



# Standard Test Methods for Gravimetric Analysis of White and Yellow Thermoplastic Traffic Marking<sup>1</sup>

This standard is issued under the fixed designation D4797; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods cover procedures for the gravimetric analysis of the binder and hydrochloric Acid (HCL) insoluble particles in white and yellow thermoplastic traffic markings. The HCL insoluble particles can be retroreflective optics, such as glass beads or some other type of retroreflective optic, or non-retroreflective particles such as silica sand, or a combination of any two or more of these materials.

1.2 This standard does not address the physical separation and the individual quantification of each component when a mixture of two or more HCL insoluble materials is present. Rather it requires the user to visually evaluate the HCL insoluble material (obtained from following this test method) and report the types of materials present.

1.3 This standard does not purport to address the titanium dioxide or lead chromate pigment measurement (after ashing) which is detailed in Test Methods [D1394](#) and [D126](#).

1.4 This standard will attempt to address the interference of organic pigments with the binder results.

1.5 The analytical procedures appear in the following order:

|   | Sections |
|---|----------|
| Percent Binder  | 10       |
| Percent Retroreflective Optics or Non-Retroreflective Particles | 11       |

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

1.7 *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.*

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.44 on Traffic Coatings.

Current edition approved Nov. 1, 2012. Published December 2012. Originally approved in 1988. Last previous edition approved in 2012 as D4797 – 12. DOI: 10.1520/D4797-12A.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- [D126 Test Methods for Analysis of Yellow, Orange, and Green Pigments Containing Lead Chromate and Chromium Oxide Green](#)
- [D1394 Test Methods for Chemical Analysis of White Titanium Pigments](#)
- [D7307 Practice for Sampling of Thermoplastic Traffic Marking Materials](#)
- [D7308 Practice for Sample Preparation of Thermoplastic Traffic Marking Materials](#)
- [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](#)

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

- 3.1.1 *ash, n*—the inorganic components of thermoplastic traffic marking including the pigment, glass spheres, and filler.
- 3.1.2 *binder, n*—the organic components (resinous components) of thermoplastic traffic marking that bind the pigments, glass spheres, and filler together as a unit.
- 3.1.3 *filler, n*—the inorganic components of thermoplastic traffic marking not including the pigments, retroreflective optics, or non-retroreflective particles that are considered functional.
- 3.1.4 *retroreflective optic, n*—functional particle that reflects and returns a relatively high proportion of light in a direction close to the light source. This characteristic is maintained over a wide variation of the angle made by the incident light ray and normal to the retroreflective surface. This includes a single component structure such as a spherical glass bead or a multi component structure with a core and a surface covered with a small retroreflector.
- 3.1.5 *non-retroreflective particles, n*—functional particle that is insoluble in HCL, such as aluminum oxide, ground

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

glass, quartz, etc., that are added for skid resistance or other non-retroreflective functional purpose.

3.1.6 *pigment, n*—titanium dioxide, lead chromate colorants, and/or organic pigments.

3.1.7 *thermoplastic, n*—See *thermoplastic traffic marking*.

3.1.8 *thermoplastic traffic marking, n*—a highly filled 100 % total solids highway marking system that when heated to a molten state can be extruded or sprayed onto a road surface and when cooled forms a solid durable delineator.

3.1.9 *hydrochloric acid (HCL) insoluble particles, n*—retroreflective optics, such as glass beads or some other type of retroreflective optic, or non-retroreflective particles such as silica sand, or a combination of any two or more of these materials.

#### 4. Summary of Test Method

4.1 Thermoplastic traffic marking material is prepared for the described test methods by melting a sample to its application temperature under continuous agitation. The specimen is then poured into round patties on a non-stick surface such as a baking pan. The patties are then broken into pieces for ignition in a muffle furnace. The percent binder is calculated from the ashed specimen and the various tests for retroreflective optics, non-retroreflective particles, titanium dioxide, and lead chromate pigment can be performed later on the ashed residue. Determining the binder content of organic pigment containing thermoplastic may not be as straight forward. Specimen selection and preparation are the same for each sample tested.

#### 5. Significance and Use

5.1 The function of these test methods is to define the percent of binder and retroreflective optics or non-retroreflective particles in the composition of the thermoplastic traffic marking as defined by the applicable specification for the manufacture of a specific thermoplastic traffic marking. The subsequent sample, as a result of ashing can be used to later test for the presence of titanium dioxide, lead chromate and possibly organic pigments.

#### 6. Apparatus

6.1 *Balance*, analytical, capable of weighing to 0.1 mg.

6.2 *Crucibles*, 30+ mL, porcelain or aluminum pan.

6.3 *Desiccator*.

6.4 *Furnace (Muffle)*, capable of maintaining 540°C (1004°F).

6.5 *Hot Plate or Heating Mantle*, capable of heating a can of thermoplastic to 218°C (425°F).

6.6 *Sieve*, 3 in., 45- $\mu$ m (No. 325) (metal).

6.7 *Buchner Funnel*.

6.8 *Vacuum Flask and Rubber Hose*.

6.9 *Vacuum Pump*.

6.10 *Oven* capable of reaching 218°C (425°F).

6.11 *Microwave Oven*.

6.12 *400 mL Beaker* or acid proof container.

6.13 *Magnetic Stirring Bar*.

6.14 *Magnetic Stirring Plate*.

6.15 *Spatula*.

#### 7. Reagents

7.1 *Hydrochloric Acid Solution (HCL)* (1 + 1 concentrated HCL diluted with equal volume of water).

7.2 *Hydrochloric Acid, Concentrated (HCL)*.

#### 8. Sampling

8.1 Samples may be obtained in accordance with Practice **D7307** by an appropriate quartering or riffle sampling method where deemed necessary considering the physical form of the material.

#### 9. Preparation of Specimens

9.1 Melt a sample of thermoplastic traffic marking in accordance with Test Method **D7308** to 218°C (425°F) (or per manufacturers recommended processing temperature) under continuous agitation on a hot plate or stir every 15 min in an oven set at 218°C (425°F) or per manufactures recommended processing temperature.

NOTE 1—Road marking thermoplastic is manufactured in a wide variety of viscosities at 218°C. Some viscosities are so low that the retroreflective optics settle quickly. In order to prevent any settlement during the sampling process, removing the test sample at a lower temperature is warranted. Some thermoplastic test samples are best poured as low as 160°C (320°F) as long as they can flow into patties.

9.2 Flow the sample out on a smooth clean non-stick surface and allow it to cool to room temperature. Patties approximately 3 mm ( $\frac{1}{8}$  in.) thick are usually easy to break up specimens for the described analysis.

9.3 Break the specimen into small pieces and weigh to the nearest 0.1 mg into a weighed crucible that is at least twice the volume of specimen. The binder test can be done on samples as small as 10 g (0.353 g) and be effective. Larger samples can supply more retroreflective optics or non-retroreflective particles for their evaluation later if required.

9.4 Cover the crucible and place into a muffle furnace preheated to 540°C (1004°F) and ash for 1 hour or until no carbonaceous material remains.

9.5 Remove the crucible with the ashed remains of the specimen and place into a desiccator and cool to room temperature.

#### 10. Percent Binder

10.1 *Interferences*—If yellow organic-pigment-containing road marking thermoplastic samples are ashed, the organic pigment may begin to degrade; therefore increasing the binder results. If the theoretical amount of organic pigment content of the sample is known and assumption can be made as to whether some or all the organic pigment has degraded (depending on its degradation temperature), then that amount can be accounted for in the calculation in **Eq 1**.

10.2 *Procedure*—Weigh the crucible and ash (see Section 9) to the nearest 0.1 mg and calculate the percent binder *D* as follows:

$$D = (1 - (S/W)) \times 100 \quad (1)$$

where:

$S$  = ashed weight of thermoplastic specimen, g, (crucible + ash wt.) – crucible wt.

$W$  = weight of thermoplastic specimen, g, (crucible + thermoplastic specimen) – crucible wt.

## 11. Percent Retroreflective Optics (RO) or Non-retroreflective Particles (NRP) using Hydrochloric Acid (HCL)

### 11.1 Procedure:

11.1.1 Weigh the crucible and ash (see Section 9) to 0.1 mg and calculate the percent ash.

11.1.2 After the ashed material has been weighed, transfer the ash to a 400-mL beaker or other acid-proof container and with minimal pressure, break apart the ashed specimen without crushing the retroreflective optics.

11.1.3 Add to the ash approximately 50 to 150 mL (1.7 to 5 oz.) of cold 1 + 1 HCL and stir occasionally until most of the effervescence has ceased. (**Warning**—This is best performed under a vented hood. Also, this procedure can be performed using warmed HCL but is not necessary.)

11.1.4 Immediately dilute the contents with as much water as possible to allow the RO or NRP to settle. Decant the water and particulate carefully so as not to lose RO or NRP.

11.1.5 If all the ash residue has not gone into solution, reintroduce HCL solution and stir. Continuous agitation can best be achieved with a magnetic stirring bar and magnetic stirrer. Stirring with a spatula can achieve similar results.

11.1.6 Continue adding HCL or diluting with water and decanting until the water is clear.

11.1.7 Then transfer the residue into a weighed 3-in. 45- $\mu$ m (No. 325) sieve or a Buchner funnel containing a weighed corrugated coffee filter and wash with enough cold water to remove any residue. If the RO or NRP do not appear clean, you should repeat the acid washing process.

11.1.8 Dry the sides and the bottom of the sieve with a paper towel and dry for 1 hour in a gravity oven preheated to 100°C (212°F). If using a Buchner funnel and coffee filters, a vacuum can be pulled on the system to evacuate the water and then the RO/NRP-containing-filters can be dried in an oven or microwave oven.

11.1.9 Place the sieve or coffee filter in a desiccator and cool to room temperature.

11.1.10 Weigh the sieve/filter and HCL insoluble particles (RO or NRP) to 0.1 mg and calculate the percent as follows (see [Note 2](#)):

NOTE 2—Most road marking thermoplastic-ashed-residue which is insoluble in HCL is a retroreflective optic.

$$\%HCL \text{ Insoluble Particles} = (R/W) \times 100 \quad (2)$$

where:

$R$  = weight of residue after acid wash (g) (not including sieve/filter wt.)

$W$  = original weight of thermoplastic specimen (g) (not including crucible wt.)

11.1.11 After completing the calculation examine the sample of acid insoluble particles obtained during the test to determine the qualitative composition of the material. Include in the report the qualitative composition of the residue. For example, the HCL insoluble particles obtained from this test are composed of 100 % retroreflective optics, or the HCL insoluble particles obtained from this test are composed of both retroreflective optics and non-retroreflective particles.

## 12. Precision and Bias<sup>3</sup>

12.1 The precision of this test method is based on an interlaboratory study of ASTM D4797–12, Standard Test Methods for Gravimetric Analysis of White and Yellow Thermoplastic Traffic Marking, conducted in 2012. Seven laboratories participated in the study, testing four different thermoplastic materials. Every analyst was instructed to report four replicate test results in this study. Practice E691 was followed for the study design; the details are given in ASTM Research Report No. RR:D01-1166.

12.1.1 *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 paint, obtained by the same operator using the same equipment on the same day in the same laboratory.

12.1.1.1 Repeatability limits are listed in [Table 1](#) and [Table 2](#).

12.1.2 *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 paint, obtained by different operators using different equipment in different laboratories.

12.1.2.1 Reproducibility limits are listed in [Table 1](#) and [Table 2](#).

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

12.1.4 Any judgment in accordance with statements [12.1.1](#) and [12.1.2](#) would have an approximate 95 % probability of being correct.

12.2 *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.

12.3 The precision statement was determined through statistical examination of 212 test results, from a total of seven laboratories, on four thermoplastic materials. The four materials were described as:

Sample A: White Road Marking Thermoplastic 18 % Binder and 30 % Insoluble Particles

Sample B: White Road Marking Thermoplastic 20 % binder and 40 % Insoluble Particles

Sample C: White Road Marking Thermoplastic 22 % Binder and 30 % Insoluble Particles

Sample D: Yellow Non-Leaded Road Marking Thermoplastic 18 % Binder and 30 % Insoluble

<sup>3</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1166.

**TABLE 1 % Binder**

| Material | Average <sup>A</sup><br>$\bar{X}$ | Repeatability<br>Standard<br>Deviation<br>$s_r$ | Reproducibility<br>Standard<br>Deviation<br>$S_R$ | Repeatability<br>Limit<br>$r$ | Reproducibility<br>Limit<br>$R$ |
|----------|-----------------------------------|---|---|-------------------------------|---------------------------------|
| Sample A | 18.2162                           | 0.1709  | 0.2205  | 0.4784                        | 0.6173                          |
| Sample B | 20.0969                           | 0.5542  | 0.5845  | 1.5517                        | 1.6366                          |
| Sample C | 22.3397                           | 0.4324  | 0.5226  | 1.2107                        | 1.4632                          |
| Sample D | 19.5027                           | 0.3939  | 0.9554  | 1.1028                        | 2.6751                          |

<sup>A</sup> The average of the laboratories' calculated averages.

**TABLE 2 % HCL Insoluble Particles**

| Material | Average <sup>A</sup><br>$\bar{X}$ | Repeatability<br>Standard<br>Deviation<br>$s_r$ | Reproducibility<br>Standard<br>Deviation<br>$S_R$ | Repeatability<br>Limit<br>$r$ | Reproducibility<br>Limit<br>$R$ |
|----------|-----------------------------------|---|---|-------------------------------|---------------------------------|
| Sample A | 30.2850                           | 0.4742  | 0.5780  | 1.3278                        | 1.6185                          |
| Sample B | 41.2402                           | 1.4415  | 2.5214  | 4.0362                        | 7.0599                          |
| Sample C | 30.1476                           | 1.1301  | 1.2345  | 3.1644                        | 3.4567                          |
| Sample D | 30.5405                           | 0.2600  | 0.3742  | 0.7279                        | 1.0478                          |

<sup>A</sup> The average of the laboratories' calculated averages.

### 13. Keywords

13.1 binder; lead chromate; non-retroreflective particles; organic pigment; retroreflective optics; thermoplastic traffic marking material; titanium dioxide

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/*