



Designation: D7767 – 11

Standard Test Method to Measure Volatiles from Radiation Curable Acrylate Monomers, Oligomers, and Blends and Thin Coatings Made from Them¹

This standard is issued under the fixed designation D7767; 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 describes a means to determine the percentage of processing, potential, and total volatiles from radiation curable acrylate monomers, oligomers, and blends. The results can be used to estimate the volatiles from thin radiation curable coatings that cannot otherwise be measured with the restriction that those coatings are not subjected to a pre-exposure water or solvent drying step. It also provides a means to determine the volatiles of thin radiation curable coatings in the absence of known interferences such as pigments in inks.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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:²

D5403 Test Methods for Volatile Content of Radiation Curable Materials

E145 Specification for Gravity-Convection and Forced-Ventilation Ovens

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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² 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.

2.2 Other Document:³

EPA Method 24 Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings

3. Terminology

3.1 Definitions:

3.1.1 *cure, n*—conversion of a coating from its application state to its final use state measured by tests generally related to end use performance and mutually agreeable to supplier and purchaser.

3.1.2 *electron beam (EB) curing, n*—conversion of a coating from its application state to its final use state by means of a mechanism initiated by electron impingement generated by equipment designed for that purpose.

3.1.3 *pigment, n*—an insoluble substance added to a formulation to modify the visual appearance of a coating made from the formulation.

3.1.4 *potential volatiles, n*—the percentage loss in specimen weight upon heating at 110°C for 60 min after radiation curing.

3.1.5 *processing volatiles, n*—the percentage loss in specimen weight under process conditions that are designed to simulate actual industrial cure processing conditions.

3.1.6 *retained weight, n*—the mass of specimen remaining after exposing to the UV source, heating in an oven, or both.

3.1.7 *thin, adj*—less than 15 micrometres in thickness.

3.1.8 *total volatiles, n*—the percentage loss in specimen weight under process conditions that are designed to simulate actual industrial cure processing conditions and after heating at 110°C for 60 min.

3.1.9 *ultraviolet (UV) curing, n*—conversion of a coating from its application state to its final use state by means of a mechanism initiated by ultraviolet radiation in the range from 200 to 400 nm generated by equipment designed for that purpose.

³ Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, <http://www.access.gpo.gov>.

3.1.10 *UVA, n*—the region of the electromagnetic spectrum comprising wavelengths falling in the range between 320 and 390 nm.

4. Summary of Test Method

4.1 A designated quantity of an acrylate-functional material (test specimen) is weighed in a container lid before and after a UV exposure step sufficient to ensure a thorough cure of the test specimen to obtain the percent solids retained. The calculated percentage weight loss is attributed to process volatiles. The test specimen and container lid are weighed again after heating for 60 min at $110 \pm 5^\circ\text{C}$ to obtain the percent solids retained. Any additional weight loss is attributed to potential volatiles. The total volatiles for a test specimen are the difference between the initial sample mass and the retained mass after exposing and heating divided by the initial mass.

5. Significance and Use

5.1 This test method is an extension of Test Method **D5403**. While Test Method **D5403** specifies that a test specimen be cured by exposure to UV or EB as prescribed by the supplier of the material, most radiation curable monomers and oligomers provided as raw materials to formulators are not designed to be used alone but rather as blends of monomers and oligomers so that there are no “supplier prescribed” exposure conditions. Test Method **D5403** is not appropriate for the measurement of volatiles from thin radiation-curable coatings because supplier prescribed cure conditions include both a thickness and an exposure specification which are difficult or impossible to achieve in a test lab. Furthermore, inks form a special class of thin radiation curable coatings because they are formulated with known interferences (for example, pigments). As a result, Test Method **D5403** does not provide a method for measuring volatiles from monomers and oligomers used as raw materials in the formulation of radiation curable coatings nor does it provide a method for measuring volatiles from thin radiation curable coatings such as inks.

5.2 This test method provides a means to measure the volatile content of individual acrylate monomers, oligomers, and blends commonly used to formulate radiation curable coatings such as printing inks. Such coatings comprise liquid or solid reactants that cure by polymerizing, crosslinking, or a combination of both and are designed to be applied as thin coatings in the absence of water or solvent and to be cured by exposing to ultraviolet radiation. There is currently no direct method for measuring the volatiles from the individual materials used or thin coatings made from them.

5.3 This test method also provides a means to measure the volatiles from acrylate monomers, oligomers, and blends cured using ultraviolet radiation from which an estimate for the volatiles from a thin coating cured using ultraviolet radiation comprising these acrylate monomers, oligomers, and blends can be calculated. A common exposure step involving a specified amount of ultraviolet radiation in a specific spectral range using a common photoinitiator is called for.

5.4 This test method further provides a means to measure the volatiles from thin radiation-curable coatings such as inks in the absence of known interferences such as pigments. A

common exposure step involving a specified amount of ultraviolet radiation in a specific spectral range using a common photoinitiator is called for.

5.5 If desired, volatile content can be determined as two separate components: processing volatiles and potential volatiles. Processing volatiles are a measure of volatile loss during the actual cure process. Potential (or residual) volatiles are a measure of volatile loss that might occur upon aging or under extreme storage conditions. These volatile content measurements may be useful to the producer of a material, a formulator using such materials, or to environmental interests for determining and reporting emissions.

5.6 The validity of this test method for non-acrylated radiation-curable chemistries such as methacrylates, thiol-ene, vinyl ethers, and epoxies cured using ultraviolet radiation has not been verified. Use of an electron beam to cure the acrylate monomers, oligomers, and blends or thin coatings made from them, including inks, has not been verified using this method and cannot be assumed.

6. Interferences

6.1 The degree to which the results of this procedure accurately measure the volatiles emitted is absolutely dependent upon proper cure during the test procedure. Although overcure will have little or no effect upon measured volatiles, undercure may lead to erroneously high values. To minimize variability in the cure conditions, an ultraviolet source providing a given irradiance in a specific spectral region and an exposure energy is specified as is a photoinitiator and concentration.

6.2 The presence of strong ultraviolet absorbing non-acrylate species such as pigments and ultraviolet blockers can interfere with the ability of this test procedure to accurately measure volatiles. These additives are designed to absorb, reflect, luminesce, or scatter visible or ultraviolet radiation. Such additives interfere with the proper cure of materials tested using this method and are to be avoided.

6.3 Photoinitiators are strong ultraviolet absorbers but their presence is required for proper curing.

7. Apparatus

7.1 *Container Lids*, metal can lids having an OD of 35 mm and a height of 14 mm with a 25 mm diameter protrusion which, when inverted, creates a 0.6 mm deep, 25 mm diameter well.⁴

7.2 *Forced Draft Oven, Type IIA or IIB* as specified in Specification **E145**.

7.3 *Ring Stand*, a device designed to support items using various clamps.

7.4 *Versatile Clamp*, a 3-pronged clamp with adjustable closure for holding items.

⁴ Metal can lids for this method can be obtained from SKS Bottle & Packaging (Watervliet, NY).

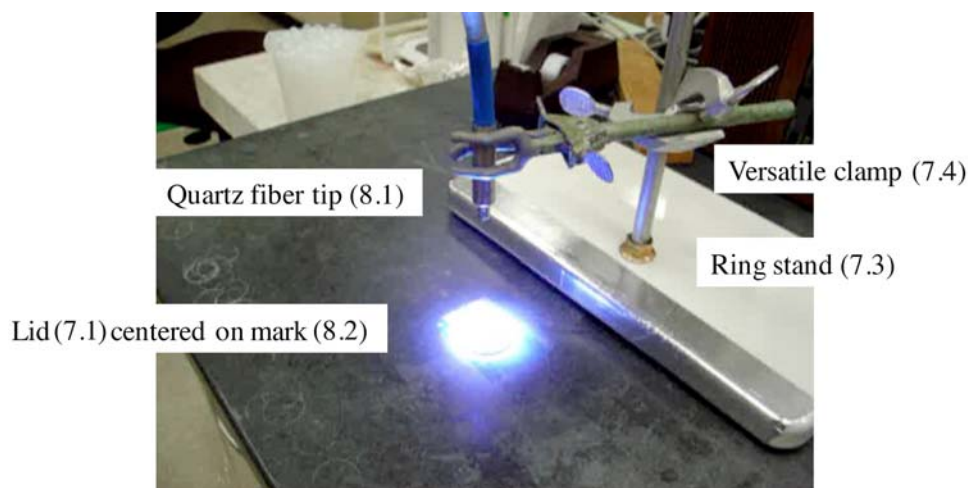


FIG. 1 Photo of Fiber Alignment Relative to Metal Lid During Exposure

7.5 *Ultraviolet Radiation Source*, the focused output from a short-arc 200W Xe/Hg bulb delivered by a quartz fiber guide.⁵

7.6 *Radiometer*, a device able to measure irradiance and energy in the UVA spectral region.⁶

7.7 *Balance*, an instrument capable of weighing a mass to the nearest 0.1 mg.

7.8 *Gloves*, personal protective wear for handling chemicals.

7.9 *Forceps or Tongs*, a means to handle a specimen without direct contact in order to minimize mass transfer.

7.10 *Spreading Tool*, a small metal or PTFE spatula or a wooden applicator stick for spreading resin.

8. Preparation of Apparatus

8.1 The tip of the quartz fiber guide shall be positioned normal to the center of a container lid (7.1) at a height of approximately 80 to 85 mm from the container lid to provide an illuminated circular area of approximately 40 to 45 mm in diameter in the plane on which the container lid (7.1) sets in order to approximate uniform irradiance of the test specimen.

8.2 Identify the approximate center of the illuminated area with a mark which will later assist in positioning of a container lid with a test specimen. A 25 mm filter paper disk taped to the work area surface works well for this. A proper setup is shown in Fig. 1.

NOTE 1—Placement of a mark is best accomplished with the shutter open. Wear appropriate eye protection before opening the shutter and placing the mark.

8.3 Center the optical window of the radiometer on the mark (8.2). Using the ultraviolet radiation source (7.5) set at 100 % power with the fiber (8.1) and radiometer optical window (7.6) properly aligned, open the shutter and measure the UVA peak irradiance at the sample plane. If necessary, adjust the fiber

height to achieve a UVA peak irradiance of $115 \pm 15 \text{ mW/cm}^2$. Once positioned, the fiber should not be moved relative to the mark (8.2).

8.4 Position the radiometer window (7.6) on the mark (8.2) and measure the UVA energy after an 80 s exposure. If necessary, adjust the exposure time to achieve a UVA target energy of $9.0 \pm 0.2 \text{ joules/cm}^2$. This determination should be repeated daily to verify proper exposure conditions.

9. Procedure

9.1 Dissolve 2.0 % by weight of ethyl-2,4,6-trimethylbenzoylphenylphosphine (TPO-L) photoinitiator in the material to be tested. Mix thoroughly to ensure homogeneity. Store the test specimen in a dark container.

9.2 Precondition the container lids for 30 min at $110 \pm 5^\circ\text{C}$ and store in a desiccator prior to use.

9.3 Weigh a preconditioned container lid (7.1) to 0.1 mg (A). Use gloves, forceps, or tongs to handle the container lid.

9.4 Place the container lid upside down on the balance pan and add $0.2 \pm 0.02 \text{ g}$ of the test specimen (9.1) to the recessed area. Spread the test specimen using a spreading tool to ensure uniform coverage of the recessed area. Do not allow the test specimen to contact any surface of the container lid outside of the recessed area. Weigh the container lid with test specimen to 0.1 mg (B).

NOTE 2—It is helpful to hold the container lid with one hand using gloves, forceps, or tongs while spreading the test specimen with the spreading tool in the other. The elapsed time between spreading and weighing should be no greater than 60 s. If the sample to be tested contains any reactive diluent with a vapor pressure at room temperature greater than 1.0 mm Hg, the elapsed time between spreading and weighing must be no greater than 30 s.

NOTE 3—Low viscosity test specimens spread easily and a uniform thickness can be obtained. High viscosity test specimens are more difficult to work with but it is important to spread as evenly as is practical. Air bubbles shall be removed, if possible.

9.5 Center the container lid with test specimen on the mark (8.2) using gloves, forceps, or tongs, being careful not to

⁵ This test method was developed using an LC-8 SpotCure source from Hamamatsu Corporation (Bridgewater, NJ).

⁶ Power Puck II from EIT (Sterling, VA).