilicate glass, approximately 8-in. long by 1-in. diameter with tapered end, for warming cryogenically ground resin samples to ambient temperature (see Fig. 1).

5.11 *Solvent Evaporation Assembly*—See Fig. 2.

5.12 *Silica Gel Purification Column.*[7,9]

6. Reagents

6.1 *Methanol,* chromatographic grade, distilled in glass.

6.2 *Acetonitrile,* chromatographic grade, distilled in glass.

6.3 *Water,* prepare Type II reagent water in accordance with Specification D1193, or distill deionized water. Filter through a 0.45-µm filter[7,10] and store in a glass container.

6.4 *Acetonitrile:Water, 70:30*—Mix 7 volumes of acetonitrile with 3 volumes of water.

6.5 *Acetonitrile:Water, 30:70*—Mix 3 volumes of acetonitrile with 7 volumes of water.

6.6 *Acetonitrile:Water, 95:5*—Mix 9.5 volumes of acetonitrile with 0.5 volumes of water.

6.7 *Methylene Chloride,* chromatographic grade, distilled in glass.

6.8 *Dibutyl Phthalate,* purified.[7,11]

6.9 *Dibutyl Phthalate Internal Standard* (approximately 7.0 mg/mL)—Weigh 7.0 ± 0.1 g of dibutyl phthalate to the nearest 0.1 mg. Dissolve in methanol and quantitatively transfer to a 1-L volumetric flask. Dilute to volume with methanol and mix thoroughly. Calculate the exact concentration of dibutyl phthalate.

6.9.1 Long-term storage of a methanolic solution of dibutyl phthalate should be avoided. Dibutyl phthalate in the presence of traces of acidic or basic impurities may transesterify. If transesterification occurs, the dibutyl phthalate peak will slowly decrease, and the appearance of the methylbutyl phthalate peak (k_1 value about 3.8) will be noted.

6.10 *Dibutyl Phthalate Internal Standard* (approximately 0.7 mg/mL)—Pipet 100 mL of dibutyl phthalate standard (6.9, approximately 7 mg/mL) into a 1-L volumetric flask. Dilute to volume with methanol and mix thoroughly. Calculate the exact concentration of dibutyl phthalate.

6.11 *Benzyl Alcohol,* purified.[7,12]

6.12 *Benzyl Alcohol Internal Standard* (approximately 15.0 mg/mL)—Weigh 15.0 ± 0.1 g of benzyl alcohol to the nearest 0.1 mg. Dissolve in methanol and quantitatively transfer to a 1-L volumetric flask. Dilute to volume with methanol and mix thoroughly. Calculate the exact concentration of benzyl alcohol.

6.13 *Benzyl Alcohol Internal Standard* (approximately 1.5 mg/mL)—Pipet 100 mL of benzyl alcohol standard (6.12, approximately 15 mg/mL) into a 1-L volumetric flask. Dilute to volume with methanol and mix thoroughly. Calculate the exact concentration of benzyl alcohol.

6.14 *Dicumyl Peroxide, Recrystallized*—Transfer 25.0 g of commercial refined dicumyl peroxide into a 100-mL Erlenmeyer flask. Add 8.0 mL of methanol and gently warm the

[5] Satisfactory results were obtained using Waters µ-Bondapak C-18 (Cat. No. 27324) and Waters Radial PAK C-18 (Cat. No. 84720) columns in a round-robin evaluation of the test method. Available from Waters Corporation, 34 Maple St., Milford, MA 01757. Equivalent results should be obtainable with other commercial C-18 reversed phase columns.

[6] The sole source of supply of the apparatus known to the committee at this time is Spex Freezer/Mill, Catalog No. 6700, available from SPEX CertiPrep, 203 Norcross Ave., Metuchen, NJ 08840, www.spexcsp.com.

[7] 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.

[8] The sole source of supply of the apparatus known to the committee at this time is Waters Associations Sample Clarification Kit, Catalog No. 26870, available from Waters Corporation, 34 Maple St., Milford, MA 01757.

[9] The sole source of supply of the apparatus known to the committee at this time is SEP-PAK silica gel cartridges, Waters No. 51-900, available from Waters Corporation, 34 Maple St., Milford, MA 01757.

[10] The sole source of supply of the apparatus known to the committee at this time is a 0.45-µm Millipore type HA filter, available from Millipore retail locations (Millipore Corporate Headquarters, 290 Concord Road, Billerica, MA 01821, www.millipore.com).

[11] The sole source of supply of the apparatus known to the committee at this time is Dibutyl phthalate, Aldrich Chemical Co. No. 15243-9, available from Aldrich Chemical Company, Inc., 940 W. St. Paul Ave., Milwaukee, WI 53233-2625, www.sigmaaldrich.com.

[12] The sole source of supply of the apparatus known to the committee at this time is Benzyl alcohol, No. B1620-8, available from Aldrich Chemical Company, Inc., 940 W. St. Paul Ave., Milwaukee, WI 53233-2625, www.sigmaaldrich.com.

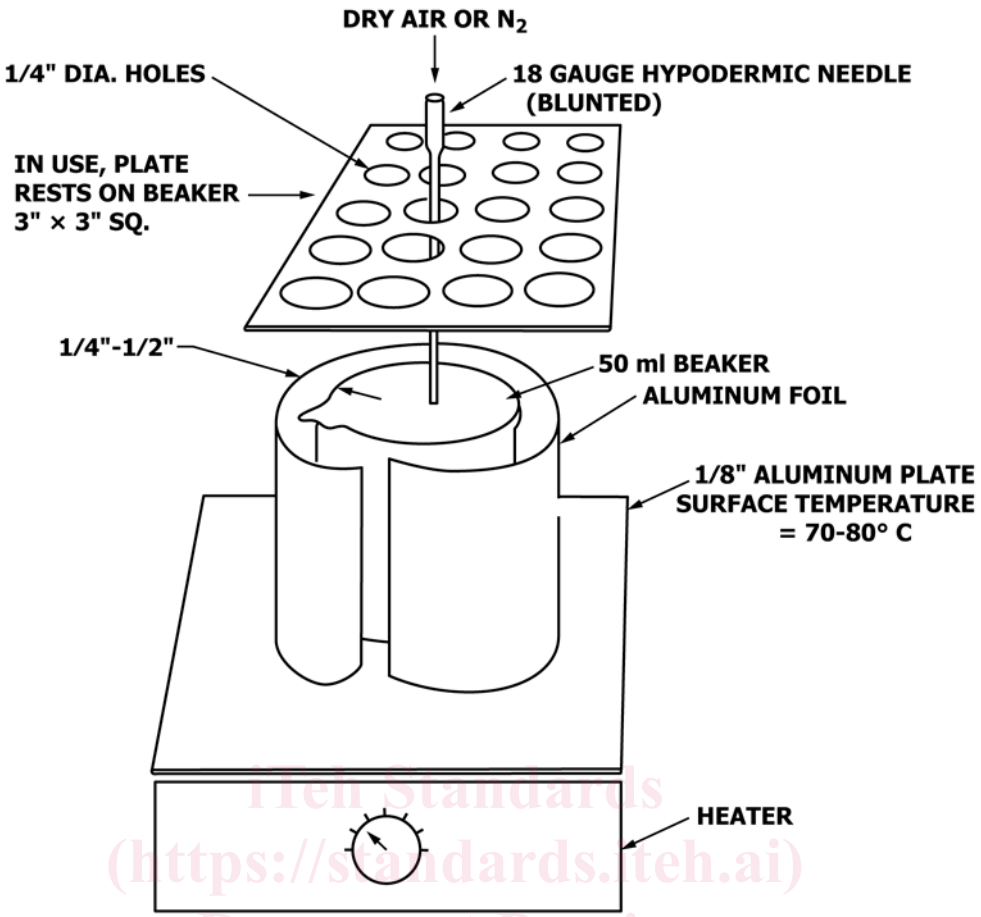

FIG. 2 Solvent Evaporation Assembly for Preventing Accumulation and Loss of Volatile Compounds

solution in a water bath while swirling, to effect complete solution. Cool to 0°C in an ice bath. Transfer the contents to a medium-porosity sintered glass crucible and vacuum filter. Allow air to pass through the filter for 10 to 15 min, to dry the peroxide. Repeat the crystallization twice using approximately 1 mL of methanol for every 3 g of peroxide. Place the recrystallized dicumyl peroxide in a tightly capped bottle and store in the refrigerator. *Caution*—see Section 7.

6.15 *Acetophenone,* purified.[7,13]

6.16 *α,α-Dimethylbenzyl Alcohol (DMBA)*—Dissolve 0.2 g of α,α-dimethylbenzyl alcohol[7,14] in 2 mL of 98:2 *n*-hexane:chloroform. Transfer the solution into a 5-mL syringe and carefully pass the solution through a SEP-PAK silica gel cartridge. Discard the eluate. Wash the column with an additional 2 mL of 98:2 *n*-hexane:chloroform and again discard the eluate. Then, elute the DMBA with 5 mL of chloroform, collecting the eluate in a 50-mL filtering flask. Stopper the flask and attach the side arm to a water aspirator. Immerse the flask in a water bath maintained at 35 to 40°C until the chloroform has completely volatilized. Store the purified DMBA in a sealed vial.

7. Hazards

7.1 Organic peroxides are strong oxidizing agents and present potential fire and explosion hazards. Reactivity varies widely and some compounds may explode when shocked. While dicumyl peroxide is one of the more stable peroxides, contact with reducing agents and sources of heat, sparks, or open flame must be avoided. Organic peroxides in general are irritating to the skin, eyes, and mucous membranes. Avoid bodily contact and handle only in a well-ventilated area.

7.2 Small quantities of solid or molten dicumyl peroxide can be safely handled at temperatures up to 55°C. Dicumyl peroxide should not be heated above 55°C as the rate of peroxide decomposition rapidly increases with increasing temperatures above this point.

7.3 Only a water bath that has been preheated to the desired temperature and removed from the heat source should be used for warming vessels containing dicumyl peroxide. Electrically heated water baths should not be used as they may cause localized hot spots. Other sources of heat considered unsafe for warming containers of dicumyl peroxide include ovens, hot plates, and direct steam.

[13] The sole source of supply of the apparatus known to the committee at this time is Acetophenone, 99 %, Aldrich Chemical Co. No. A1,070-1, available from Aldrich Chemical Company, Inc., 940 W. St. Paul Ave., Milwaukee, WI 53233-2625, www.sigmaaldrich.com.

[14] The sole source of supply of the apparatus known to the committee at this time is α,α-Dimethylbenzyl alcohol, 99 %, Fluka Chemical Corp. No. 78940, available from Fluka Chemical Corp., 1001 W Saint Paul Ave., Milwaukee, WI 53233-2641, www.sigmaaldrich.com.