Designation: D6093 – 97 (Reapproved 2022)

Standard Test Method for Percent Volume Nonvolatile Matter in Clear or Pigmented Coatings Using a Helium Gas Pycnometer[1]

This standard is issued under the fixed designation D6093; 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 the determination of the percent volume nonvolatile matter of a variety of clear and pigmented coatings. The approach used should provide faster and more accurate results than the use of the liquid displacement technique in Test Method D2697, particularly for coatings that are difficult to wet or that contain voids, cracks or other defects. The improvement in accuracy stems from the superior ability of helium gas under pressure to penetrate very small pores and surface irregularities in dried films. This provides a more accurate determination of void volumes than can be obtained via liquid displacement.

1.2 The technique will provide results under the following constraints:

1.2.1 The stability of the helium gas pycnometer is greater than ±0.005 cm^3.

1.2.2 Test specimen weights are greater than 1 g.

1.3 The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are mathematical conversions to SI units that are provided for information only and are not considered standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1475 Test Method for Density of Liquid Coatings, Inks, and Related Products

D2369 Test Method for Volatile Content of Coatings

D2697 Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings

D3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings

D4708 Practice for Preparation of Uniform Free Films of Organic Coatings

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

2.2 *Other Documents:*

2.2.1 Directions for obtaining appropriate instruction manuals on the use, care, and operation of the instruments and equipment are listed in Section 5, (Apparatus).

3. Summary of Test Method

3.1 This procedure measures the volume of nonvolatile material in a dried or baked coating film. A helium gas pycnometer is used to determine the volume occupied by a film by measuring the reduction of gas capacity in the pycnometer sample chamber caused by the presence of the test specimen. (The actual measurement is accomplished with a pressure transducer that measures the difference in pressure between the empty sample compartment and when loaded. The volume occupied by the coating sample is then calculated from the Ideal Gas Law.) The weight of the specimen is also measured and the two values are used to calculate the dry film density.

3.2 The percent volume nonvolatile content of a coating is calculated using the dry film density, liquid coating density, and the weight percent nonvolatile content of the coating.

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

4. Significance and Use

4.1 This test method measures the volume of dry coating obtainable from a given volume of liquid coating. This value is useful for calculating the volatile organic content (VOC) of a coating and could be used to estimate the coverage (square feet of surface covered at a specified dry film thickness per unit volume) obtainable with different coating products.

NOTE 1—In Practice D3960 paragraph 10.3.1, the equation for calculating the VOC content using the percent volume nonvolatile is given. Prior to this method a satisfactory procedure for measuring percent volume nonvolatile did not exist (see Note 11 in Practice D3960).

NOTE 2—Since the actual coverage of a coating includes the void volume and the porosity of the film, the coverage value calculated from this method will be inaccurate by that amount, that is, the actual coverage will be greater. The higher the pigment to binder ratio (P/B) of a coating or the higher content of void containing material (latices, hollow beads, etc.) or both, the greater will be the deviation of the coverage calculation (This is also true to a lesser degree with Test Method D2697).

4.2 For various reasons the volume nonvolatile value obtained for a coating is often not equal to that predicted from simple linear addition of the weights and volumes of the raw materials in a formulation. One reason is that the volume occupied by a solution of resin in solvent may be the same, greater, or less than the total volume of the separate ingredients. Such contraction or expansion of resin solutions is governed by a number of factors, one of which is the extent and direction of spread between solubility parameters of the resin and solvent.

4.3 The spatial configuration of the pigment particles and the degree to which the pigment particles are filled with the binder also affect the volume of a dry coating film. Above the critical pigment volume concentration, the apparent volume of the dry film is significantly greater than theoretical due to the increase in unfilled voids between pigment particles. The use of volume nonvolatile matter values in such instances should be carefully considered as the increased volume is largely due to air trapped in these voids.

4.4 For thin films, the issue of critical pigment volume effects is usually not a concern. With high poly(vinyl chloride) (PVC) films, however, liquid displacement of air voids takes place with difficulty even under high pressures. Helium solves this problem since, as a gas, it readily penetrates and displaces air, water, and volatile solvents even at low pressures. Purging the gas pycnometer flushes these materials from the film.

5. Apparatus and Reagents

5.1 *Gas Pycnometer,* equipped with a suitably sized cup.

NOTE 3—The data from the round robin was obtained using a 5-mL cup instrument. [4]

5.2 *Panels,* steel or aluminum, 4 in. by 12 in. (102 mm by 305 mm).

5.3 *Sheeting*[5], approximately 1.5-mils (38-µm) thick.

5.4 *Doctor Blades,* 5 mils to 8 mils (127 µm to 203 µm), appropriate to give 1.0 mils to 1.8 mils (25 µm to 46 µm) dry film thickness). A 3 in. (76 mm) wide, multiple clearance applicator is recommended.

5.5 *Standard Spray Equipment,* capable of obtaining a uniform film of 1.0 mil to 1.8 mil (25 µm to 46 µm) dry film thickness after baking.

5.6 *Forced Draft Oven,* capable of maintaining 110 °C ± 5 °C.

5.7 *Single Edge Razor Blades* or *Scalpels,*

5.8 *Anti-Static Instrument.*[6]

5.9 *Analytical Balance,* capable of weighing to ±0.0001 g.

5.10 *A Paper/Thin Film Cutter,* equipped with a rolling blade, available from most office supply centers.

5.11 *Polyethylene Gloves* and *Plastic Tweezers.*

6. Procedure

6.1 Determine the wet coating density (pounds per gallon) in accordance with Test Method D1475.

6.2 Determine the weight percent nonvolatile content of the liquid sample in accordance with Test Method D2369.

6.3 Wrap 4-in. by 12-in. panels (102-mm by 305-mm), (two per sample) with sheeting [5] and tape the sheeting to the back of the panels with masking tape. Do not overlap the sheeting on the backs of the panels.

NOTE 4—The objective of this procedure is to obtain the coating free of substrate. Other collection methods, such as scraping the coating from glass plates or using release paper instead of sheeting[5] are acceptable. See also Practice D4708 for other film preparation techniques.

6.4 Place the wrapped panels on a panel rack and bake at 160 °C, for 10 min to 15 min. Baking will tighten the sheeting[5] and remove any wrinkles. After baking, allow panels to cool at room temperature for at least 15 min.

6.5 Prepare a thin, uniform, bubble-free film on the wrapped panels either by spraying or with a drawdown blade, to obtain a dry film thickness of 1.0 mils to 1.8 mils (25 µm to 46 µm). Thinner films of 1.0 mils to 1.2 mils (25 µm to 31 µm) have fewer potential problems with entrapped solvents.

6.6 Bake the coated panels for 60 min at 110 °C in a forced draft oven, then cool at room temperature for 20 min to 30 min.

6.7 Cut a slit across the top or bottom, about ½ in. from the edge of the film. Separate a small portion of the film from the

[4] The sole source of supply of the 5–mL cup, Model 1305 known to the committee at this time is the Micromeritics Instrument Corp., One Micromeritics Drive, Norcross, GA 30093–1877. 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.

[5] The sole source of sheeting, Tedlar, a registered trademark of E. I. du Pont de Nemours and Company, PC105M3, known to the committee at this time is the Dupont Company. 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.

[6] The sole source of supply of the anti-static instrument, Zerostat 3, known to the committee at this time is the Aldrich Chemical Co., Inc., (address). 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.

sheeting[5] with a scalpel or razor blade. Work a thin narrow spatula blade (about 4-½ in.-long (115-mm)) under the separated portion of the file then remove the film by working the spatula blade between the film and substrate along and across each side and end of the panel.

6.8 Place the film on a piece of sheeting[5] or plain paper that has been treated with the anti-static device. Treat the film with the device in accordance with the manufacturer's instructions.

NOTE 5—Using metal lab benches helps reduce static problems.

6.9 Cut the film into strips, approximately ¼ in. by ¾ in. (6 mm by 19 mm).

NOTE 6—Alternatively, if the film does not cut well or crumbles, the film may be loosely packed into the cup.

6.10 Weigh the dried, empty cup and record.

6.11 Place the film strips vertically into a sample cup until there is between 1.0 g to 2.0 g of film in the 5-mL cup (If a different size cup is used, use a proportional amount of film sample.). Use the anti-static device as often as necessary. The film strips should not be protruding from the cup.

6.12 Weigh the sample strips and cup to verify there is at least 1.0 g of the test specimen. Samples should be run in duplicate.

6.13 Conduct the experiment in accordance with the Gas Pycnometer Instruction Manual.

6.14 Take at least five consecutive readings, in accordance with instrument instructions. Variation in readings should be random. A consistent volume increase indicates loss of trapped solvent and results should be considered suspect. Refer to the instrument instruction manual.

6.15 Weigh the cup after finishing the instrument readings.

6.16 Subtract the weight of the empty cup to obtain the film weight.

7. Calculation

7.1 Calculate the dry film density, *Df*, from the pycnometer volume displacement (6.14) and film weight (6.15) as follows:

$$Df = \frac{\text{Film weight} \quad (\text{g})}{\text{Volume displacement} \quad (\text{mL})} \tag{1}$$

NOTE 7—If the film density of duplicate runs differs by more than 0.05 g/mL, the test should be repeated.

7.2 Calculate dry film specific gravity, *Sgf*, as follows:

$$Sgf = \frac{Df(\text{g/mL})}{0.9971\ (\text{g/mL})} \tag{2}$$

where 0.9971 = Density of distilled water at 25 °C in g/mL.

7.3 Calculate the dry film weight per gallon, *Wgf*, as follows:

$$Wgf = Sgf \times 8.312\ (\text{lb./gal}) \tag{3}$$

where 8.312 = weight of 1 gal of distilled water at 24 °C (lb./gal).

7.4 Calculate percent volume solids nonvolatile content (*VNV, %*) as follows:

$$VNV,\ \% = \frac{\text{weight \% nonvolatiles} \times \text{weight per gal (liquid sample)}}{Wgf} \tag{4}$$

NOTE 8—If the wet sample density is determined by a device directly reading out in g/L, the following equation can be used which generates identical VNV, % results as follows:

$$VNV,\ \% = \frac{\text{weight percent NV} \times \text{wet coating density (g/mL)}}{\text{dry film density (g/mL)}} \tag{5}$$

7.5 *Example calculation:*

Df	= 1.452 g/mL
Weight percent nonvolatiles	= 61.3 %
Gallon weight (liquid sample)	= 9.55 lb/gal
Sgf	= 1.452 g/mL 0.997 g/mL = 1.456
Wgf	= 1.456 × 8.312 lb /gal = 12.102 lb/gal
VNV, %	= 61.3 % × 9.55/12.102 = 48.4 %

8. Precision and Bias

8.1 *Precision* (In accordance with Practice E180). In an inter laboratory study of this test method five laboratories analyzed in duplicate on two days, three coatings (one solvent-based and two water-reducible) with nonvolatile contents ranging from 27 to 48 volume percent. The pooled within-laboratory coefficient of variation was 1.16 % with 14 df and the pooled between laboratories coefficient of variation 2.46 % with 11 df. Based on these coefficients of variation, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

8.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 3.5 % relative.

8.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 7.67 % relative.

8.2 *Bias*—No general statement of bias can be made because no reference material is available.

9. Keywords

9.1 coatings; helium gas pycnometer; paint film density, coverage; percent volume nonvolatile matter; VOC, volatile organic compound content