Designation: D7767 – 11

Standard Test Method to Measure Volatiles from Radiation Curable Acrylate Monomers, Oligomers, and Blends and Thin Coatings Made from Them[1]

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

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.

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[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials.

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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.

[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 ± 5°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.

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

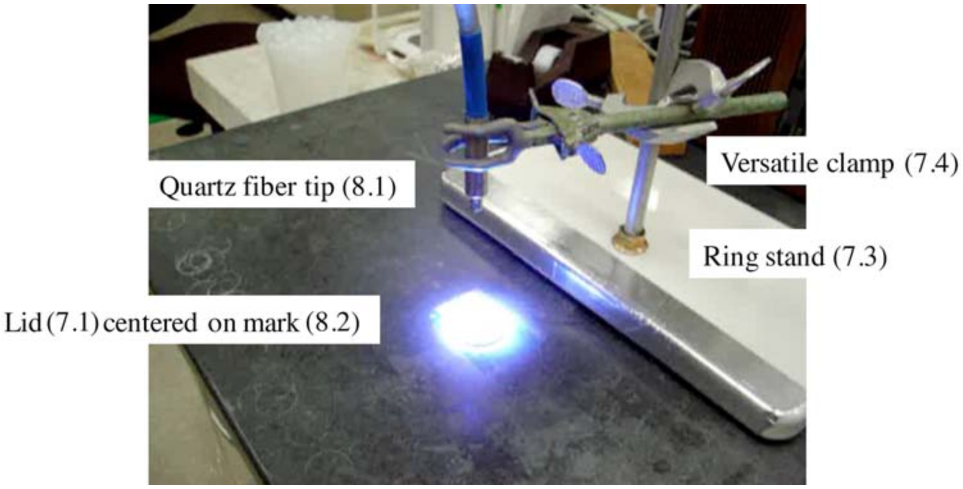

FIG. 1 Photo of Fiber Alignment Relative to Metal Lid During Exposure

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 ± 15 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 ± 0.2 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-trimethylbenzoyphenylphosphinate (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 ± 5°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 ± 0.02 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

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[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).

TABLE 1 Calculation of Estimated Volatiles for a Coating using Method A

Reactive Components in Composition	Weight Percentage of each Monomer, Oligomer, or Blend in the Composition	Total Percent Volatiles for each Monomer, Oligomer, or Blend in the Composition (10.2.1)	Total Percent Volatiles in Composition based on Weight Percentages
Acrylate 1	30.0	1.67	0.50
Acrylate 2	60.0	0.43	0.26
Acrylate 3	10.0	3.14	0.31
Totals	100.0	NA	1.07

TABLE 2 Determination of Volatiles from Blends and Fully Formulated Coatings using Method B

Components in Composition (I)	Weight Percentage of each Component in Fully Formulated Ink (II)	Weight Percentage of each Component in Test Specimen (III)	Total Percent Volatiles of Test Specimen (IV)
Acrylate 1	22.5	24.0	
Acrylate 2	45.0	49.0	
Acrylate 3	7.5	8.2	
Inert Filler	5.8	6.3	
Photoinitiator 1	6.0	6.5	
Amine Synergist	3.0	3.3	
Flow Aid	0.2	0.2	
Photoinitiator (Note 7)	0.0	2.0	
Pigment	10.0	0.0	
Totals	100.0	100.0	1.50

TABLE 3 R_{bake}

Expected R_{bake}	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{X}$	s_r	S_R	r	R
>99 %	99.6358	0.1654	0.2195	0.4631	0.6147
98 % – 99 %	98.5094	0.4852	0.5469	1.3586	1.5314
<98 %	96.0745	0.2169	0.4887	0.6075	1.3685

[A] The average of the laboratories' calculated averages.

disrupt the area of the container lid in contact with the test specimen. This is critical to ensure good repeatability.

NOTE 4—If the test specimen flows beyond the recessed area of the container lid during transport from the balance to the mark, the sample must be discarded and the procedure repeated.

9.6 Open the shutter for the exposure time determined in 8.4 to provide 9.0 ± 0.2 joules/cm ^{2} UVA energy.

NOTE 5—Acrylate polymerization is accompanied by a reaction exotherm. Some very reactive monomers such as 1,6-hexanediol diacrylate react extremely fast and generate enough heat such that the cured test specimen can shatter, sometimes resulting in expulsion of some of the cured test specimen from the container lid. If this occurs, the sample must be discarded and a fresh specimen tested.

9.7 If determination of process and potential volatiles is desired, cool the test specimen for 15 min in a desiccator then reweigh the container lid with test specimen to 0.1 mg (*C*).

9.8 Repeat steps 9.3-9.7 until each of three container lids with exposed specimen is deemed acceptable per Note 4 and Note 5.

9.9 Heat the container lids with test specimen in a forced draft oven (7.2) for 60 min at 110 ± 5°C.

9.10 Allow the container lid with test specimen to cool to room temperature in a desiccator for 15 min and reweigh to 0.1 mg (*D*).

10. Calculation or Interpretation of Results

10.1 Determine the retained weight percentage after UV exposure (R_{UV}) and after baking (R_{bake}) and calculate the weight percent volatiles using the following equations:

$$R_{UV} = 100\left[(C - A)/(B - A)\right] \tag{1}$$

$$R_{bake} = 100\left[(D - A)/(B - A)\right] \tag{2}$$

$$\textit{Processing Percent Volatiles} = 100 - R_{UV} \tag{3}$$

$$\textit{Potential Percent Volatiles} = R_{UV} - R_{bake} \tag{4}$$

$$\textit{Total Percent Volatiles} = 100 - R_{bake} \tag{5}$$

where:

A = weight of container lid, g
B = weight of container lid plus test specimen, g
C = weight of container lid plus test specimen after UV cure, g, and
D = weight of container lid plus cured test specimen after heating, g.

10.2 Measurement of total percent volatiles for a neat monomer, oligomer or blend.

10.2.1 This test method allows the total percent volatiles of an acrylate monomer, oligomer, or blend to be determined based on the retained test specimen weights after exposing and baking. Representative materials include acrylate-functional raw materials that are used in formulating radiation curable coatings and inks such as tripropyleneglycol diacrylate, a polyurethane acrylate oligomer, and an epoxy acrylate oligomer diluted with trimethylolpropane triacrylate.

NOTE 6—The total percent volatiles includes a small contribution from the photoinitiator (9.1) which was measured using EPA Method 24 in which a sample of ethyl-2,4,6-trimethylbenzoylphenylphosphinate (9.1) was heated in a forced draft oven (7.2) for 60 min at 110 ± 5°C. The weight loss from the neat photoinitiator was found to be 1.11 %. Thus, the contribution from the ethyl-2,4,6-trimethylbenzoylphenylphosphinate present at the 2 % level in a test specimen contributes 0.02 % to the total percent volatiles using this test method.

10.3 Determination of total percent volatiles for a UV-curable acrylate coating.

10.3.1 *Method A — Estimating the Total Percent Volatiles for a UV-Curable Coating based on the Weighted Contribution of the Individual Components*—Table 1 illustrates how to estimate the total percent volatiles for a thin radiation curable coating using a weighted contribution of the total percent volatiles from each acrylate component present in the coating as determined using 10.2. In this example, the estimated total percent volatiles for the coating based on the individual acrylate components is 1.07 %. The same procedure can be applied to estimate a processing percent volatiles and potential percent volatiles for the coating, if desired. Note that Method A does not include contributions from other photoinitiators and non-acrylate additives including interferences that might be present in a fully formulated coating or synergistic effects of blending high and low functionality monomers, oligomers or blends and is therefore likely to provide the least accurate value of the actual total percent volatiles.

10.3.2 *Method B — Determining the Total Percent Volatiles for a UV-Curable Coating based on Testing a Blend of the Individual Components*—While 10.3.1 can be used to estimate the total percent volatiles for a UV-curable coating, a more preferred method is to measure the total percent volatiles on a fully formulated coating, less any known interferences. This method is most appropriate for UV inks or acrylate blends where synergistic effects due to functionality are expected. The blend shown in Table 2 contains all of the acrylate components listed in Table 1 in the same relative amounts in addition to a variety of non-acrylate components such as a photoinitiator package, flow aids, and amine synergists. Note that the addition of the 2.0% ethyl-2,4,6-trimethylbenzoylphenylphosphinate (9.1) is still required in the test specimen. Method B can be used to determine the total percent volatiles for a formulation that eliminates the need to measure the total percent volatiles of the individual components. The processing percent volatiles and potential percent volatiles can also be determined, if desired.

NOTE 7—If interferences are present in the fully formulated coating, the total percent volatiles value calculated for the blend less the interferences must be corrected by multiplying the total percent volatiles by one minus the percentage of interferences in the coating. Thus, if the volatiles for a fully formulated ink having the composition shown in Table 2 column II were to be determined using Method B, the composition without pigment shown in column III would be tested in which the compositional weight percentages remain the same and the required photoinitiator (9.1) is added. If the total percent volatiles were determined to be 1.50 %, then the total percent volatiles for the fully formulated composition with 10 % pigment would be 90 % of the value measured or 1.35 %. Correcting this value for the 0.02 % volatiles contribution from the required photoinitiator (Note 6), the reported value would be 1.33 %. This assumes that the total percent volatiles for the interferences is zero. If desired, a total percent volatiles contribution for these interferences can be measured using alternative methods such as EPA Method 24.

11. Precision and Bias[7]

11.1 The precision of this test method is based on an intralaboratory study of ASTM D7767, Test Method to Measure Volatiles from Radiation Curable Acrylate Monomers, Oligomers, and Blends and Thin Coatings Made from Them, conducted in 2010. Nine laboratories participated in this study, analyzing materials representing three different property types. Each "test result" reported represents an individual determination and the participating labs reported three to twelve replicate test results for each material type. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report No. D01–1159.

11.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

11.1.1.1 Repeatability limits are listed in Table 3.

11.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

11.1.2.1 Reproducibility limits are listed in Table 3.

11.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

11.1.4 Any judgment in accordance with statements 11.1.1 and 11.1.2 would have an approximate 95 % probability of being correct.

11.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

11.3 The precision statement was determined through statistical examination of 189 test results, reported by nine laboratories, on three types of materials.

12. Keywords

12.1 acrylic monomers; acrylics; blends; electron beam curing; inks; oligomers; photoinitiator; pigmented coatings; radiation curable material; radiation curing; ultraviolet curing; volatile content

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1159.

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