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Test Procedure for

**DETERMINING POLYMER ADDITIVE  
PERCENTAGES IN POLYMER MODIFIED ASPHALT  
CEMENTS**



TxDOT Designation: Tex-533-C

Effective Date: August 1999

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**1. SCOPE**

- 1.1 Use this procedure to determine the concentrations of various polymeric additives in asphalt binder, including the following:
- styrene-butadiene rubber (SBR) latex,
  - styrene-butadiene-styrene block copolymer (SBS),
  - ethylene acrylic acid (EAA), and
  - ethylene vinyl acetate (EVA).
- 1.2 Use the methods discussed for detection of other additives, if a consistently measurable infrared response is observed and calibrated.
- 1.3 This test procedure is in several parts:
- Part I—Determining polymer content of an unknown sample
  - Part II—Generating calibration curves for specific asphalt/additive combinations
  - Part III—General procedure for collecting sample data by attenuated total reflectance (ATR) method
  - Part IV—General procedure for collecting sample data by light transmission through a salt plate. (This part is an alternative to Part III.)
- 1.4 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.

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## PART I—DETERMINING POLYMER CONTENT OF AN UNKNOWN SAMPLE

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### 2. SCOPE

- 2.1 Use the following procedure to measure the polymer content of an unknown sample of modified asphalt.

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### 3. PROCEDURE

- 3.1 If one does not exist, generate a calibration curve for the polymer-modified asphalt using the method described in Part II. (The background collection method used by the infrared spectrophotometer (IR) may account for variations in the prisms or salt plates. If so, calibration curves need generation only periodically. Refer to the instrument manufacturer's recommendations to determine the necessary frequency of calibrations.)
- 3.2 Generate an IR spectrum using either the method described in Part III or the one described in Part IV.
- 3.3 Integrate the appropriate peak, or calculate the peak height ratio, for the appropriate polymer type in the unknown.
- 3.4 Calculate the polymer content from the measured peak height ratio or peak area using the previously generated calibration curve.

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## PART II—GENERATING CALIBRATION CURVES

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### 4. SCOPE

- 4.1 Because the infrared response is different for each asphalt crude source and each polymer brand, generate a calibration curve for each asphalt/polymer combination. The producer of the modified asphalt is required to submit samples of the asphalt and the polymer for generation of a calibration curve.

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### 5. APPARATUS

- 5.1 *Plastic squeeze bottle.*
- 5.2 *Sample can, 1 L (1 qt.)*
- 5.3 *Thermometer, capable of measuring 4–304°C (40–580°F).*
- 5.4 *Rotary mixer.*

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## 6. PREPARING STANDARD BLENDS

- 6.1 Weigh approximately 400 g of asphalt into a 1-L (1-qt.) can.
- 6.2 Record the sample weight under Section 8.
- 6.3 Heat the asphalt to 160°C (320°F) in a heating mantle. As soon as the material is fluid enough, begin stirring with a rotary mixer.
- 6.4 Maintain the temperature between 149 and 177°C (300 and 350°F).
- 6.5 Calculate the amount of polymer needed, using the equations in Section 8.
- 6.6 Add polymer to the asphalt.  
**Note 1**—For solid polymers, weigh the appropriate amount and add about a third of the material at a time, allowing polymer to disperse for a few seconds between additions. Add emulsified polymers by the drop from a squeeze bottle, and back weigh the bottle for the weight of polymer. Adding too much emulsified material at once can cause the sample to boil over.
- 6.7 Allow materials to continue mixing for 20 min. after addition of polymer is complete.
- 6.8 By repeating Sections 6.1–6.7, produce four standards with 1, 2, 3, and 4% polymer.
- 6.9 Allow all of the standards to cool before use.

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## 7. DATA COLLECTION AND CURVE GENERATION

- 7.1 Prepare standard blends as described in Section 6.
- 7.2 Perform IR scans of all standards and of the unmodified asphalt, using the method described in Part III or Part IV.
- 7.3 When using the ATR method (Part III), integrate the appropriate peak. (If the software is not equipped to do this, multiply the peak height by the width of the peak at half height.) The peaks for some types of polymer are:
- SBR and SBS peaks are 965 wave numbers, (due to butadiene mid-block),
  - EAA peak is 1700 wave numbers, (due to carbonyl bond), and
  - EVA peak is 1735 wave numbers, (due to carbonyl bond).
- 7.4 When using the salt plate method (Part IV), calculate the ratio of the polymer peak to the asphalt peak. The asphalt peak is 1375 wave numbers.
- 7.5 Plot peak area (for the ATR method) or peak height ratio (for the salt plate method) versus polymer concentration, and perform a curve fit by using linear least squares or other convenient method. (IR software may be equipped to do this.) The resulting equation is the calibration curve.

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## 8. CALCULATIONS

8.1 Calculate the amount of polymer to be added as a percentage of the final weight of the blend.

8.1.1 Calculate for solid polymers:

$$W_p = \frac{PW_a}{100 - P}$$

Where:

$W_p$  = weight of polymer to be added

$W_a$  = weight of asphalt

$P$  = percentage of polymer to be used (i.e., 1, 2, 3, or 4%).

8.1.2 For emulsified polymers, the take polymer content of the emulsion into account. Calculate the amount of emulsion to be added:

$$W_e = \frac{W_p}{C_p}$$

Where:

$W_e$  = amount of emulsion to be added

$C_p$  = polymer content of the emulsion

$W_p$  = weight of polymer, from the previous equation.

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## PART III—ATTENUATED TOTAL REFLECTANCE METHOD

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### 9. SCOPE

9.1 Use this method of gathering data when the instrument available has attenuated total reflectance (ATR) capability. If the instrument does not have ATR capability, use the method described in Part IV or other approved method of collecting IR spectra.

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### 10. APPARATUS

10.1 *Infrared spectrophotometer (IR)*, with ATR capability and some means of background correction.

10.2 *Prisms.*

10.3 *Spatula.*

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## 11. MATERIALS

- 11.1 *Cleaning solvent*, (trichlorethylene, dichloromethane, or other suggested clean evaporating solvent).
- 11.2 *Release paper*, (such as wax paper).
- 11.3 *Tape*, (such as masking tape).

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## 12. PREPARING ATR SAMPLE

- 12.1 Acquire a sample of at least 10 g of polymer-modified asphalt.
- 12.2 Cut a strip of release paper approximately 10 mm × 60 to 80 mm long (0.4 in. × 2.3 to 3.2 in.) (Use an appropriate size for the prism, ensuring that the paper is slightly larger than the prism face.)
- 12.3 Affix one end of the paper to a lab table with tape.
- 12.4 Heat the sample in a 177°C (320°F) oven for approximately 5 min., or until liquefied.
- 12.5 Pour the sample over the release paper and spread with a spatula.
- 12.5.1 Use enough material to cover the paper, but leave about 10 mm (0.4 in.) uncovered on each end.
- 12.5.2 The test procedure requires a sample thickness on the prism of only several microns. A thickness on the paper of about 1 mm (0.04 in.) is suggested. Additional material will not alter the test result, but it will make cleaning more difficult.
- 12.6 Allow the sample to cool for several minutes.
- 12.7 Peel the paper with the sample from the table and trim the excess material with a hot spatula.

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## 13. BACKGROUND COLLECTION

- 13.1 A background spectrum allows the user to make corrections for differences in each prism used and for varying atmospheric conditions inside the instrument. Use the same prism for the background collection as for the sample analysis. Perform the background collection before analyzing a sample.
- 13.2 Start the software for controlling the IR, if necessary.
- 13.3 Place a clean, dry ATR prism over the sample chamber.
- 13.4 Begin collection of background spectrum. The computer software may be set up to do this automatically as part of the data collection process.

13.5 When the computer is finished with the background, remove the prism.

13.6 If necessary, save the background spectrum.

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## 14. SAMPLE ANALYSIS

14.1 Prepare the sample as described in Section 12.

14.2 Collect a background as described in Section 13.

14.3 Affix the release paper with the material sample to the prism so that the asphalt is in direct contact with the top face of the prism.

14.4 Apply finger pressure to the top of the sample to push out any air bubbles. (Air bubbles in the sample are visible from the underside of the prism.)

14.5 Replace the prism over the sample chamber and begin collection of the sample spectrum.

14.6 When data collection is finished, remove the prism from the sample chamber and peel away the release paper.

14.7 Place the prism in a cleaning solvent bath to remove the asphalt.

14.7.1 Use an ultrasonic bath to reduce cleaning time.

14.7.2 Avoid scrubbing, scraping, or brushing prisms, as they may scratch easily.

14.8 Perform background correction with the background spectrum collected earlier and by the method recommended by the instrument manufacturer. The instrument may be equipped do this as a normal part of data collection.

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## PART IV—SALT PLATE METHOD

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### 15. SCOPE

15.1 This is the general procedure for collecting IR data by light transmission through a salt plate. Use this method when there is no ATR-capable instrument available.

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### 16. APPARATUS

16.1 *Infrared spectrophotometer (IR)*, with some means of background correction.

16.2 *Salt plate*, for use with the IR.

16.3 *Heating mantle*, with stirrer.

16.4 *Balance*, Class A in accordance with Tex-901-K.

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- 16.5            *Balance*, Class G1 in accordance with Tex-901-K.
- 16.6            *Test tubes*, 150 mL (5 oz.), with screw caps and Teflon seal.
- 16.7            *Pipette*, 10 mL (0.3 oz.)
- 16.8            *Pipettes*, disposable.
- 16.9            *Heat lamp*.
- 16.10          *Spatula*.
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## 17.            **MATERIAL**

- 17.1            *Chromatography-grade tetrahydrofuran (THF)*.
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## 18.            **PREPARING SAMPLES**

- 18.1            *Soluble Samples*—for samples that dissolve completely in THF, (i.e., those containing SBR, SBS, or EVA).
- 18.1.1          Weigh  $0.995 \pm 0.005$  g of sample into a test tube.
- 18.1.2          Pipette 10 mL (0.3 oz.) of THF into the test tube.
- 18.1.3          Shake until the asphalt dissolves completely.
- 18.1.4          Let the solution stand for 15–30 min. to allow any solids to settle.
- 18.1.5          Place 5–9 drops of the solution on a salt plate using a disposable pipette.
- 18.1.6          Allow the THF to evaporate at room temperature until the film of material begins to solidify.
- 18.1.7          Put the salt plate under a heat lamp to drive away any residual solvent.
- 18.2            *Insoluble Samples*—for samples that do not dissolve completely in THF, (i.e., those containing EAA).
- 18.2.1          Heat approximately 50 g of sample in a 160°C (320°F) oven until fluid.
- 18.2.2          Place a salt plate under a heat lamp for approximately 10 min. or until hot to the touch.
- 18.2.3          Remove the sample from the oven and stir to ensure that the polymer has dispersed.
- 18.2.4          Place hot salt plate on a clean, dry cloth.
- 18.2.5          Remove a drop of the sample with a warm spatula and place it on the center of the salt plate.

- 18.2.6 Smooth out the material in a radial direction to achieve a film on the salt plate that is thin enough for light to pass through.
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**19. SAMPLE ANALYSIS**

- 19.1 Prepare the sample using one of the two methods described in Section 18.
- 19.2 Place the salt plate in the cell holder and position the most uniform region of the film in the path of the beam.
- 19.3 Set the baseline to 80% transmittance at 4000 wave numbers. (This is dependent on the transmittance characteristics of the salt plate; the manufacturer may recommend a different setting.)
- 19.4 Scan the sample from 4000 to 200 wave numbers, and record the data.