METHOD 313B—THE DETERMINATION OF RESIDUAL HYDROCARBON IN SOLUTION POLYMERS BY CAPILLARY GAS CHROMATOGRAPHY

1.0 Scope

1.1 This method is applicable to solution polymerized polybutadiene (PBD).

1.2 This method quantitatively determines n-hexane in wet crumb polymer at levels from 0.08 to 0.15% by weight.

1.3 This method may be extended to the determination of other hydrocarbons in solution produced polymers with proper experimentation and documentation.

2.0 Principle of Method

2.1 A weighed sample of polymer is dissolved in chloroform and the cement is coagulated with an isopropyl alcohol solution containing a specific amount of alpha-methyl styrene (AMS) as the internal standard. The extract of this coagulation is then injected into a gas chromatograph and separated into individual components. Quantification is achieved by the method of internal standardization.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences [Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

6.0 Equipment and Supplies

6.1 Analytical balance, 160 g capacity, 0.1 mg resolution

6.2 Bottles, 2-oz capacity with poly-cap screw lids

6.3 Mechanical shaker

6.4 Syringe, 10-ul capacity

6.5 Syringe, 2.5-ml capacity, with 22 gauge 1.25 inch needle, PP/PE material, disposable

6.6 Gas chromatograph, Hewlett-Packard model 5890, or equivalent, configured with FID, split injector packed with silanized glass wool.

6.6.1 Establish the following gas chromatographic conditions, and allow the system to thoroughly equilibrate before use.

6.6.2 Injector parameters:

Injection technique = Split

Injector split flow = 86 ml/min

Injector temperature = 225 deg C

6.6.3 Oven temperature program:

Initial temperature = 40 deg C

Initial time = 6 min

Program rate = 10 deg C/min

Upper limit temperature = 175 deg C

Upper limit interval = 10 min

6.6.4 Detector parameters:

Detector temperature = 300 deg C

Hydrogen flow = 30 ml/min

Air flow = 350 ml/min

Nitrogen make up = 26 ml/min

6.7 Gas chromatographic columns: SE-54 (5%-phenyl) (1%-vinyl)-methylpolysiloxane, 15 M × 0.53 mm ID with a 1.2 micron film thickness, and a Carbowax 20M (polyethylene glycol), 15 M × 0.53 mm ID with a 1.2 micron film thickness.

6.7.1 Column assembly: using a 0.53 mm ID butt connector union, join the 15 M × 0.53 mm SE-54 column to the 15 M × 0.53 mm Carbowax 20M. The SE-54 column will be inserted into the injector and the Carbowax 20M inserted into the detector after they have been joined.

6.7.2 Column parameters:

Helium flow = 2.8 ml/min

Helium headpressure = 2 psig

6.8 Centrifuge

6.9 Data collection system, Hewlett-Packard Model 3396, or equivalent

6.10 Pipet, 25-ml capacity, automatic dispensing, and 2 liter reservoir

6.11 Pipet, 2-ml capacity, volumetric delivery, class A

6.12 Flasks, 100 and 1000-ml capacity, volumetric, class A

6.13 Vial, serum, 50-ml capacity, red rubber septa and crimp ring seals

6.14 Sample collection basket fabricated out of wire mesh to allow for drainage

7.0 Chemicals and Reagents

CHEMICALS:

7.1 alpha-Methyl Styrene, C_9H_{10}, 99 + % purity, CAS 98-83-9

7.2 n-Hexane, C_6H_{14}, 99 + % purity, CAS 110-54-3

7.3 Isopropyl alcohol, C_3H_8O 99.5 + % purity, reagent grade, CAS 67-63-0

7.4 Chloroform, $CHCl_3$, 99% min., CAS 67-66-3

REAGENTS:

7.5 Internal Standard Stock Solution: 10 mg/25 ml AMS in isopropyl alcohol.

7.5.1 Into a 25-ml beaker, weigh 0.4 g of AMS to the nearest 0.1 mg.

7.5.2 Quantitatively transfer this AMS into a 1-L volumetric flask. Dilute to the mark with isopropyl alcohol.

7.5.3 Transfer this solution to the automatic dispensing pipet reservoir. This will be labeled the AMS STOCK SOLUTION.

7.6 n-Hexane Stock Solution: 13mg/2ml hexane in isopropyl alcohol.

7.6.1 Into a 100-ml volumetric flask, weigh 0.65 g of n-hexane to the nearest 0.1 mg.

7.6.2 Dilute to the mark with isopropyl alcohol. This solution will be labeled the n-HEXANE STOCK SOLUTION.

8.0 Sample Collection, Preservation and Storage

8.1 A sampling device similar to Figure 1 is used to collect a non-vented crumb rubber sample at a location that is after the stripping operation but before the sample is exposed to the atmosphere.

8.2 The crumb rubber is allowed to cool before opening the sampling device and removing the sample.

8.3 The sampling device is opened and the crumb rubber sample is collected in the sampling basket.

8.4 One pound of crumb rubber sample is placed into a polyethylene bag. The bag is labeled with the time, date and sample location.

8.5 The sample should be delivered to the laboratory for testing within one hour of sampling.

8.6 Laboratory testing will be done within 3 hours of the sampling time.

8.7 No special storage conditions are required unless the storage time exceeds 3 hours in which case refrigeration of the samples is recommended.

9.0 Quality Control

9.1 For each sample type, 12 samples shall be obtained from the process for the recovery study. Half of the vials and caps shall be tared, labeled “spiked”, and numbered 1 through 6. The other vials shall be labeled “unspiked” and need not be tared, but are also numbered 1 through 6.

9.2 Determine the % moisture content of the crumb sample. After determining the % moisture content, the correction factor for calculating the dry crumb weight can be determined by using the equation in section 12.2 of this method.

9.3 Run the spiked and unspiked samples in the normal manner. Record the concentrations of the n-hexane content of the mixed hexane reported for each pair of spiked and unspiked samples.

9.4 For the recovery study, each sample of crumb shall be dissolved in chloroform containing a known amount of mixed hexane solvent.

9.5 For each hydrocarbon, calculate the recovery efficiency (R) using the following equations:

$M_r = M_s - M_u$

$R = M_r / S$

Where:

M_u = Measured amount of compound in the unspiked sample

M_s = Measured amount of compound in the spiked sample

M_r = Measured amount of the spiked compound

S = Amount of compound added to the spiked sample

R = Fraction of spiked compound recovered

9.6 Normally a value of R between 0.70 and 1.30 is acceptable.

9.7 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration

10.1 Using the AMS STOCK SOLUTION equipped with the automatic dispensing pipet (7.5.3 of this method), transfer 25.0 ml of the internal standard solution into an uncapped 50-ml serum vial.

10.2 Using a 2.0 ml volumetric pipet, quantitatively transfer 2.0 ml of the n-HEXANE STOCK SOLUTION (7.6.2 of this method) into the 50-ml serum vial and cap. This solution will be labeled the CALIBRATION SOLUTION.

10.3 Using the conditions prescribed (6.6 of this method), inject 1 µl of the supernate.

10.4 Obtain the peak areas and calculate the response factor as described in the calculations section (12.1 of this method).

11.0 Procedure

11.1 Determination of Dry Polymer Weight

11.1.1 Remove wet crumb from the polyethylene bag and place on paper towels to absorb excess surface moisture.

11.1.2 Cut small slices or cubes from the center of the crumb sample to improve sample uniformity and further eliminate surface moisture.

11.1.3 A suitable gravimetric measurement should be made on a sample of this wet crumb to determine the correction factor needed to calculate the dry polymer weight.

11.2 Determination of n-Hexane in Wet Crumb

11.2.1 Remove wet crumb from the polyethylene bag and place on paper towels to absorb excess surface moisture.

11.2.2 Cut small slices or cubes from the center of the crumb sample to improve sample uniformity and further eliminate surface moisture.

11.2.3 Into a tared 2 oz bottle, weigh 1.5 g of wet polymer to the nearest 0.1 mg.

11.2.4 Add 25 ml of chloroform to the 2 oz bottle and cap.

11.2.5 Using a mechanical shaker, shake the bottle until the polymer dissolves.

11.2.6 Using the autodispensing pipet, add 25.0 ml of the AMS STOCK SOLUTION (7.5.3 of this method) to the dissolved polymer solution and cap.

11.2.7 Using a mechanical shaker, shake the bottle for 10 minutes to coagulate the dissolved polymer.

11.2.8 Centrifuge the sample for 3 minutes at 2000 rpm.

11.2.9 Using the conditions prescribed (6.6 of this method), chromatograph 1 µl of the supernate.

11.2.10 Obtain the peak areas and calculate the concentration of the component of interest as described in the calculations (12.2 of this method).

12.0 Calculations

12.1 Calibration:

$RF_x = (W_x \times A_{is}) / (W_{is} \times A_x)$

Where:

RF_x = the relative response factor for n-hexane

W_x = the weight (g) of n-hexane in the CALIBRATION

SOLUTION

A_{is} = the area of AMS

W_{is} = the weight (g) of AMS in the CALIBRATION SOLUTION

A_x = the area of n-hexane

12.2 Procedure:

12.2.1 Correction Factor for calculating dry crumb weight.

$F = 1—(\%\ moisture / 100)$

Where:

F = Correction factor for calculating dry crumb weight

% moisture determined by appropriate method

12.2.2 Moisture adjustment for chromatographic determination.

$W_s = F \times W_c$

Where:

W_s = the weight (g) of the dry polymer corrected for moisture

F = Correction factor for calculating dry crumb weight

W_c = the weight (g) of the wet crumb in section 9.6

12.2.3 Concentration (ppm) of hexane in the wet crumb.

$ppm_x = (A_x * RF_x * W_{is} * 10000) / (A_{is} * W_s)$

Where:

ppm_x = parts per million of n-hexane in the polymer

A_x = the area of n-hexane

RF_x = the relative response factor for n-hexane

W_{is} = the weight (g) of AMS in the sample solution

A_{is} = the area of AMS

W_s = the weight (g) of the dry polymer corrected for moisture

13.0 Method Performance

13.1 Precision for the method was determined at the 0.08% level.

The standard deviation was 0.01 and the percent relative standard deviation (RSD) was 16.3 % with five degrees of freedom.

14.0 Waste Generation

14.1 Waste generation should be minimized where possible.

15.0 Waste Management

15.1 Discard liquid chemical waste into the chemical waste drum.

15.2 Discard polymer waste into the polymer waste container.

16.0 References

16.1 This method is based on Goodyear Chemical Division Test Method E-964.