



Designation: E 1090 – 96

Standard Test Method for Dicumyl Peroxide and Dicumyl Peroxide Decomposition Products in Resins¹

This standard is issued under the fixed designation E 1090; 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 is applicable to the determination of dicumyl peroxide² 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 *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 7.

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

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

E 300 Practice for Sampling Industrial Chemicals⁴

E 682 Practice for Liquid Chromatography Terms and Relationships⁵

E 685 Practice for Testing Fixed-Wavelength Photometric Detectors Used in Liquid Chromatography⁵

E 755 Test Method For Assay of Dicumyl Peroxide by Liquid Chromatography⁴

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 E 755.

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 E 682 and E 685.)

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 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.⁶

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.

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.

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² Dicumyl peroxide; peroxide, bis(1-methyl-1-phenylethyl) C₁₈H₂₂O₂; CAS Registry No. 80-43-3.

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

⁴ *Annual Book of ASTM Standards*, Vol 15.05.

⁵ *Annual Book of ASTM Standards*, Vol 14.01.

⁶ 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. Equivalent results should be obtained with other commercial C-18 reversed phase columns.

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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.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- μ m filter assembly to remove microparticulate matter from the prepared sample solution.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*.⁹

6. Reagents

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

⁷ A Spex Freezer/Mill, Catalog No. 6700, has been found to be satisfactory for this purpose. This mill is available from Spex Industries, Inc., Metuchen, NJ.

⁸ Waters Associations Sample Clarification Kit, Catalog No. 26870, was found to be satisfactory for this purpose.

⁹ SEP-PAK silica gel cartridges, Waters No. 51-900, have been found to be suitable for this purpose.

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

6.3 *Water*, prepare Type II reagent water in accordance with Specification D 1193, or distill deionized water. Filter through a 0.45- μ m filter¹⁰ 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.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

¹⁰ A 0.45- μ m Millipore type HA filter was found to be satisfactory for this purpose.

¹¹ Dibutyl phthalate, Aldrich Chemical Co. No. 15243-9, was found to be satisfactory for this use.

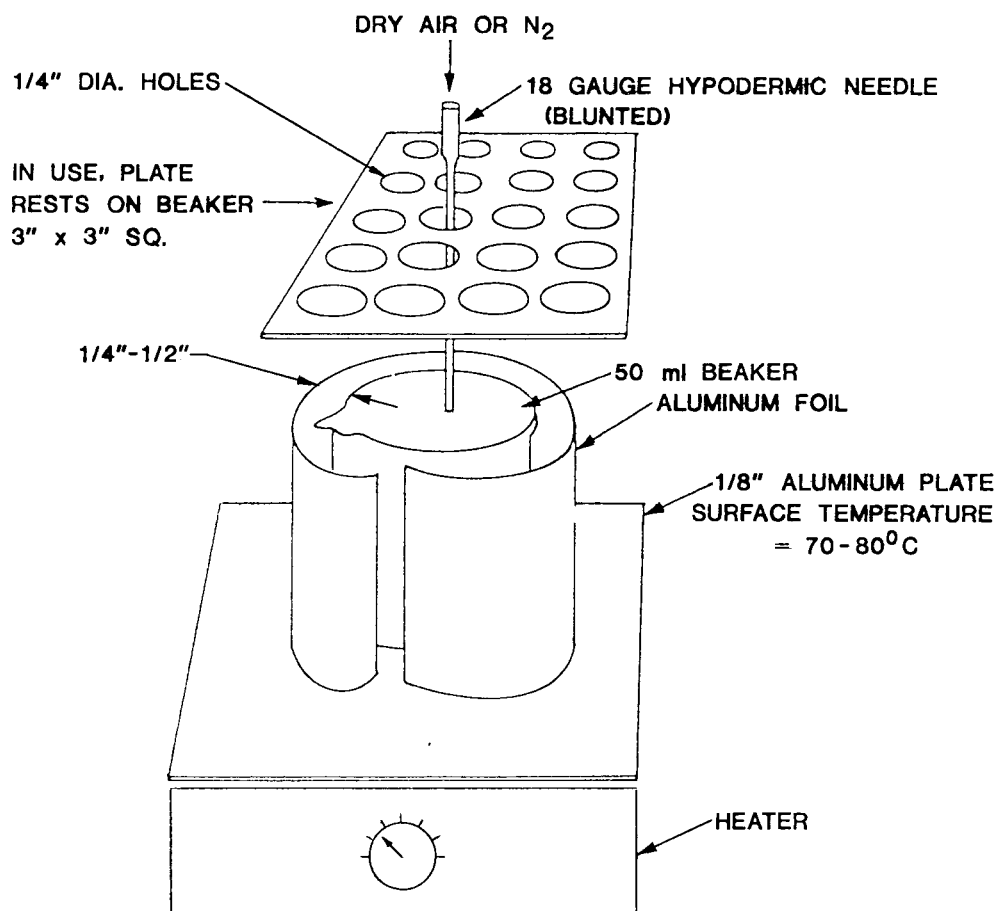


FIG. 2 Solvent Evaporation Assembly for Preventing Accumulation and Loss of Volatile Compounds