Test Procedure for

ANALYSIS OF THERMOPLASTIC PIGMENTS USING X-RAY FLUORESCENCE SPECTROSCOPY

TxDOT Designation: Tex-627-J

Effective Date: October 2011

1. SCOPE

1.1 Use this method as a quantitative technique for preparing and testing thermoplastic paint pigments using X-ray fluorescence spectroscopy.

1.2 The values given in parentheses (if provided) are not standard and may not be exact mathematical conversions. Use each system of units separately. Combining values from the two systems may result in nonconformance with the standard.

PART I—TESTING SAMPLES

2. APPARATUS

2.1 Mechanical grinder.

2.2 Ring press, with die of corresponding size to the X-ray spectrometer sample holder and capable of achieving 20 tons of force.

2.3 X-ray fluorescence spectrometer (XRF), wavelength dispersive, able to operate with the analysis chamber evacuated and detect the spectral lines of titanium and lead.

2.4 Aluminum sample cup, approximate 2 in. in diameter and 0.6 in. deep.

2.5 Brush and rag, clean, for dusting.

2.6 Gloves, disposable latex or nitrile.

2.7 Sample die, used to make pressed pellets of the appropriate size to fit in the X-ray fluorescence spectrometer.

3. MATERIALS

3.1 Thermoplastic pigment sample, prepared in accordance with Tex-863-B.

3.2 Acetic anhydride, 97%.
3.3 *Grinding and briquetting additive for XRF sample preparation*, 500-mg tablet.

3.4 *Clean sand*, any type.

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### 4. PREPARING SAMPLES

#### 4.1 Grind samples:

4.1.1 Ensure that the grinder is free of contamination.

4.1.2 Pour sample into grinder. Add two to three drops of acetic anhydride and a grinding tablet.

4.1.3 Close and secure grinder components. Start the grinder and pulverize for 50 sec.

4.1.4 Open the grinder and collect the sample into a sample container. Dust off each component with a small, clean brush. Label the sample, and set it aside.

4.1.5 Clean the remaining residue off each component of the grinder. After every sample, run clean sand through the grinding procedure. This will ensure there is no cross-contamination between thermoplastic samples. Repeat pulverizing procedure for remainder of the samples.

#### 4.2 Press pellets:

4.2.1 Take the pulverized sample to the ring press to make pressed pellets.

4.2.2 Ensure that the press and die are free of contamination.

4.2.3 Load a sample into the die and the die into the press. Ensure all components are secure before applying force.

4.2.4 Apply 18 tons of force to sample for 1 min.

**Note 1**—The amount of applied force and hold time may vary for different sample sizes.

4.2.5 Slowly release the force, allowing at least 30 sec. to pass during release.

4.2.6 Remove pelletized sample from the ring press and place in a labeled aluminum sample cup. Using a clean rag, dust off any residue on the ring press and die to prevent cross-contamination. Repeat pressing procedure for remaining samples, if necessary.

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### 5. PROCEDURE

5.1 Before running samples for pigment determination, calibrate the XRF spectrometer in accordance with Part II of this test procedure.

5.2 Ensure equipment is on and running at an optimum level according to the manufacturer's instructions. Start up data collection software.
5.3 Load samples, being careful not to contaminate the surface of the sample. Use gloves when handling the samples.

5.4 Operate the spectrometer according to the manufacturer's instructions. Set the instrument to measure the percent lead content for yellow thermoplastic, and the titanium content for white thermoplastic samples.

5.5 When the instrument has completed the measurement, unload the samples and obtain the appropriate data.

6. **CALCULATIONS**

6.1 Calculate the percent pigment in the original thermoplastic sample:

\[
C = P \left( \frac{10(1-R)+0.5}{10} \right)
\]

Where:

- \(C\) = Percent pigment in the original thermoplastic sample
- \(P\) = Percent pigment in the pelletized sample determined by XRF spectrometer
- \(R\) = Fraction of resin content in the sample, calculated in accordance with Tex-863-B.

**PART II—XRF CALIBRATION**

7. **SCOPE**

7.1 Use this method to calibrate the XRF to measure the titanium and lead pigments in thermoplastic samples.

8. **APPARATUS**

8.1 Apparatus listed in Section 2, with the addition of the following items:

8.1.1 *Friction-top cans, 1 pt, with lids.*

8.1.2 *Analytical balance, Class A in accordance with Tex-901-K.*

8.1.3 *Convection oven, capable of maintaining 210 ± 6°C (415 ± 10°F).*

8.1.4 *Mortar and pestle.*

8.1.5 *Shaker mill.*

8.1.6 *Muffle furnace, capable of maintaining 1000 ± 10°C (1,800 ± 20°F).*
8.1.7 *Silicone-coated paper roll*, minimum 6 in. (150 mm) wide.

8.1.8 *Weighted can*, 1 pt., filled with solid thermoplastic, for use as a rolling pin.

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### MATERIALS

9.1 *Alkyd resin.*

9.2 *Polyethylene beads.*

9.3 *Phthalate plasticizer.*

9.4 *Medium chrome yellow pigment.*

9.5 *Titanium dioxide pigment.*

9.6 *Calcium carbonate.*

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### PREPARING STANDARDS

10.1 *Preparing the Resin Mixture:*

10.1.1 Obtain a friction-top pint can. Remove the friction top to produce a smooth lip.

10.1.2 Place can on an analytical balance. Tare the balance.

10.1.3 Into the pint can, weigh 15 ± 0.1 g of the polyethylene beads and 240 ± 0.1 g of the alkyd resin.

10.1.4 Lift the can and gently swirl to mix the two resins as much as possible. Replace the can on the balance.

10.1.5 Add 45 ± 0.1 g of liquid phthalate plasticizer into the can. The can should contain 300 g of total material.

10.1.6 Remove the can from the balance and swirl to mix the components as much as possible.

10.1.7 Place the can in an oven set at 210 ± 6°C and melt the sample for a total of 2 hr. Stir the sample thoroughly with a spatula approximately every 15 min. to prevent scorching and to obtain a uniform mixture.

10.1.8 Cut approximately 2 sq. ft. of silicone-coated paper, staple edges to a cardboard substrate for rigidity, and place on a tabletop or other suitable flat surface.

10.1.9 After 2 hr., remove the sample from the oven, stir well, and pour the remaining contents over the silicone-coated paper. Using the spatula, spread the sample to a depth of about 1/8 in. (3 mm) on the silicone paper and allow it to cool.
10.1.10 Break the cooled sample into small pieces averaging 0.5 × 0.5 in. (13 × 13 mm), using the weighted can as a rolling pin. Place the pieces into a clean, empty pint can.

**Note 2**—These chips are the resin component of the thermoplastic standards.

10.2 **Preparing the Pigment, Calcium Carbonate, Glass Bead, and Resin Mixture:**

10.2.1 Obtain ten clean, empty friction-top pint cans and label as appropriate for five standards each of yellow and white thermoplastic.

10.2.2 Place a can on an analytical balance. Tare the balance.

10.2.3 Place approximately 50 g of calcium carbonate (CaCO₃) into a mortar. Grind with the pestle until there are no visible lumps.

10.2.4 Weigh into the can the amount of CaCO₃ required for the standard as listed in Table 1 or Table 2. Weigh to the nearest 0.01 g.

**Note 3**—Use Table 1 for yellow thermoplastic standards; use Table 2 for white thermoplastic standards.

**Table 1—Component Amounts for Yellow Thermoplastic Standards**

<table>
<thead>
<tr>
<th>No.</th>
<th>Medium Chrome Yellow Pigment (g)</th>
<th>CaCO₃ (g)</th>
<th>Glass Beads (g)</th>
<th>Resin (g)</th>
<th>Total (g)</th>
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<tr>
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<td>38</td>
<td>30</td>
<td>20</td>
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</table>

**Table 2—Component Amounts for White Thermoplastic Standards**

<table>
<thead>
<tr>
<th>No.</th>
<th>Titanium Dioxide Pigment (g)</th>
<th>CaCO₃ (g)</th>
<th>Glass Beads (g)</th>
<th>Resin (g)</th>
<th>Total (g)</th>
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</table>

10.2.5 Lift the can from the balance and gently swirl to coat the bottom and sides of the can with CaCO₃. This will prevent the resin and other materials from sticking to the sides of the can. Replace the can on the balance.
10.2.6 Add the prime pigment, (titanium dioxide or medium chrome yellow), in the amount indicated in Table 1 or 2. Lift the can, swirl to mix, and replace on the balance.

10.2.7 Add 20 g of resin blend. Lift the can, swirl to mix, and replace on the balance.

10.2.8 Add 30 g of glass beads.

10.2.9 Place a lid on the can and seal the can. Shake the can by hand to mix, turning it upside down.

10.2.10 Place the can on a shaker mill and shake for 1 min. Do not over shake, as this will fracture the resin.

10.2.11 Repeat Sections 10.2.2–10.2.10 for the remaining standard mixtures.

10.2.12 Remove the lids, and remove the friction-top of each can to produce a smooth lip.

10.2.13 Prepare chips as described in Sections 10.1.7–10.1.10. Make sure to keep chips from each standard separate.

10.3 Preparing Thermoplastic Standards for XRF Analysis:

10.3.1 For each standard, weigh 10 g of chips into a crucible. Record the weight of the chips to the nearest 0.01 g.

10.3.2 Place the crucibles into a muffle furnace at 1,000 ± 10°C for 1 hr.

10.3.3 Remove the crucibles from the muffle furnace and allow the crucibles to cool to room temperature.

10.3.4 Weigh the crucibles to the nearest 0.01 g and calculate the resin content of each standard in accordance with Section 11.1.

10.3.5 Determine the percent pigment in each pellet in accordance with Section 11.2.

10.3.6 Grind and pelletize the standards as described in Section 4.

10.3.7 Follow the manufacturer’s instructions to analyze the standards in the XRF spectrometer and create a calibration curve for the percent pigment contained in each pellet.
11. **CALCULATIONS**

11.1 Calculate resin content:

\[ R = 1 - \left( \frac{W_{RC} - W_C}{W_{SC} - W_C} \right) \]

Where:
- \( R \) = resin content of the sample
- \( W_{RC} \) = Weight of the residue and crucible
- \( W_{SC} \) = Weight of the sample and crucible
- \( W_C \) = Weight of the crucible.

11.2 Calculate the percent pigment in a pelletized sample:

\[ P = \left( \frac{W_s \times C}{W_s(1 - R) + 0.5} \right) \]

Where:
- \( P \) = Percent pigment in the pellet
- \( W_s \) = Weight of the sample before placing in the muffle furnace
- \( C \) = Percent pigment in the original sample
- \( R \) = Resin content of the sample determined in Section 11.1.

12. **ARCHIVED VERSIONS**

12.1 Archived versions are available.