

revision to the state implementation plan shall be considered separately in light of specific technical, economic, and environmental factors and in relation to relevant statutory and regulatory requirements.

EPA is publishing this action without prior proposal because the Agency views this as a noncontroversial amendment and anticipates no adverse comments. However, in a separate document in this Federal Register publication, the EPA is proposing to approve the SIP revision should adverse or critical comments be filed. This action will be effective May 16, 1997, unless, by April 16, 1997, adverse or critical comments are received.

If the EPA receives such comments, this action will be withdrawn before the effective date by publishing a subsequent document that will withdraw the final action. All public comments received will then be addressed in a subsequent final rule based on this action serving as a proposed rule. The EPA will not institute a second comment period on this action. Any parties interested in commenting on this action should do so at this time. If no such comments are received, the public is advised that this action will be effective May 16, 1997.

Regulatory Process

Under the Regulatory Flexibility Act, 5 U.S.C. 600 *et seq.*, EPA must prepare a regulatory flexibility analysis assessing the impact of any proposed or final rule on small entities. 5 U.S.C. 603 and 604. Alternatively, EPA may certify that the rule will not have a significant impact on a substantial number of small entities. Small entities include small businesses, small not-for-profit enterprises and government entities with jurisdiction over a population of less than 50,000.

SIP approvals under sections 110 and 301(a) and subchapter I, Part D of the CAA do not create any new requirements, but simply approve requirements that the State is already imposing. Therefore, because the Federal SIP-approval does not impose any new requirements, I certify that it does not have a significant impact on any small entities affected. Moreover, due to the nature of the Federal-state relationship under the CAA, preparation of a regulatory flexibility analysis would constitute Federal inquiry into the economic reasonableness of state action.

The CAA forbids EPA to base its actions concerning SIPs on such grounds. *Union Electric Co. v. U.S. E.P.A.*, 427 U.S. 246, 256-66 (S. Ct. 1976); 42 U.S.C. 7410 (a)(2).

Unfunded Mandates

Under Sections 202, 203, and 205 of the Unfunded Mandates Reform Act of 1995 ("Unfunded Mandates Act"), signed into law on March 22, 1995, EPA must undertake various actions in association with proposed or final rules that include a Federal mandate that may result in estimated costs of \$100 million or more to the private sector or to State, local, or tribal governments in the aggregate.

Through submission of this state implementation plan or plan revision, the State and any affected local or tribal governments have elected to adopt the program provided for under Part D of the Clean Air Act. These rules may bind State, local, and tribal governments to perform certain actions and also require the private sector to perform certain duties. The rule being approved by this action will impose no new requirements because affected sources are already subject to these regulations under State law. Therefore, no additional costs to State, local, or tribal governments or to the private sector result from this action. EPA has also determined that this final action does not include a mandate that may result in estimated costs of \$100 million or more to State, local, or tribal governments in the aggregate or to the private sector.

Under 5 U.S.C. 801(a)(1)(A) as added by the Small Business Regulatory Enforcement Fairness Act of 1996, EPA submitted a report containing this rule and other required information to the U.S. Senate, the U.S. House of Representatives and the Comptroller General of the General Accounting Office prior to publication of the rule in today's Federal Register. This rule is not a "major rule" as defined by 5 U.S.C. 804(2).

This action has been classified as a Table 3 action for signature by the Regional Administrator under the procedures published in the Federal Register on January 19, 1989 (54 FR 2214-2225), as revised by a July 10, 1995 memorandum from Mary Nichols, Assistant Administrator for Air and Radiation. The Office of Management and Budget (OMB) has exempted this regulatory action from Executive Order 12866 review.

List of Subjects in 40 CFR Part 52

Environmental protection, Air pollution control, Hydrocarbons, Incorporation by reference, Intergovernmental relations, Ozone, Reporting and recordkeeping requirements, Volatile organic compounds.

Note: Incorporation by reference of the State Implementation Plan for the State of California was approved by the Director of the Federal Register on July 1, 1982.

Dated: February 19, 1997.

Nora L. McGee,
Acting Regional Administrator.

Part 52, chapter I, title 40 of the Code of Federal Regulations is amended as follows:

PART 52—[AMENDED]

1. The authority citation for Part 52 continues to read as follows:

Authority: 42 U.S.C. 7401-7671q

Subpart D—Arizona

2. Section 52.120 is amended by adding paragraph (c)(82) to read as follows:

§ 52.120 Identification of plan.

* * * * *

(c) * * *

(82) New and amended rules and regulations for the Maricopa County Environmental Services Department—Air Pollution Control were submitted on August 31, 1995, by the Governor's designee.

(i) Incorporated by reference.

(A) Rule 343, adopted on February 15, 1995.

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BILLING CODE 6560-50-P

40 CFR Part 63

[FRL-5700-9]

RIN 2060-AE37

Test Methods for the Polymers and Resins I Rule; Appendix A, Test Methods 310 A, B, C, 312 A, B, C, 313 A, B

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This action promulgates test methods 310 a, b and c, 312 a, b and c, and 313 a and b for the detection of residual amounts of hazardous air pollutants (HAPs) in conjunction with the recently issued National Emission Standards for Hazardous Air Pollutants (NESHAP) for the Manufacture of Major Elastomers, (commonly referred to as Polymers and Resins I). The methods were adapted from industrial methods submitted by the facilities in the polymers and resins industry and were published for public comment as part of the Polymers and Resins I proposed rulemaking action. The methods will be

promulgated, in conjunction with the Polymers and Resins I rule, as EPA methods 310 a, b and c, 312 a, b and c, and 313 a and b, and will be codified at 40 CFR Part 63, Appendix A.

Methods 310 a, b, and c are applicable for determining the residual amount of solvent (hexane being the most commonly used solvent) and diene monomer in ethylene-propylene terpolymer (EPDM) as produced in the solution polymerization process. Methods 312 a, b, and c are applicable for determining the residual amount of styrene in styrene-butadiene rubber (SBR) as produced in the emulsion polymerization process. Methods 313 a and b are applicable for determining the residual amount of toluene, dimer, and styrene in polybutadiene rubber (PBR) and SBR crumb as produced in the solution polymerization process. All of the methods analyses are through the use of gas chromatography.

EFFECTIVE DATE: These methods are effective March 17, 1997.

ADDRESS: The background information for the promulgated test methods may be obtained from: Air Docket Section (LE-131), Attention: Docket No. A-92-44, U.S. Environmental Protection Agency, 401 M Street SW., Washington, DC 20460.

The docket is located at the above address in room M-1500, Waterside Mall (ground floor), and may be inspected from 8 a.m. to 4 p.m., Monday through Friday; telephone number (202) 382-7548. A reasonable fee may be charged for copying docket materials.

FOR FURTHER INFORMATION CONTACT: For information concerning the methods, contact Mr. Solomon Ricks at (919) 541-5242, Emission Measurement Center, Emission Monitoring and Analysis Division (MD-19), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 27711.

SUPPLEMENTARY INFORMATION: *Response to Comments:* Concurrent with the proposal of subpart U, the EPA proposed three test residual HAP test methods—one each for SBRE, PBR/SBRS, and EPR. In determining the methods to be included in the proposal, the industry was given the opportunity to submit test methods for evaluation and approval by the EPA. The EPA selected the test methods submitted by the Exxon Chemical Company (Method 310), the Goodyear Tire and Rubber Company (Method 312), and the American Synthetic Rubber Corporation (Method 313) as the test methods to be used to determine residual HAP concentration.

After proposal of the test methods, several commenters stated that no single

analytical method would produce consistent results for all polymers. It was suggested by the companies that each company should be allowed to demonstrate compliance using a company-specific method that is comparable to the EPA test method. The EPA agreed with the commenters and concluded that it was appropriate to allow every interested company to validate their own test method using a modified version of 40 CFR part 63, Appendix A, Method 301.

A total of eight test methods were submitted by seven different companies. Throughout the process, the affected industry has been involved with all activity associated with the EPA's promulgation of the residual organic HAP test methods. The EPA held meetings with industry representatives to discuss their comments on the proposed methods, and to discuss procedures for validating company test methods. Representatives of each of those three companies which did not submit test methods were in attendance at one or more of the meetings.

This notice with the promulgated regulatory language is also available on the Technology Transfer Network (TTN) on the EPA's electronic bulletin boards. The TTN provides information and technology exchange in various areas of air pollution control. The service is free, except for the cost of a telephone call. Dial (919) 541-5742 for up to a 14,400 bps modem. If more information on TTN is needed, call the HELP line at (919) 541-5384.

Other materials related to this rulemaking are available for review in the docket.

Judicial Review: Under section 307(b)(1) of the Act, judicial review of the final rule is available only by filing a petition for review in the U. S. Court of Appeals for the District of Columbia Circuit within 60 days of today's publication of this final rule. Under section 307(b)(2) of the Act, the requirements that are the subject of today's notice may not be challenged later in civil or criminal proceedings brought by the EPA to enforce these requirements.

I. Introduction

The methods being promulgated are to be used in testing for residual amounts of HAPs to determine compliance with the standards in the promulgated Polymers and Resins I rule (September 5, 1996, 61 FR 46906). The methods were published for comment along with the Polymers and Resins I proposal under the authority of section 112(d) of the Clean Air Act as amended in 1990. Section 112(d) requires the

Administrator to regulate emissions of HAP listed in section 112(b) of the Clean Air Act. The Polymers and Resins I proposal was published for public comment on June 12, 1995 (60 FR 30801).

The methods being promulgated will apply to ethylene-propylene elastomers production, polybutadiene rubber production, and styrene-butadiene rubber and latex production, using stripping technology as the method of compliance. As stated in the promulgated Polymers and Resins I rule, if compliance is to be demonstrated by sampling, samples of the stripped wet crumb or stripped latex must be taken after the stripper and analyzed to determine the residual HAP content.

II. Summary of Test Methods

A. Methods 310 a, b, and c

The promulgated methods are adapted from test methods submitted to the EPA by DSM Copolymer, Uniroyal Chemical, and Exxon. These companies are involved in the manufacture of EPDM rubber. The basic principle of DSM Copolymer's methods involve heating a sample in a sealed bottle with an internal standard and analyzing the vapor by gas chromatography. Uniroyal Chemical extracts residual hexane contained in wet pieces of EPDM polymer with methyl isobutyl ketone (MIBK). The extract is then analyzed by gas chromatography. Exxon's principle involves dissolving an EPDM crumb rubber sample in toluene to which heptane has been added as an internal standard. Acetone is then added to the solution to precipitate the crumb, and the supernatant is then analyzed for hexane and diene by a gas chromatograph with a flame ionization detector (FID).

B. Methods 312 a, b, and c

The promulgated methods are adapted from a test methods submitted to the EPA by Goodyear Tire and Rubber Company, Ameripol Synpol Corporation, and DSM Copolymer. The basic principle of the Goodyear method is to coagulate the SBR latex sample with an ethyl alcohol solution containing a specific amount of alpha-methyl styrene as the internal standard, and analyzing the extract to determine styrene concentration using a gas chromatograph with a FID. Ameripol Synpol coagulates the latex sample in propanol which contains alpha-methyl styrene as the internal standard. The extract is then analyzed by a gas chromatograph to determine the residual styrene from the latex. DSM Copolymer utilizes a packed column gas chromatograph with a FID to determine

the concentration of residual styrene in the latex samples.

C. Methods 313 a and b

The promulgated methods are adapted from test methods submitted to the EPA by the American Synthetic Rubber Corporation (ASRC) and the Goodyear Tire and Rubber Company. The basic principle of the ASRC method involves placing the wet crumb sample in a sealed vial and running on a headspace sampler which heats the vial to a specified temperature for a specific time and then injects a known volume of vapor into a capillary gas chromatograph. The method determines residual toluene and styrene in the stripper crumb derived from solution polymerization processes that utilize toluene as the polymerization solvent. The Goodyear method uses the principle of dissolving the polymer sample in chloroform and coagulating the cement with an isopropyl alcohol solution containing a specific amount of alpha-methyl styrene as the internal standard. The extract of this coagulation is then injected into a gas chromatograph and separated into individual components.

III. Significant Comments and Changes to Test Methods

When published with the Polymers and Resins I proposal, the methods were proposed as methods 310, 312, and 313. The industry submitted their test methods for EPA review, and it was left to the EPA to decide which method would be acceptable as the test methods to be used for compliance purposes. However, after proposal, the companies who submitted their methods for consideration, and whose methods were not selected, raised the issue that no single analytical method would produce consistent results for all polymers. After review and consideration of this issue, the EPA concluded that it was appropriate to allow every interested company to validate their own test method using a modified version of 40 CFR part 63, Appendix A, Method 301. The results of this effort was to have a total of eight methods submitted as validated test methods by seven companies. Only three affected companies decided not to submit methods. Therefore, the final methods rule include methods 310a, b, and c for EPR, methods 312a, b, and c for SBRE, and methods 313a and b for PBR/SBRS, as acceptable residual organic HAP test methods.

IV. Administrative Requirements

A. Docket

The docket is an organized and complete file for all information submitted or otherwise considered by EPA in the development of this promulgated rulemaking. The principal purposes of the docket are: (1) to allow interested parties to identify and locate documents so that they can effectively participate in the rulemaking process, and (2) to serve as the record in case of judicial review (except for interagency review materials) [Clean Air Act Section 307(d)(7)(A)].

B. Office of Management and Budget Review

Under Executive Order 12866 (58 FR 51735 October 4, 1993), the EPA is required to judge whether a regulation is "significant" and therefore subject to Office of Management and Budget (OMB) review and the requirements of this Executive Order to prepare a regulatory impact analysis (RIA). The Order defines "significant regulatory action" as one that is likely to result in a rule that may: (1) Have an annual effect on the economy of \$100 million or more or adversely affect in a material way the economy, a sector of the economy, productivity, competition, jobs, the environment, public health or safety, or State, local, or tribal governments or communities; (2) create a serious inconsistency or otherwise interfere with an action taken or planned by another agency; (3) materially alter the budgetary impact of entitlements, grants, user fees, or loan programs, or the rights and obligation of recipients thereof; or (4) raise novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order.

Pursuant to the terms of the Executive Order, this action has been determined to be "not significant."

C. Regulatory Flexibility Act

The EPA has determined that it is not necessary to prepare a regulatory flexibility analysis in connection with this final rule. The EPA has also determined that this rule will not have a significant adverse impact on a substantial number of small businesses. This rulemaking does not impose emission measurement requirements beyond those specified in the current regulations, nor does it change any emission standard, rather it provides acceptable test methods that the businesses regulated by Polymers and Resins I may use to comply with that rule. As such, it will not present a

significant economic impact on a substantial number of small businesses.

D. Small Business Regulatory Enforcement Fairness Act of 1996 (SBREFA)

Under 5 U.S.C. 801(a)(1)(A) as added by the Small Business Regulatory Enforcement Fairness Act of 1996, EPA submitted a report containing this rule and other required information to the U.S. Senate, the U.S. House of Representatives and the Comptroller General of the General Accounting Office prior to publication of the rule in today's Federal Register. This rule is not a "major rule" as defined by 5 U.S.C. 804(2).

E. Paperwork Reduction Act

The rule does not impose or change any information collection requirements subject to Office of Management and Budget review under the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.*

F. Unfunded Mandates

Under Section 202 of the Unfunded Mandates Reform Act of 1995 ("Unfunded Mandates Act"), signed into law on March 22, 1995, EPA must prepare a budgetary impact statement to accompany any proposed or final rule that includes a Federal mandate that may result in estimated costs to State, local, or tribal governments in the aggregate; or to the private sector, of \$100 million or more. Under Section 205, EPA must select the most cost-effective and least burdensome alternative that achieves the objectives of the rule and is consistent with statutory requirements. Section 203 requires EPA to establish a plan for significantly or uniquely impacted by the rule.

EPA has determined that the action proposed today does not include a Federal mandate that may result in estimated costs of \$100 million or more to either State, local, or tribal governments in the aggregate, or to the private sector, nor does this action significantly or uniquely impact small governments, because this action contains no requirements that apply to such governments or impose obligations upon them. Therefore, the requirements of the Unfunded Mandates Act do not apply to this action.

List of Subjects in 40 CFR Part 63

Environmental protection, Emulsion polymerization, Gas chromatography, Residual Hydrocarbon, Styrene, Solution polymerization.

Dated: March 4, 1997.

Carol M. Browner,
Administrator.

For the reasons set out in the preamble, Appendix A of Part 63 of Title 40 of the CFR is amended as follows:

PART 63—[AMENDED]

1. The authority citation for Part 63 continues to read as follows:

Authority: 42 U.S.C. 7401, *et seq.*

2. Appendix A of Part 63 is amended by adding methods 310, 312, and 313 to read as follows:

APPENDIX A—TEST METHODS

* * * * *

METHOD 310A—DETERMINATION OF RESIDUAL HEXANE THROUGH GAS CHROMATOGRAPHY

1.0 Scope and Application

- 1.1 This method is used to analyze any crumb rubber or water samples for residual hexane content.
- 1.2 The sample is heated in a sealed bottle with an internal standard and the vapor is analyzed by gas chromatography.

2.0 Summary of Method

- 2.1 This method, utilizing a capillary column gas chromatograph with a flame ionization detector, determines the concentration of residual hexane in rubber crumb samples.

3.0 Definitions

- 3.1 The definitions are included in the text as needed.

4.0 Interferences

- 4.1 There are no known interferences.

5.0 Safety

- 5.1 It is the responsibility of the user of this procedure to establish safety and health practices applicable to their specific operation.

6.0 Equipment and Supplies

- 6.1 Gas Chromatograph with a flame ionization detector and data handling station equipped with a capillary column 30 meters long.
- 6.2 Chromatograph conditions for Sigma 1:
 - 6.2.1 Helium pressure: 50# inlet A, 14# aux
 - 6.2.2 Carrier flow: 25 cc/min
 - 6.2.3 Range switch: 100x
 - 6.2.4 DB: 1 capillary column
- 6.3 Chromatograph conditions for Hewlett-Packard GC:
 - 6.3.1 Initial temperature: 40 °C

- 6.3.2 Initial time: 8 min

- 6.3.3 Rate: 0

- 6.3.4 Range: 2

- 6.3.5 DB: 1705 capillary column

- 6.4 Septum bottles and stoppers

- 6.5 Gas Syringe—0.5 cc

7.0 Reagents and Standards

- 7.1 Chloroform, 99.9+%, A.S.C. HPLC grade

8.0 Sample Collection, Preservation, and Storage

- 8.1 A representative sample should be caught in a clean 8 oz. container with a secure lid.

- 8.2 The container should be labeled with sample identification, date and time.

9.0 Quality Control

- 9.1 The instrument is calibrated by injecting calibration solution (Section 10.2 of this method) five times.

- 9.2 The retention time for components of interest and relative response of monomer to the internal standard is determined.

- 9.3 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.

- 9.3.1 Determine the percent hexane in three separate dried rubber crumb samples.

- 9.3.2 Weigh a portion of each crumb sample into separate sample bottles and add a known amount of hexane (10 microliters) by microliter syringe and 20 microliters of internal standard. Analyze each by the described procedure and calculate the percent recovery of the known added hexane.

- 9.3.3 Repeat the previous step using twice the hexane level (20 microliters), analyze and calculate the percent recovery of the known added hexane.

- 9.3.4 Set up two additional sets of samples using 10 microliters and 20 microliters of hexane as before, but add an amount of water equal to the dry crumb used. Analyze and calculate percent recovery to show the effect of free water on the results obtained.

- 9.3.5 A value of R between 0.70 and 1.30 is acceptable.

- 9.3.6 R shall be 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 and Instrument Settings

- 10.1 Calibrate the chromatograph using a standard made by injecting 10 µl of fresh hexane and 20 µl of chloroform into a sealed septum bottle. This standard will be 0.6 wt.% total hexane based on 1 gram of dry rubber.

- 10.2 Analyze the hexane used and calculate the percentage of each hexane isomer (2-methylpentane, 3-methylpentane, n-hexane, and methylcyclopentane). Enter these percentages into the method calibration table.

- 10.3 Heat the standard bottle for 30 minutes in a 105 °C oven.

- 10.4 Inject about 0.25 cc of vapor into the gas chromatograph and after the analysis is finished, calibrate according to the procedures described by the instrument manufacturer.

11.0 Procedure

- 11.1 Using a cold mill set at a wide roller gap (125–150 mm), mill about 250 grams of crumb two times to homogenize the sample.

- 11.2 Weigh about 2 grams of wet crumb into a septum bottle and cap with a septum ring. Add 20 µl of chloroform with a syringe and place in a 105 °C oven for 45 minutes.

- 11.3 Run the moisture content on a separate portion of the sample and calculate the grams of dry rubber put into the septum bottle.

- 11.4 Set up the data station on the required method and enter the dry rubber weight in the sample weight field.

- 11.5 Inject a 0.25 cc vapor sample into the chromatograph and push the start button.

- 11.6 At the end of the analysis, the data station will print a report listing the concentration of each identified component.

- 11.7 To analyze water samples, pipet 5 ml of sample into the septum bottle, cap and add 20 µl of chloroform. Place in a 105 °C oven for 30 minutes.

- 11.8 Enter 5 grams into the sample weight field.

- 11.9 Inject a 0.25 cc vapor sample into the chromatograph and push the start button.

- 11.10 At the end of the analysis, the data station will print a report listing the concentration of each identified component.

12.0 Data Analysis and Calculation

- 12.1 For samples that are prepared as in section 11 of this method, ppm

n-hexane is read directly from the computer.

12.2 The formulas for calculation of the results are as follows:

$$\text{ppm}_{\text{hexane}} = (\text{A}_{\text{hexane}} \times \text{R}_{\text{hexane}}) / (\text{A}_{\text{is}} \times \text{R}_{\text{is}})$$

Where:

A_{hexane} = area of hexane

R_{hexane} = response of hexane

A_{is} = area of the internal standard

R_{is} = response of the internal standard

% hexane in crumb = $(\text{ppm}_{\text{hexane}} / \text{sample amount}) \times 100$

12.3 Correct the results by the value of R (as determined in sections 9.3.4, 9.3.5, and 9.3.6 of this method).

13.0 Method Performance

13.1 The test has a standard deviation of 0.14 wt% at 0.66 wt% hexane. Spike recovery of 12 samples at two levels of hexane averaged 102.3%. Note: Recovery must be determined for each type of sample. The values given here are meant to be examples of method performance.

14.0 Pollution Prevention

14.1 Waste generation should be minimized where possible. Sample size should be an amount necessary to adequately run the analysis.

15.0 Waste Management

15.1 All waste shall be handled in accordance with federal and state environmental regulations.

16.0 References and Publications

16.1 DSM Copolymer Test Method T-3380.

METHOD 310B—DETERMINATION OF RESIDUAL HEXANE THROUGH GAS CHROMATOGRAPHY

1.0 Scope and Application

Analyte	CAS No.	Matrix	Method sensitivity (5.5g sample size)
Hexane	110-54-3	Rubber crumb01 wt%.
Ethylidene norbornene (ENB)	16219-75-3	Rubber crumb001 wt%.

1.1 Data Quality Objectives:

In the production of ethylene-propylene terpolymer crumb rubber, the polymer is recovered from solution by flashing off the solvent with steam and hot water. The resulting water-crumb slurry is then pumped to the finishing units. Certain amounts of solvent (hexane being the most commonly used solvent) and diene monomer remain in the crumb. The analyst uses the following procedure to determine those amounts.

2.0 Summary of Method

2.1 The crumb rubber sample is dissolved in toluene to which heptane has been added as an internal standard. Acetone is then added to this solution to precipitate the crumb, and the supernatant is analyzed for hexane and diene by a gas chromatograph equipped with a flame ionization detector (FID).

3.0 Definitions

3.1 Included in text as needed.

4.0 Interferences

4.1 None known.

4.2 Benzene, introduced as a contaminant in the toluene solvent, elutes between methyl cyclopentane and cyclohexane. However, the benzene peak is completely resolved.

4.3 2,2-dimethyl pentane, a minor component of the hexane used in our process, elutes just prior to methyl cyclopentane. It is included as "hexane" in the analysis whether it is integrated separately or included in the methyl cyclopentane peak.

5.0 Safety

5.1 This procedure does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

5.2 Chemicals used in this analysis are flammable and hazardous (see specific toxicity information below). Avoid contact with sources of ignition during sample prep. All handling should be done beneath a hood. Playtex or nitrile gloves recommended.

5.3 Hexane is toxic by ingestion and inhalation. Vapor inhalation causes irritation of nasal and respiratory passages, headache, dizziness, nausea, central nervous system depression. Chronic overexposure can cause severe nerve damage. May cause irritation on contact with skin or eyes. May cause damage to kidneys.

5.3 ENB may be harmful by inhalation, ingestion, or skin absorption. Vapor or mist is irritating to the eyes, mucous membranes, and upper respiratory tract. Causes skin irritation.

5.4 Toluene is harmful or fatal if swallowed. Vapor harmful if inhaled. Symptoms: headache, dizziness, hallucinations, distorted perceptions, changes in motor activity, nausea, diarrhea, respiratory irritation, central nervous system depression, unconsciousness, liver, kidney and lung damage. Contact can cause severe eye irritation. May cause

skin irritation. Causes irritation of eyes, nose, and throat.

5.5 Acetone, at high concentrations or prolonged overexposure, may cause headache, dizziness, irritation of eyes and respiratory tract, loss of strength, and narcosis. Eye contact causes severe irritation; skin contact may cause mild irritation. Concentrations of 20,000 ppm are immediately dangerous to life and health.

5.6 Heptane is harmful if inhaled or swallowed. May be harmful if absorbed through the skin. Vapor or mist is irritating to the eyes, mucous membranes, and upper respiratory tract. Prolonged or repeated exposure to skin causes defatting and dermatitis.

5.7 The steam oven used to dry the polymer in this procedure is set at 110° C. Wear leather gloves when removing bottles from the oven.

6.0 Equipment and Supplies

6.1 4000-ml volumetric flask

6.2 100-ml volumetric pipette

6.3 1000-ml volumetric flask

6.4 8-oz. French Square sample bottles with plastic-lined caps

6.5 Top-loading balance

6.6 Laboratory shaker

6.7 Laboratory oven set at 110° C (steam oven)

6.8 Gas chromatograph, Hewlett-Packard 5890A, or equivalent, interfaced with HP 7673A (or equivalent) autosampler (equipped with nanoliter adapter and robotic arm), and HP 3396 series II or 3392A (or equivalent) integrator/controller.

6.9 GC column, capillary type, 50m × 0.53mm, methyl silicone, 5 micron

- film thickness, Quadrex, or equivalent.
- 6.10 Computerized data acquisition system, such as CIS/CALS
- 6.11 Crimp-top sample vials and HP p/n 5181-1211 crimp caps.
- 6.12 Glass syringes, 5-ml, with "Luer-lock" fitting
- 6.13 Filters, PTFE, .45µm pore size, Gelman Acrodisc or equivalent, to fit on Luer-lock syringes (in 6.12, above).
- 7.0 Reagents and Standards**
- 7.1 Reagent toluene, EM Science Omnisolv
Purity Check: Prior to using any bottle of reagent toluene, analyze it according to section 11.2 of this method. Use the bottle only if hexane, heptane, and ENB peak areas are less than 15 each (note that an area of 15 is equivalent to less than 0.01 wt% in a 10g sample).
- 7.2 Reagent acetone, EM Science Omnisolv HR-GC
Purity Check: Prior to using any bottle of reagent acetone, analyze it according to section 11.2 of this method. Use the bottle only if hexane, heptane, and ENB peak areas are less than 15 each.
- 7.3 Reagent heptane, Aldrich Chemical Gold Label, Cat #15,487-3
Purity Check: Prior to using any bottle of reagent heptane, analyze it according to section 11.2 of this method. Use the bottle only if hexane and ENB peak areas are less than 5 each.
- 7.4 Internal standard solution—used as a concentrate for preparation of the more dilute Polymer Dissolving Solution. It contains 12.00g heptane/100ml of solution which is 120.0g per liter.
Preparation of internal standard solution (polymer dissolving stock solution):

Action	Notes
7.4.1 Tare a clean, dry 1-liter volumetric flask on the balance. Record the weight to three places.	If the 1-liter volumetric flask is too tall to fit in the balance case, you can shield the flask from drafts by inverting a paint bucket with a hole cut in the bottom over the balance cover. Allow the neck of the flask to project through the hole in the bucket.
7.4.2 Weigh 120.00 g of n-heptane into the flask. Record the total weight of the flask and heptane as well as the weight of heptane added.	Use 99+% n-heptane from Aldrich or Janssen Chimica.
7.4.3 Fill the flask close to the mark with toluene, about 1 to 2" below the mark.	Use EM Science Omnisolve toluene, Grade TX0737-1, or equivalent.
7.4.4 Shake the flask vigorously to mix the contents	Allow any bubbles to clear before proceeding to the next step.
7.4.5 Top off the flask to the mark with toluene. Shake vigorously, as in section 5.4.4 of this method, to mix well.	
7.4.6 Weigh the flask containing the solution on the three place balance record the weight	
7.4.7 Transfer the contents of the flask to a 1 qt Boston round bottle	Discard any excess solution
7.4.8 Label the bottle with the identity of the contents, the weights of heptane and toluene used, the date of preparation and the preparer's name.	Be sure to include the words "Hexane in Crumb Polymer Dissolving Stock Solution" on the label.
7.4.9 Refrigerate the completed blend for the use of the routine Technicians.	

- 7.5 Polymer Dissolving Solution ("PDS")—Heptane (as internal standard) in toluene. This solution contains 0.3g of heptane internal standard per 100 ml of solution.
- 7.5.1 Fill a 4000ml volumetric flask about ¾ full with toluene.
- 7.5.2 Add 100 ml of the internal standard solution (section 7.4 of this method) to the flask using the 100ml pipette.
- 7.5.3 Fill the flask to the mark with toluene. Discard any excess.
- 7.5.4 Add a large magnetic stirring bar to the flask and mix by stirring.
- 7.5.5 Transfer the polymer solvent solution to the one-gallon labeled container with 50ml volumetric dispenser attached.
- 7.5.6 Purity Check: Analyze according to section 11.2. *NOTE:* You must "precipitate" the sample with an equal part of acetone (thus duplicating actual test conditions—see section 11.1 of this method, sample prep) before analyzing. Analyze the reagent 3 times to quantify the C₆ and ENB
- interferences. Inspect the results to ensure good agreement among the three runs (within 10%).
- 7.5.7 Tag the bottle with the following information:
POLYMER DISSOLVING
SOLUTION FOR C₆ IN CRUMB
ANALYSIS
PREPARER'S NAME
DATE
CALS FILE ID'S OF THE THREE
ANALYSES FOR PURITY (from
section 7.5.6 of this method)
- 7.6 Quality Control Solution: the quality control solution is prepared by adding specific amounts of mixed hexanes (barged hexane), n-nonane and ENB to some polymer dissolving solution. Nonane elutes in the same approximate time region as ENB and is used to quantify in that region because it has a longer shelf life. ENB, having a high tendency to polymerize, is used in the QC solution only to ensure that both ENB isomers elute at the proper time.
First, a concentrated stock solution is prepared; the final QC solution can then be prepared by diluting the stock solution.
- 7.6.1 In preparation of stock solution, fill a 1-liter volumetric flask partially with polymer dissolving solution (PDS)—see section 7.5 of this method. Add 20.0 ml barged hexane, 5.0 ml n-nonane, and 3 ml ENB. Finish filling the volumetric to the mark with PDS.
- 7.6.2 In preparation of quality control solution, dilute the quality control stock solution (above) precisely 1:10 with PDS, i.e. 10 ml of stock solution made up to 100 ml (volumetric flask) with PDS. Pour the solution into a 4 oz. Boston round bottle and store in the refrigerator.
- 8.0 Sample Collection, Preservation and Storage**
- 8.1 Line up facility to catch crumb samples. The facility is a special facility where the sample is drawn.
- 8.1.1 Ensure that the cock valve beneath facility is closed.

- 8.1.2 Line up the system from the slurry line cock valve to the cock valve at the nozzle on the stripper.
- 8.1.3 Allow the system to flush through facility for a period of 30 seconds.
- 8.2 Catch a slurry crumb sample.
 - 8.2.1 Simultaneously close the cock valves upstream and downstream of facility.
 - 8.2.2 Close the cock valve beneath the slurry line in service.
 - 8.2.3 Line up the cooling tower water through the sample bomb water jacket to the sewer for a minimum of 30 minutes.
 - 8.2.4 Place the sample catching basket beneath facility and open the cock valve underneath the bomb to retrieve the rubber crumb.
 - 8.2.5 If no rubber falls by gravity into the basket, line up nitrogen to the bleeder upstream of the sample bomb and force the rubber into the basket.
 - 8.2.6 Close the cock valve underneath the sample bomb.
- 8.3 Fill a plastic "Whirl-pak" sample bag with slurry crumb and send it to the lab immediately.
- 8.4 Once the sample reaches the lab, it should be prepped as soon as possible to avoid hexane loss through evaporation. Samples which have lain untouched for more than 30 minutes should be discarded.

9.0 Quality Control

Quality control is monitored via a computer program that tracks analyses of a prepared QC sample (from section 7.6.2 of this method). The QC sample result is entered daily into the program, which plots the result as a data point on a statistical chart. If the data point does not satisfy the "in-control" criteria (as defined by the lab quality facilitator), an "out-of-control" flag appears, mandating corrective action.

In addition, the area of the n-heptane peak is monitored so that any errors in making up the polymer dissolving solution will be caught and corrected. Refer to section 12.4 of this method.

- 9.1 Fill an autosampler vial with the quality control solution (from section 7.6.2 of this method) and analyze on the GC as normal (per section 11 of this method).
- 9.2 Add the concentrations of the 5 hexane isomers as they appear on the CALS printout. Also include the 2,2-dimethyl-pentane peak just ahead of the methyl cyclopentane (the fourth major isomer) peak in the event that the peak integration split this peak out. Do not include the benzene peak in the sum. Note

the nonane concentration. Record both results (total hexane and nonane) in the QC computer program. If out of control, and GC appears to be functioning within normal parameters, reanalyze a fresh control sample. If the fresh QC is not in control, check stock solution for contaminants or make up a new QC sample with the toluene currently in use. If instrument remains out-of-control, more thorough GC troubleshooting may be needed.

Also, verify that the instrument has detected both isomers of ENB (quantification not necessary—see section 7.0 of this method).

- 9.3 Recovery efficiency must be determined for each sample type and whenever modifications are made to the method. Recovery shall be between 70 and 130 percent. All test results must be corrected by the recovery efficiency value (R).

9.3.1 Approximately 10 grams of wet EPDM crumb (equivalent to about 5 grams of dry rubber) shall be added to six sample bottles containing 100 ml of hexane in crumb polymer dissolving solution (toluene containing 0.3 gram n-heptane/100 ml solution). The polymer shall be dissolved by agitating the bottles on a shaker for 4 hours. The polymer shall be precipitated using 100 ml acetone.

9.3.2 The supernatant liquid shall be decanted from the polymer. Care shall be taken to remove as much of the liquid phase from the sample as possible to minimize the effect of retained liquid phase upon the next cycle of the analysis. The supernatant liquid shall be analyzed by gas chromatography using an internal standard quantitation method with heptane as the internal standard.

9.3.3 The precipitated polymer from the steps described above shall be re-dissolved using toluene as the solvent. The toluene solvent and acetone precipitant shall be determined to be free of interfering compounds.

9.3.4 The rubber which was dissolved in the toluene shall be precipitated with acetone as before, and the supernatant liquid decanted from the precipitated polymer. The liquid shall be analyzed by gas chromatography and the rubber phase dried in a steam-oven to determine the final polymer weight.

9.3.5 The ratios of the areas of the hexane peaks and of the heptane internal standard peak shall be calculated for each of the six

samples in the two analysis cycles outlined above. The area ratios of the total hexane to heptane (R1) shall be determined for the two analysis cycles of the sample set. The ratio of the values of R1 from the second analysis cycle to the first cycle shall be determined to give a second ratio (R2).

10.0 Calibration and Standardization

The procedure for preparing a Quality Control sample with the internal standard in it is outlined in section 7.6 of this method.

10.1 The relative FID response factors for n-heptane, the internal standard, versus the various hexane isomers and ENB are relatively constant and should seldom need to be altered. However Baseline construction is a most critical factor in the production of good data. For this reason, close attention should be paid to peak integration. Procedures for handling peak integration will depend upon the data system used.

10.2 If recalibration of the analysis is needed, make up a calibration blend of the internal standard and the analytes as detailed below and analyze it using the analytical method used for the samples.

10.2.1 Weigh 5 g heptane into a tared scintillation vial to five places.

10.2.2 Add 0.2 ml ENB to the vial and reweigh.

10.2.3 Add 0.5 ml hexane to the vial and reweigh.

10.2.4 Cap, and shake vigorously to mix.

10.2.5 Calculate the weights of ENB and of hexane added and divide their weights by the weight of the n-heptane added. The result is the known of given value for the calibration.

10.2.6 Add 0.4 ml of this mixture to a mixture of 100 ml toluene and 100 ml of acetone. Cap and shake vigorously to mix.

10.2.7 Analyze the sample.

10.2.8 Divide the ENB area and the total areas of the hexane peaks by the n-heptane area. This result is the "found" value for the calibration.

10.2.9 Divide the appropriate "known" value from 10.2.5 by the found value from 10.2.8. The result is the response factor for the analyte in question. Previous work has shown that the standard deviation of the calibration method is about 1% relative.

11.0 Procedure

11.1 SAMPLE PREPARATION

- 11.1.1 Tare an 8oz sample bottle—Tag attached, cap off; record weight and sample ID on tag in pencil.
- 11.1.2 Place crumb sample in bottle: RLA-1: 20g; RLA-3: 10g—(gives a dry wt of ~10g); (gives a dry wt of ~5.5g).
- 11.1.3 Dispense 100ml of PDS into each bottle. **SAMPLE SHOULD BE PLACED INTO SOLUTION ASAP TO AVOID HEXANE LOSS**—Using “Dispensette” pipettor. *Before dispensing, “purge” the dispensette (25% of its volume) into a waste bottle to eliminate any voids.*
- 11.1.4 Tightly cap bottles and load samples into shaker.
- 11.1.5 Insure that “ON-OFF” switch on the shaker itself is “ON.”
- 11.1.6 Locate shaker timer. Insure that toggle switch atop timer control box is in the middle (“off”) position. If display reads “04:00” (4 hours), move toggle switch to the left position. Shaker should begin operating.
- 11.1.7 After shaker stops, add 100 ml acetone to each sample to precipitate polymer. Shake minimum of 5 minutes on shaker—Vistalon sample may not have fully dissolved; nevertheless, for purposes of consistency, 4 hours is the agreed-upon dissolving time.
- 11.1.8 Using a 5-ml glass Luer-lock syringe and Acrodisc filter, filter some of the supernatant liquid into an autosampler vial; crimp the vial and load it into the GC autosampler for analysis (section 11.2 of this method)—The samples are filtered to prevent polymer buildup in the GC. Clean the syringes in toluene.
- 11.1.9 Decant remaining supernatant into a hydrocarbon waste sink, being careful not to discard any of the polymer. Place bottle of precipitate into the steam oven and dry for six hours—Some grades of Vistalon produce very small particles in the precipitate, thus making complete decanting impossible without discarding some polymer. In this case, decant as much as possible and put into the oven as is, allowing the oven to drive off remaining supernatant (this practice is avoided for environmental reasons). **WARNING: OVEN IS HOT—110 °C (230° F).**
- 11.1.10 Cool, weigh and record final weight of bottle.
- 11.2 GC ANALYSIS
- 11.2.1 Initiate the CALS computer channel.
- 11.2.2 Enter the correct instrument method into the GC’s integrator.
- 11.2.3 Load sample vial(s) into autosampler.

- 11.2.4 Start the integrator.
- 11.2.5 When analysis is complete, plot CALS run to check baseline skim.

12.0 Data Analysis and Calculations

- 12.1 Add the concentrations of the hexane peaks as they appear on the CALS printout. Do not include the benzene peak in the sum.
- 12.2 Subtract any hexane interferences found in the PDS (see section 7.5.6 of this method); record the result.
- 12.3 Note the ENB concentration on the CALS printout. Subtract any ENB interference found in the PDS and record this result in a “% ENB by GC” column in a logbook.
- 12.4 Record the area (from CALS printout) of the heptane internal standard peak in a “C7 area” column in the logbook. This helps track instrument performance over the long term.
- 12.5 After obtaining the final dry weight of polymer used (section 11.1.10 of this method), record that result in a “dry wt.” column of the logbook.
- 12.6 Divide the %C6 by the dry weight to obtain the total PHR hexane in crumb. Similarly, divide the %ENB by the dry weight to obtain the total PHR ENB in crumb. Note that PHR is an abbreviation for “parts per hundred”. Record both the hexane and ENB results in the logbook.
- 12.7 Correct all results by the recovery efficiency value (R).

13.0 Method Performance

- 13.1 The method has been shown to provide 100% recovery of the hexane analyte. The method was found to give a 6% relative standard deviation when the same six portions of the same sample were carried through the procedure. Note: These values are examples; each sample type must be tested for sample recovery.

14.0 Pollution Prevention

- 14.1 Dispose of all hydrocarbon liquids in the appropriate disposal sink system; never pour hydrocarbons down a water sink.
- 14.2 As discussed in section 11.1.9 of this method, the analyst can minimize venting hydrocarbon vapor to the atmosphere by decanting as much hydrocarbon liquid as possible before oven drying.

15.0 Waste Management

- 15.1 The Technician conducting the analysis should follow the proper waste management practices for their laboratory location.

16.0 References

- 16.1 Baton Rouge Chemical Plant Analytical Procedure no. BRCP 1302
- 16.2 Material Safety Data Sheets (from chemical vendors) for hexane, ENB, toluene, acetone, and heptane

METHOD 310C—DETERMINATION OF RESIDUAL N-HEXANE IN EPDM RUBBER THROUGH GAS CHROMATOGRAPHY

1.0 Scope and Application

- 1.1 This method describes a procedure for the determination of residual hexane in EPDM wet crumb rubber in the 0.01—2% range by solvent extraction of the hexane followed by gas chromatographic analysis where the hexane is detected by flame ionization and quantified via an internal standard.
- 1.2 This method may involve hazardous materials operations and equipment. This method does not purport to address all the safety problems associated with its use, if any. It is the responsibility of the user to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2.0 Summary

- 2.1 Residual hexane contained in wet pieces of EPDM polymer is extracted with MIBK. A known amount of an internal standard (IS) is added to the extract which is subsequently analyzed via gas chromatography where the hexane and IS are separated and detected utilizing a megabore column and flame ionization detection (FID). From the response to the hexane and the IS, the amount of hexane in the EPDM polymer is calculated.

3.0 Definitions

- 3.1 Hexane—refers to n-hexane
- 3.2 Heptane—refers to n-heptane
- 3.3 MIBK—methyl isobutyl ketone (4 methyl 2—Pentanone)

4.0 Interferences

- 4.1 Material eluting at or near the hexane and/or the IS will cause erroneous results. Prior to extraction, solvent blanks must be analyzed to confirm the absence of interfering peaks.

5.0 Safety

- 5.1 Review Material Safety Data Sheets of the chemicals used in this method.

6.0 Equipment and Supplies

- 6.1 4 oz round glass jar with a wide mouth screw cap lid.
- 6.2 Vacuum oven.
- 6.3 50 ml pipettes.
- 6.4 A gas chromatograph with an auto sampler and a 50 meter, 0.53 ID, methyl silicone column with 5 micron phase thickness.
- 6.5 Shaker, large enough to hold 10, 4 oz. jars.
- 6.6 1000 and 4000 ml volumetric flasks.
- 6.7 Electronic integrator or equivalent data system.
- 6.8 GC autosampler vials.
- 6.9 50 uL syringe.

7.0 Reagents and Standards

- 7.1 Reagent grade Methyl-Iso-Butyl-Ketone (MIBK)
- 7.2 n-heptane, 99% + purity
- 7.3 n-hexane, 99% + purity

8.0 Sample Collection

- 8.1 Trap a sample of the EPDM crumb slurry in the sampling apparatus. Allow the crumb slurry to circulate through the sampling apparatus for 5 minutes; then close off the valves at the bottom and top of the sampling apparatus, trapping the crumb slurry. Run cooling water through the water jacket for a minimum of 30 minutes. Expel the cooled crumb slurry into a sample catching basket. If the crumb does not fall by gravity, force it out with demineralized water or nitrogen. Send the crumb slurry to the lab for analysis.

9.0 Quality Control

- 9.1 The Royalene crumb sample is extracted three times with MIBK containing an internal standard. The hexane from each extraction is added together to obtain a total hexane content. The percent hexane in the first extraction is then calculated and used as the recovery factor for the analysis.
- 9.2 Follow this test method through section 11.4 of the method. After removing the sample of the first extraction to be run on the gas chromatograph, drain off the remainder of the extraction solvent, retaining the crumb sample in the sample jar. Rinse the crumb with demineralized water to remove any MIBK left on the surface of the crumb. Repeat the extraction procedure with fresh MIBK with internal standard two more times.
- 9.3 After the third extraction, proceed to section 11.5 of this method and obtain the percent hexane in each extraction. Use the sample weight

obtained in section 12.1 of this method to calculate the percent hexane in each of the extracts.

- 9.4 Add the percent hexane obtained from the three extractions for a total percent hexane in the sample.
- 9.5 Use the following equations to determine the recovery factor (R):

$$\% \text{ Recovery of the first extraction} = (\% \text{ hexane in the first extract} / \text{total } \% \text{ hexane}) \times 100$$

$$\text{Recovery Factor (R)} = (\% \text{ Hexane Recovered in the first extract}) / 100$$

10.0 Calibration**10.1 Preparation of Internal Standard (IS) solution:**

Accuracy weigh 30 grams of n-heptane into a 1000 ml volumetric flask. Dilute to the mark with reagent grade MIBK. Label this Solution "A". Pipette 100 mls. of Solution A into a 4 liter volumetric flask. Fill the flask to the mark with reagent MIBK. Label this Solution "B". Solution "B" will have a concentration of 0.75 mg/ml of heptane.

10.2 Preparation of Hexane Standard Solution (HS):

Using a 50 uL syringe, weigh by difference, 20 mg of n-hexane into a 50 ml volumetric flask containing approximately 40 ml of Solution B. Fill the flask to the mark with Solution B and mix well.

10.3 Conditions for GC analysis of standards and samples:

Temperature:
 Initial=40 °C
 Final=150 °C
 Injector=160 °C
 Detector=280 °C
 Program Rate=5.0 °C/min

Initial Time=5 minutes Final Time=6 minutes

Flow Rate=5.0 ml/min

Sensitivity=detector response must be adjusted to keep the hexane and IS on scale.

10.4 Fill an autosampler vial with the HS, analyze it three times and calculate a Hexane Relative Response Factor (RF) as follows:

$$RF = (A_{IS} \times C_{HS} \times P_{HS}) / (A_{HS} \times C_{IS} \times P_{IS})$$

Where:

A_{IS} =Area of IS peak (Heptane)

A_{HS} =Area of peak (Hexane Standard)

C_{HS} =Mg of Hexane/50 ml HS

C_{IS} =Mg of Heptane/50 ml IS Solution B

P_{IS} =Purity of the IS n-heptane

P_{HS} =Purity of the HS n-hexane

11.0 Procedure

- 11.1 Weight 10 grams of wet crumb into a tared (W1), wide mouth 4 oz. jar.
- 11.2 Pipette 50 ml of Solution B into the jar with the wet crumb rubber.

- 11.3 Screw the cap on tightly and place it on a shaker for 4 hours.
- 11.4 Remove the sample from the shaker and fill an autosampler vial with the MIBK extract.
- 11.5 Analyze the sample two times.
- 11.6 Analyze the HS twice, followed by the samples. Inject the HS twice at the end of each 10 samples or at the end of the run.

12.0 Calculations

- 12.1 Drain off the remainder of the MIBK extract from the polymer in the 4 oz. jar. Retain all the polymer in the jar. Place the uncovered jar and polymer in a heated vacuum oven until the polymer is dry. Reweigh the jar and polymer (W2) and calculate the dried sample weight of the polymer as follows:

$$\text{Dried SW} = W2 - W1 \quad (2)$$

- 12.2 Should the polymer be oil extended, pipette 10 ml of the MIBK extract into a tared evaporating dish (W1) and evaporate to dryness on a steam plate.

Reweigh the evaporating dish containing the extracted oil (W2). Calculate the oil content of the polymer as follows:

$$\text{Gram of oil extracted} = 5 (W2 - W1) \quad (3)$$

$$\% \text{ Hexane in polymer} = (A_s \times RF \times C_{IS} \times P_{IS}) / (A_{IS} \times SW) \quad (4)$$

Where:

A_s =Area of sample hexane sample peak.

A_{IS} =Area of IS peak in sample.

C_{IS} =Concentration of IS in 50 ml.

P_{IS} =Purity of IS.

SW=Weight of dried rubber after extraction. (For oil extended polymer, the amount of oil extracted is added to the dry rubber weight).

$$\% \text{ Corrected Hexane} = (\% \text{ Hexane in Polymer}) / R \quad (5)$$

R=Recovery factor determined in section 9 of this method.

13.0 Method Performance

- 13.1 Performance must be determined (1) for each sample type by following the procedures in section 9 of this method.

14.0 Waste Generation

- 14.1 Waste generation should be minimized where possible.

15.0 Waste Management

- 15.1 All waste shall be handled in accordance with Federal and State environmental regulations.

16.0 References

(Reserved)

METHOD 312A—DETERMINATION OF STYRENE IN LATEX STYRENE-BUTADIENE RUBBER, THROUGH GAS CHROMATOGRAPHY

1. Scope and Application

- 1.1 This method describes a procedure for determining parts per million (ppm) styrene monomer (CAS No. 100-42-5) in aqueous samples, including latex samples and styrene stripper water.
- 1.2 The sample is separated in a gas chromatograph equipped with a packed column and a flame ionization detector.

2.0 Summary of Method

- 2.1 This method utilizes a packed column gas chromatograph with a flame ionization detector to determine the concentration of residual styrene in styrene butadiene rubber (SBR) latex samples.

3.0 Definitions

- 3.1 The definitions are included in the text as needed.

4.0 Interferences

- 4.1 In order to reduce matrix effects and emulsify the styrene, similar styrene free latex is added to the internal standard. There are no known interferences.
- 4.2 The operating parameters are selected to obtain resolution necessary to determine styrene monomer concentrations in latex.

5.0 Safety

- 5.1 It is the responsibility of the user of this procedure to establish appropriate safety and health practices.

6.0 Equipment and Supplies

- 6.1 Adjustable bottle-top dispenser, set to deliver 3 ml. (for internal standard), Brinkmann Dispensette, or equivalent.
- 6.2 Pipettor, set to 10 ml., Oxford Macro-set, or equivalent.
- 6.3 Volumetric flask, 100-ml, with stopper.
- 6.4 Hewlett Packard Model 5710A dual channel gas chromatograph equipped with flame ionization detector.
- 6.4.1 11 ft. \times 1/8 in. stainless steel column packed with 10% TCEP on 100/120 mesh Chromosorb P, or equivalent.
- 6.4.2 Perkin Elmer Model 023 strip chart recorder, or equivalent.
- 6.5 Helium carrier gas, zero grade.
- 6.6 Liquid syringe, 25- μ l.

- 6.7 Digital MicroVAX 3100 computer with VG Multichrom software, or equivalent data handling system.

- 6.6 Wire Screens, circular, 70-mm, 80-mesh diamond weave.

- 6.7 DEHA—(N,N-Diethyl hydroxylamine), 97+% purity, CAS No. 3710-84-7

- 6.8 p-Dioxane, CAS No. 123-91-1

7.0 Reagents and Standards

- 7.1 Internal standard preparation.
- 7.1.1 Pipette 5 ml p-dioxane into a 1000-ml volumetric flask and fill to the mark with distilled water and mix thoroughly.

- 7.2 Calibration solution preparation.

- 7.2.1 Pipette 10 ml styrene-free latex (eg: NBR latex) into a 100-ml volumetric flask.

- 7.2.2 Add 3 ml internal standard (section 7.1.1 of this method).

- 7.2.3 Weigh exactly 10 μ l fresh styrene and record the weight.

- 7.2.4 Inject the styrene into the flask and mix well.

- 7.2.5 Add 2 drops of DEHA, fill to the mark with water and mix well again.

- 7.2.6 Calculate concentration of the calibration solution as follows:
mg/l styrene=(mg styrene added)/0.1 L

8.0 Sample Collection, Preservation, and Storage

- 8.1 A representative SBR emulsion sample should be caught in a clean, dry 6-oz. teflon lined glass container. Close it properly to assure no sample leakage.
- 8.2 The container should be labeled with sample identification, date and time.

9.0 Quality Control

- 9.1 The instrument is calibrated by injecting calibration solution (Section 7.2 of this method) five times.
- 9.2 The retention time for components of interest and relative response of monomer to the internal standard is determined.
- 9.3 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.
- 9.3.1 A set of six latex samples shall be collected. Two samples shall be prepared for analysis from each sample. Each sample shall be analyzed in duplicate.
- 9.3.2 The second set of six latex samples shall be analyzed in duplicate before spiking each sample with approximately 1000 ppm styrene. The spiked samples shall be analyzed in duplicate.

- 9.3.3 For each hydrocarbon, calculate the average recovery efficiency (R) using the following equations:

where:

$$R = \Sigma(R_n)/6$$

where:

$$R_n = (c_{ns} - c_v)/S_n$$

n=sample number

c_{ns} =concentration of compound measured in spiked sample number n.

c_{nu} = concentration of compound measured in unspiked sample number n.

S_n =theoretical concentration of compound spiked into sample n.

- 9.3.4 A value of R between 0.70 and 1.30 is acceptable.

- 9.3.5 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 and Instrument Settings

- 10.1 Injection port temperature, 250°C.
- 10.2 Oven temperature, 110°C, isothermal.
- 10.3 Carrier gas flow, 25 cc/min.
- 10.4 Detector temperature, 250°C.
- 10.5 Range, 1X.

11.0 Procedure

- 11.1 Turn on recorder and adjust baseline to zero.
- 11.2 Prepare sample.
- 11.2.1 For latex samples, add 3 ml Internal Standard (section 7.1 of this method) to a 100-ml volumetric flask. Pipet 10 ml sample into the flask using the Oxford pipettor, dilute to the 100-ml mark with water, and shake well.
- 11.2.2 For water samples, add 3 ml Internal Standard (section 7.1 of this method) to a 100-ml volumetric flask and fill to the mark with sample. Shake well.
- 11.3 Flush syringe with sample.
- 11.4 Carefully inject 2 μ l of sample into the gas chromatograph column injection port and press the start button.
- 11.5 When the run is complete the computer will print a report of the analysis.

12.0 Data Analysis and Calculation

- 12.1 For samples that are prepared as in section 11.2.1 of this method:

$$\text{ppm styrene} = A \times D$$

Where:

A = "ppm" readout from computer

D = dilution factor (10 for latex samples)

- 12.2 For samples that are prepared as in section 11.2.2 of this method,

ppm styrene is read directly from the computer.

13.0 Method Performance

13.1 This test has a standard deviation (1) of 3.3 ppm at 100 ppm styrene. The average Spike Recovery from six samples at 1000 ppm Styrene was 96.7 percent. The test method was validated using 926 ppm styrene standard. Six analysis of the same standard provided average 97.7 percent recovery. Note: These are example recoveries and do not replace quality assurance procedures in this method.

14.0 Pollution Prevention

14.1 Waste generation should be minimized where possible. Sample size should be an amount necessary to adequately run the analysis.

15.0 Waste Management

15.1 All waste shall be handled in accordance with Federal and State environmental regulations.

16.0 References and Publications

- 16.1 40 CFR 63 Appendix A—Method 301 Test Methods Field Validation of Pollutant Measurement
- 16.2 DSM Copolymer Test Method T-3060, dated October 19, 1995, entitled: *Determination of Residual Styrene in Latex*, Leonard, C.D., Vora, N.M. *et al*

METHOD 312B—DETERMINATION OF RESIDUAL STYRENE IN STYRENE-BUTADIENE (SBR) RUBBER LATEX BY CAPILLARY GAS CHROMATOGRAPHY

1.0 Scope

- 1.1 This method is applicable to SBR latex solutions.
- 1.2 This method quantitatively determines residual styrene concentrations in SBR latex solutions at levels from 80 to 1200 ppm.

2.0 Principle of Method

2.1 A weighed sample of a latex solution is coagulated with an ethyl alcohol (EtOH) 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, and 0.1 mg resolution
- 6.2 Bottles, 2-oz capacity, with poly-cap screw lids
- 6.3 Mechanical shaker
- 6.4 Syringe, 10- μ l capacity
- 6.5 Gas chromatograph, Hewlett Packard model 5890A, or equivalent, configured with FID with a megabore jet, splitless injector packed with silanized glass wool.
- 6.5.1 Establish the following gas chromatographic conditions, and allow the system to thoroughly equilibrate before use.

Injection technique = Splitless
Injector temperature = 225 deg C
Oven temperature = 70 deg C (isothermal)

Detector: temperature = 300 deg C
range = 5
attenuation = 0
Carrier gas: helium = 47 ml/min
Detector gases: hydrogen = 30 ml/min
air = 270 ml/min
make-up = 0 ml/min
Analysis time: = 3.2 min at the specified carrier gas flow rate and column temperature.

- 6.6 Gas chromatographic column, DB-1, 30 M X 0.53 ID, or equivalent, with a 1.5 micron film thickness.
- 6.7 Data collection system, Perkin-Elmer/Nelson Series Turbochrom 4 Series 900 Interface, or equivalent.
- 6.8 Pipet, automatic dispensing, 50-ml capacity, and 2-liter reservoir.
- 6.9 Flasks, volumetric, class A, 100-ml and 1000-ml capacity.
- 6.10 Pipet, volumetric delivery, 10-ml capacity, class A.

7.0 Chemicals and Reagents

CHEMICALS:

- 7.1 Styrene, C₈H₈, 99+%, CAS 100-42-5
- 7.2 Alpha methyl styrene, C₉H₁₀, 99%, CAS 98-83-9
- 7.3 Ethyl alcohol, C₂H₅OH, denatured formula 2B, CAS 64-17-5

REAGENTS:

- 7.4 Internal Standard Stock Solution: 5.0 mg/ml AMS in ethyl alcohol.
- 7.4.1 Into a 100-ml volumetric flask, weigh 0.50 g of AMS to the nearest 0.1 mg.
- 7.4.2 Dilute to the mark with ethyl alcohol. This solution will contain 5.0 mg/ml AMS in ethyl alcohol and will be labeled the AMS STOCK SOLUTION.
- 7.5 Internal Standard Working Solution: 2500 μ g/50 ml of AMS in ethyl alcohol.
- 7.5.1 Using a 10 ml volumetric pipet, quantitatively transfer 10.0 ml of the AMS STOCK SOLUTION into a 1000-ml volumetric flask.
- 7.5.2 Dilute to the mark with ethyl alcohol. This solution will contain 2500 μ g/50ml of AMS in ethyl alcohol and will be labeled the AMS WORKING SOLUTION.
- 7.5.3 Transfer the AMS WORKING SOLUTION to the automatic dispensing pipet reservoir.
- 7.6 Styrene Stock Solution: 5.0 mg/ml styrene in ethyl alcohol.
- 7.6.1 Into a 100-ml volumetric flask, weigh 0.50 g of styrene to the nearest 0.1 mg.
- 7.6.2 Dilute to the mark with ethyl alcohol. This solution will contain 5.0 mg/ml styrene in ethyl alcohol and will be labeled the STYRENE STOCK SOLUTION.
- 7.7 Styrene Working Solution: 5000 μ g/10 ml of styrene in ethyl alcohol.
- 7.7.1 Using a 10-ml volumetric pipet, quantitatively transfer 10.0 ml of the STYRENE STOCK SOLUTION into a 100-ml volumetric flask.
- 7.7.2 Dilute to the mark with ethyl alcohol. This solution will contain 5000 μ g/10 ml of styrene in ethyl alcohol and will be labeled the STYRENE WORKING SOLUTION.
- 8.0 Sample Collection, Preservation and Storage
- 8.1 Label a 2-oz sample poly-cap lid with the identity, date and time of the sample to be obtained.
- 8.2 At the sample location, open sample valve for at least 15 seconds to ensure that the sampling pipe has been properly flushed with fresh sample.
- 8.3 Fill the sample jar to the top (no headspace) with sample, then cap it tightly.
- 8.4 Deliver sample to the Laboratory for testing within one hour of sampling.
- 8.5 Laboratory testing will be done within two hours of the sampling time.
- 8.6 No special storage conditions are required unless the storage time

exceeds 2 hours in which case refrigeration of the sample is recommended.

9.0 Quality Control

- 9.1 For each sample type, 12 samples of SBR latex shall be obtained from the process for the recovery study. Half the vials and caps shall be tared, labeled "spiked", and numbered 1 through 6. The other vials are labeled "unspiked" and need not be tared, but are also numbered 1 through 6.
- 9.2 The six vials labeled "spiked" shall be spiked with an amount of styrene to approximate 50% of the solution's expected residual styrene level.
- 9.3 The spiked samples shall be shaken for several hours and allowed to cool to room temperature before analysis.
- 9.4 The six samples of unspiked solution shall be coagulated and a mean styrene value shall be determined, along with the standard deviation, and the percent relative standard deviation.
- 9.5 The six samples of the spiked solution shall be coagulated and the results of the analyses shall be determined using the following equations:

$$M_r = M_s - M_u$$

$$R = M_r / S$$

where:

M_u = Mean value of styrene in the unspiked sample

M_s = Measured amount of styrene in the spiked sample

M_r = Measured amount of the spiked compound

S = Amount of styrene added to the spiked sample

R = Fraction of spiked styrene recovered

- 9.6 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 a 10-ml volumetric pipet, quantitatively transfer 10.0 ml of the STYRENE WORKING SOLUTION (section 7.7.2 of this method) into a 2-oz bottle.
- 10.2 Using the AMS WORKING SOLUTION equipped with the automatic dispensing pipet (section 7.5.3 of this method), transfer 50.0 ml of the internal standard solution into the 2-oz bottle.
- 10.3 Cap the 2-oz bottle and swirl. This is the calibration standard,

which contains 5000 µg of styrene and 2500 µg of AMS.

- 10.4 Using the conditions prescribed (section 6.5 of this method), chromatograph 1 µl of the calibration standard.
- 10.5 Obtain the peak areas and calculate the relative response factor as described in the calculations section (section 12.1 of this method).

11.0 Procedure

- 11.1 Into a tared 2-oz bottle, weigh 10.0 g of latex to the nearest 0.1 g.
- 11.2 Using the AMS WORKING SOLUTION equipped with the automatic dispensing pipet (section 7.5.3 of this method), transfer 50.0 ml of the internal standard solution into the 2-oz bottle.
- 11.3 Cap the bottle. Using a mechanical shaker, shake the bottle for at least one minute or until coagulation of the latex is complete as indicated by a clear solvent.
- 11.4 Using the conditions prescribed (section 6.5 of this method), chromatograph 1 µl of the liquor.
- 11.5 Obtain the peak areas and calculate the concentration of styrene in the latex as described in the calculations section (Section 12.2 of this method).

12.0 Calculations

12.1 Calibration:

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

where:

RF = the relative response factor for styrene

W_x = the weight (µg) of styrene

A_{is} = the area of AMS

W_{is} = the weight (µg) of AMS

A_x = the area of styrene

12.2 Procedure:

$$\text{ppm}_{\text{styrene}} = (A_x RF \times W_{is}) / (A_{is} \times W_s)$$

where:

$\text{ppm}_{\text{styrene}}$ = parts per million of styrene in the latex

A_x = the area of styrene

RF = the response factor for styrene

W_{is} = the weight (µg) of AMS

A_{is} = the area of AMS

W_s = the weight (g) of the latex sample

- 12.3 Correct for recovery (R) as determined by section 9.0 of this method.

13.0 Precision

- 13.1 Precision for the method was determined at the 80, 144, 590, and 1160 ppm levels. The standard deviations were 0.8, 1.5, 5 and 9 ppm respectively. The percent relative standard deviations (%RSD) were 1% or less at all levels. Five degrees of freedom were

used for all precision data except at the 80 ppm level, where nine degrees of freedom were used. Note: These are example results and do not replace quality assurance procedures in this method.

14.0 Pollution Prevention

- 14.1 Waste generation should be minimized where possible. Sample size should be an amount necessary to adequately run the analysis.

15.0 Waste Management

- 15.1 Discard liquid chemical waste into the chemical waste drum.
- 15.2 Discard latex sample waste into the latex waste drum.
- 15.3 Discard polymer waste into the polymer waste container.

16.0 References

- 16.1 This method is based on Goodyear Chemical Division Test Method E-889.

METHOD 312C—DETERMINATION OF RESIDUAL STYRENE IN SBR LATEX PRODUCED BY EMULSION POLYMERIZATION

1.0 Scope

- 1.1 This method is applicable for determining the amount of residual styrene in SBR latex as produced in the emulsion polymerization process.

2.0 Principle of Method

- 2.1 A weighed sample of latex is coagulated in 2-propanol which contains alpha-methyl styrene as an Internal Standard. The extract from the coagulation will contain the alpha-methyl styrene as the Internal Standard and the residual styrene from the latex. The extract is analyzed by a Gas Chromatograph. Percent styrene is calculated by relating the area of the styrene peak to the area of the Internal Standard peak of known concentration.

3.0 Definitions

- 3.1 The definitions are included in the text as needed.

4.0 Interferences

(Reserved)

5.0 Safety

- 5.1 When using solvents, avoid contact with skin and eyes. Wear hand and eye protection. Wash thoroughly after use.
- 5.2 Avoid overexposure to solvent vapors. Handle only in well ventilated areas.

6.0 Equipment and Supplies

- 6.1 *Gas Chromatograph*—Hewlett Packard 5890, Series II with flame ionization detector, or equivalent.
Column—HP 19095F-123, 30m × 0.53mm, or equivalent. Substrate HP FFAP (cross-linked) film thickness 1 micrometer. Glass injector port liners with silanized glass wool plug.
Integrator—HP 3396, Series II, or equivalent.
- 6.2 Wrist action shaker
- 6.3 Automatic dispenser
- 6.4 Automatic pipet, calibrated to deliver 5.0 ± 0.01 grams of latex
- 6.5 Four-ounce wide-mouth bottles with foil lined lids
- 6.6 Crimp cap vials, 2ml, teflon lined septa
- 6.7 Disposable pipets
- 6.8 Qualitative filter paper
- 6.9 Cap crimper
- 6.10 Analytical balance
- 6.11 10ml pipette
- 6.12 Two-inch funnel

7.0 Reagents and Standards

- 7.1 2-Propanol (HP2C grade)
- 7.2 Alpha methyl styrene (99+% purity)
- 7.3 Styrene (99+% purity)
- 7.4 Zero air
- 7.5 Hydrogen (chromatographic grade)
- 7.6 Helium
- 7.7 Internal Standard preparation
- 7.7.1 Weigh 5.000–5.005 grams of alpha-methyl styrene into a 100ml volumetric flask and bring to mark with 2-propanol to make Stock “A” Solution.

Note: Shelf life—6 months.

- 7.7.2 Pipette 10ml of Stock “A” Solution into a 100ml volumetric flask and bring to mark with 2-propanol to prepare Stock “B” Solution.
- 7.7.3 Pipette 10ml of the Stock “B” solution to a 1000ml volumetric flask and bring to the mark with 2-propanol. This will be the Internal Standard Solution (0.00005 grams/ml).
- 7.8 Certification of Internal Standard—Each batch of Stock “B” Solution will be certified to confirm concentration.
- 7.8.1 Prepare a Standard Styrene Control Solution in 2-propanol by the following method:
- 7.8.1.1 Weigh 5.000 ± 0.005g of styrene to a 100ml volumetric flask and fill to mark with 2-propanol to make Styrene Stock “A” Solution.
- 7.8.1.2 Pipette 10ml of Styrene Stock “A” Solution to a 100ml volumetric flask and fill to mark with 2-propanol to make Styrene Stock

“B” Solution.

- 7.8.1.3 Pipette 10ml of Styrene Stock “B” solution to a 250ml volumetric flask and fill to mark with 2-propanol to make the Certification Solution.
- 7.8.2 Certify Alpha-Methyl Styrene Stock “B” Solution.
- 7.8.2.1 Pipette 5ml of the Certification Solution and 25ml of the Alpha Methyl Styrene Internal Standard Solution to a 4-oz. bottle, cap and shake well.
- 7.8.2.2 Analyze the resulting mixture by GC using the residual styrene method. (11.4–11.6 of this method)
- 7.8.2.3 Calculate the weight of alpha methyl styrene present in the 25ml aliquot of the new Alpha Methyl Styrene Standard by the following equation:

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

Where

A_x = Peak area of alpha methyl styrene

A_{is} = Peak area of styrene

W_x = Weight of alpha methyl styrene

W_{is} = Weight of styrene (.00100)

F_x = Analyzed response factor = 1

The Alpha Methyl Styrene Stock Solution used to prepare the Internal Standard Solution may be considered certified if the weight of alpha methyl styrene analyzed by this method is within the range of .00121g to .00129g.

8.0 Sampling

- 8.1 Collect a latex sample in a capped container. Cap the bottle and identify the sample as to location and time.
- 8.2 Deliver sample to Laboratory for testing within one hour.
- 8.3 Laboratory will test within two hours.
- 8.4 No special storage conditions are required.

9.0 Quality Control

- 9.1 The laboratory is required to operate a formal quality control program. This consists of an initial demonstration of the capability of the method as well as ongoing analysis of standards, blanks, and spiked samples to demonstrate continued performance.
- 9.1.1 When the method is first set up, a calibration is run and the recovery efficiency for each type of sample must be determined.
- 9.1.2 If new types of samples are being analyzed, then recovery efficiency for each new type of sample must be determined. New type includes any change, such as polymer type, physical form or a significant change in the

composition of the matrix.

- 9.2 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.
- 9.2.1 In determining the recovery efficiency, the quadruplet sampling system shall be used. Six sets of samples (for a total of 24) shall be taken. In each quadruplet set, half of the samples (two out of the four) shall be spiked with styrene.
- 9.2.2 Prepare the samples as described in section 8 of this method. To the vials labeled “spiked”, add a known amount of styrene that is expected to be present in the latex.
- 9.2.3 Run the spiked and unspiked samples in the normal manner. Record the concentrations of styrene reported for each pair of spiked and unspiked samples with the same vial number.
- 9.2.4 For each hydrocarbon, calculate the average recovery efficiency (R) using the following equation:

$$R = \Sigma(R_n) / 12$$

Where: n = sample number

$$R_n = (M_s - M_u) / S$$

M_s = total mass of compound (styrene) measured in spiked sample (μg)

M_u = total mass of compound (styrene) measured in unspiked sample (μg)

S = theoretical mass of compound (styrene) spiked into sample (μg)

R = fraction of spiked compound (styrene) recovered

- 9.2.5 A different R value should be obtained for each sample type. A value of R between 0.70 and 1.30 is acceptable.
- 9.2.6 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

A styrene control sample will be tested weekly to confirm the FID response and calibration.

- 10.1 Using the Styrene Certification Solution prepared in 7.8.1, perform test analysis as described in 7.8.2 using the equation in 7.8.2.3 to calculate results.
- 10.2 Calculate the weight of styrene in the styrene control sample using the following equation:

$$W_{sty} = (F_x \times A_{sty} \times W_{is}) / A_{is}$$

The instrument can be considered calibrated if the weight of the styrene analyzed is within range of 0.00097–0.00103gms.

11.0 Procedure

- 11.1 Using an auto pipet, add 25ml of Internal Standard Solution to a 4 oz. wide-mouth bottle.
- 11.2 Using a calibrated auto pipet, add 5.0 ± 0.01 g latex to the bottle containing the 25ml of Internal Standard Solution.
- 11.3 Cap the bottle and place on the wrist action shaker. Shake the sample for a minimum of five minutes using the timer on the shaker. Remove from shaker.
- 11.4 Using a disposable pipet, fill the 2ml sample vial with the clear alcohol extract. (If the extract is not clear, it should be filtered using a funnel and filter paper.) Cap and seal the vial.
- 11.5 Place the sample in the autosampler tray and start the GC and Integrator. The sample will be injected into the GC by the auto-injector, and the Integrator will print the results.
- 11.6 *Gas Chromatograph Conditions*
 Oven Temp—70 °C
 Injector Temp—225 °C
 Detector Temp—275 °C
 Helium Pressure—500 KPA
 Column Head Pressure—70 KPA
 Makeup Gas—30 ml/min.
 Column—HP 19095F—123, 30m x 0.53mm Substrate: HP—FFAP (cross-linked) 1 micrometer film thickness

12.0 Calculations

- 12.1 The integrator is programmed to do the following calculation at the end of the analysis:

$$\% \text{Residual Styrene} = (A_x X W_x) / (A_{is} X W_{is}) \times 100$$

Where:

A_x = Peak area of styrene

A_{is} = Peak area of internal standard

W_x = Weight of sample = 5g

W_{is} = Weight of internal std. = 0.00125g

F_x = Analyzed response factor = 1.0

- 12.2 The response factor is determined by analyzing a solution of 0.02g of styrene and 0.02g of alpha methyl styrene in 100ml of 2-propanol. Calculate the factor by the following equation:

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

Where:

W_x = Weight of styrene

A_x = Peak area of styrene

W_{is} = Weight of alpha methyl styrene

A_{is} = Peak area of alpha methyl styrene

13.0 Method Performance

- 13.1 Performance must be determined for each sample type by following the procedures in section 9 of this method.

14.0 Waste Generation

- 14.1 Waste generation should be minimized where possible.

15.0 Waste Management

- 15.1 All waste shall be handled in accordance with Federal and State environmental regulations.

16.0 References
(Reserved)**METHOD 313A—DETERMINATION OF RESIDUAL HYDROCARBONS IN RUBBER CRUMB****1.0 Scope and Application**

1.1 This method determines residual toluene and styrene in stripper crumb of the of the following types of rubber: polybutadiene (PBR) and styrene/butadiene rubber (SBR), both derived from solution polymerization processes that utilize toluene as the polymerization solvent.

1.2 The method is applicable to a wide range of concentrations of toluene and styrene provided that calibration standards cover the desired range. It is applicable at least over the range of 0.01 to 10.0 % residual toluene and from 0.1 to 3.0 % residual styrene. It is probably applicable over a wider range, but this must be verified prior to use.

1.3 The method may also be applicable to other process samples as long as they are of a similar composition to stripper crumb. See section 3.1 of this method for a description of stripper crumb.

2.0 Summary of Method

2.1 The wet crumb is placed in a sealed vial and run on a headspace sampler which heats the vial to a specified temperature for a specific time and then injects a known volume of vapor into a capillary GC. The concentration of each component in the vapor is proportional to the level of that component in the crumb sample and does not depend on water content of the crumb.

2.2 Identification of each component is performed by comparing the retention times to those of known standards.

2.3 Results are calculated by the external standard method since injections are all performed in an identical manner. The response for each component is compared with that obtained from dosed samples of crumb.

2.4 Measured results of each compound are corrected by dividing each by the average recovery efficiency determined for the same compound in the same sample type.

3.0 Definitions

- 3.1 Stripper crumb refers to pieces of rubber resulting from the steam

stripping of a toluene solution of the same polymer in a water slurry. The primary component of this will be polymer with lesser amounts of entrained water and residual toluene and other hydrocarbons. The amounts of hydrocarbons present must be such that the crumb is a solid material, generally less than 10 % of the dry rubber weight.

4.0 Interferences

4.1 Contamination is not normally a problem since samples are sealed into vials immediately on sampling.

4.2 Cross contamination in the headspace sampler should not be a problem if the correct sampler settings are used. This should be verified by running a blank sample immediately following a normal or high sample. Settings may be modified if necessary if this proves to be a problem, or a blank sample may be inserted between samples.

4.3 Interferences may occur if volatile hydrocarbons are present which have retention times close to that of the components of interest. Since the solvent makeup of the processes involved are normally fairly well defined this should not be a problem. If it is found to be the case, switching to a different chromatographic column will probably resolve the situation.

5.0 Safety

5.1 The chemicals specified in this method should all be handled according to standard laboratory practices as well as any special precautions that may be listed in the MSDS for that compound.

5.2 Sampling of strippers or other process streams may involve high pressures and temperatures or may have the potential for exposure to chemical fumes. Only personnel who have been trained in the specific sampling procedures required for that process should perform this operation. An understanding of the process involved is necessary. Proper personal protective equipment should be worn. Any sampling devices should be inspected prior to use. A detailed sampling procedure which specifies exactly how to obtain the sample must be written and followed.

6.0 Equipment and Supplies

6.1 Hewlett Packard (HP) 7694 Headspace sampler, or equivalent, with the following conditions:

Times (min.): GC cycle time 6.0, vial equilibration 30.0, pressurization 0.25, loop fill 0.25, loop equilibration 0.05, inject 0.25
 Temperatures (deg C): oven 70, loop 80, transfer line 90
 Pressurization gas: He @ 16 psi

6.2 HP 5890 Series II capillary gas chromatograph, or equivalent, with the following conditions:

Column: Supelco SPB-1, or equivalent, 15m × .25mm × .25μ film

Carrier: He @ 6 psi

Run time: 4 minutes

Oven: 70 deg C isothermal

Injector: 200 deg C split ratio 50:1

Detector: FID @ 220 deg C

6.3 HP Chemstation consisting of computer, printer and Chemstation software, or an equivalent chromatographic data system.

6.4 20 ml headspace vials with caps and septa.

6.5 Headspace vial crimper.

6.6 Microliter pipetting syringes.

6.7 Drying oven at 100 deg C vented into cold trap or other means of trapping hydrocarbons released.

6.8 Laboratory shaker or tumbler suitable for the headspace vials.

6.9 Personal protective equipment required for sampling the process such as rubber gloves and face and eye protection.

7.0 Reagents and Standards

7.1 Toluene, 99.9+% purity, HPLC grade.

7.2 Styrene, 99.9+% purity, HPLC grade.

7.3 Dry rubber of same type as the stripper crumb samples.

8.0 Sample Collection, Preservation and Storage

8.1 Collect a sample of crumb in a manner appropriate for the process equipment being sampled.

8.1.1 If conditions permit, this may be done by passing a stream of the crumb slurry through a strainer, thus separating the crumb from the water. Allow the water to drain freely, do not attempt to squeeze any water from the crumb. Results will not depend on the exact water content of the samples. Immediately place several pieces of crumb directly into a headspace vial. This should be done with rubber gloves to protect the hands from both the heat and from contact with residual hydrocarbons. The vial should be between 1/4 and 1/3 full. Results do not depend on sample size as long as there is sufficient sample to reach an equilibrium vapor pressure in the headspace of the vial. Cap and seal the vial. Prepare each sample at least in duplicate. This is to minimize the effect of the variation that naturally occurs in the composition of non homogeneous crumb. The free water is not analyzed by this method and should be disposed of appropriately along with any unused rubber crumb.

8.1.2 Alternatively the process can be sampled in a specially constructed sealed bomb which can then be transported to the laboratory. The bomb is then cooled to ambient temperature by applying a stream of running water. The bomb can then be opened and the crumb separated from the water and the vials filled as described in section 8.1.1 of this method. The bomb may be stored up to 8 hours prior to transferring the crumb into vials.

8.2 The sealed headspace vials may be run immediately or may be stored up to 72 hours prior to running. It is possible that even longer storage times may be acceptable, but this must be verified for the particular type of sample being analyzed (see section 9.2.3 of this method). The main concern here is that some types of rubber eventually may flow, thus compacting the crumb so that the surface area is reduced. This may have some effect on the headspace equilibration.

9.0 Quality Control

9.1 The laboratory is required to operate a formal quality control program. This consists of an initial demonstration of the capability of the method as well as ongoing analysis of standards, blanks and spiked samples to demonstrate continued performance.

9.1.1 When the method is first set up a calibration is run (described in section 10 of this method) and an initial demonstration of method capability is performed (described in section 9.2 of this method). Also recovery efficiency for each type of sample must be determined (see section 9.4 of this method).

9.1.2 It is permissible to modify this method in order to improve separations or make other improvements, provided that all performance specifications are met. Each time a modification to the method is made it is necessary to repeat the calibration (section 10 of this method), the demonstration of method performance (section 9.2 of this method) and the recovery efficiency for each type of sample (section 9.4 of this method).

9.1.3 Ongoing performance should be monitored by running a spiked rubber standard. If this test fails to demonstrate that the analysis is in control, then corrective action must be taken. This method is described in section 9.3 of this method.

9.1.4 If new types of samples are being analyzed then recovery efficiency for each new type of sample must be determined. New type includes any change, such as polymer type, physical form or a significant change in the composition of the matrix.

9.2 Initial demonstration of method capability to establish the accuracy and precision of the method. This is to be run following the calibration described in section 10 of this method.

9.2.1 Prepare a series of identical spiked rubber standards as described in section 9.3 of this method. A sufficient number to determine statistical information on the test should be run. Ten may be a suitable number, depending on the quality control methodology used at the laboratory running the tests. These are run in the same manner as unknown samples (see section 11 of this method).

9.2.2 Determine mean and standard deviation for the results. Use these to determine the capability of the method and to calculate suitable control limits for the ongoing performance check which will utilize the same standards.

9.2.3 Prepare several additional spiked rubber standards and run 2 each day to determine the suitability of storage of the samples for 24, 48 and 72 hours or longer if longer storage times are desired.

9.3 A spiked rubber standard should be run on a regular basis to verify system performance. This would probably be done daily if samples are run daily. This is prepared in the same manner as the calibration standards (section 10.1 of this method), except that only one concentration of toluene and styrene is prepared. Choose concentrations of toluene and styrene that fall in the middle of the range expected in the stripper crumb and then do not change these unless there is a major change in the composition of the unknowns. If it becomes necessary to change the composition of this standard the initial performance demonstration must be repeated with the new standard (section 9.2 of this method).

9.3.1 Each day prepare one spiked rubber standard to be run the following day. The dry rubber may be prepared in bulk and stored for any length of time consistent with the shelf life of the product. The addition of water and hydrocarbons must be performed daily and all the steps described under section 10.1 of this method must be followed.

9.3.2 Run the spiked rubber standard prepared the previous day. Record the results and plot on an appropriate control chart or other means of determining statistical control.

9.3.3 If the results for the standard indicate that the test is out of control then corrective action must be taken. This may include a check on procedures, instrument settings, maintenance or recalibration. Samples may be stored (see section 8.2 of this

method) until compliance is demonstrated.

9.4 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.

9.4.1 For each sample type collect 12 samples from the process (section 8.1 of this method). This should be done when the process is operating in a normal manner and residual hydrocarbon levels are in the normal range. Half the vials and caps should be tared, labeled "spiked" and numbered 1 through 6. The other vials are labeled "unspiked" and need not be tared but are also numbered 1 through 6. Immediately on sampling, the vials should be capped to prevent loss of volatiles. Allow all the samples to cool completely to ambient temperature. Reweigh each of the vials labeled "spiked" to determine the weight of wet crumb inside.

9.4.2 The dry weight of rubber present in the wet crumb is estimated by multiplying the weight of wet crumb by the fraction of nonvolatiles typical for the sample. If this is not known, an additional quantity of crumb may be sampled, weighed, dried in an oven and reweighed to determine the fraction of volatiles and nonvolatiles prior to starting this procedure.

9.4.3 To the vials labeled "spiked" add an amount of a mixture of toluene and styrene that is between 40 and 60 % of the amount expected in the crumb. This is done by removing the cap, adding the mixture by syringe, touching the tip of the needle to the sample in order to remove the drop and then immediately recapping the vials. The mixture is not added through the septum, because a punctured septum may leak and vent vapors as the vial is heated. The weights of toluene and styrene added may be calculated from the volumes of the mixture added, its composition and density, or may be determined by the weight of the vials and caps prior to and after addition. The exact dry weight of rubber present and the concentration of residual toluene and styrene are not known at this time so an exact calculation of the concentration of hydrocarbons is not possible until the test is completed.

9.4.4 Place all the vials onto a shaker or tumbler for 24 ± 2 hours. This is essential in order for the hydrocarbons to be evenly distributed and completely absorbed into the rubber. If this is not followed the toluene and styrene will be mostly at the surface of the rubber and high results will be obtained.

9.4.5 Remove the vials from the shaker and tap them so that all the crumb settles to the bottom of the vials.

Allow them to stand for 1 hour prior to analysis to allow any liquid to drain fully to the bottom.

9.4.6 Run the spiked and unspiked samples in the normal manner. Record the concentrations of toluene and styrene reported for each pair of spiked and unspiked samples with the same vial number.

9.4.7 Open each of the vials labeled "spiked", remove all the rubber crumb and place it into a tared drying pan. Place in a 100 deg C oven for two hours, cool and reweigh. Subtract the weight of the tare to give the dry weight of rubber in each spiked vial. Calculate the concentration of toluene and styrene spiked into each vial as percent of dry rubber weight. This will be slightly different for each vial since the weights of dry rubber will be different.

9.4.8 For each hydrocarbon calculate the average recovery efficiency (R) using the following equations:

$$R = R_{\text{avg}} \sum (P_n)^{1/6} \quad (\text{average of the 6 individual } R_n \text{ values})$$

Where:

$$R_n = (C_{ns} - C_{nu}) / S_n$$

Where:

n=vial number

C_{ns}=concentration of compound measured in spiked sample number n.

C_{nu}=concentration of compound measured in unspiked sample number n.

S_n=theoretical concentration of compound spiked into sample n calculated in step 9.4.7

9.4.9 A different R value should be obtained for each compound (styrene and toluene) and for each sample type.

9.4.10 A value of R between 0.70 and 1.30 is acceptable.

9.4.11 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 (see section 12.2 of this method.)

10.0 Calibration

10.1 Calibration standards are prepared by dosing known amounts of the hydrocarbons of interest into vials containing known amounts of rubber and water.

10.1.1 Cut a sufficient quantity of dry rubber of the same type as will be analyzed into pieces about the same size as that of the crumb. Place these in a single layer on a piece of aluminum foil or other suitable surface and place into a forced air oven at 100° C for four hours. This is to remove any residual hydrocarbons that may be present. This step may be performed in advance.

10.1.2 Into each of a series of vials add 3.0 g of the dry rubber.

10.1.3 Into each vial add 1.0 ml distilled water or an amount that is close to the amount that will be present in the unknowns. The exact amount of water present does not have much effect on the analysis, but it is necessary to have a saturated environment. The water will also aid in the uniform distribution of the spiked hydrocarbons over the surface of the rubber after the vials are placed on the shaker (in step 10.1.5 of this method).

10.1.4 Into each vial add varying amounts of toluene and styrene by microliter syringe and cap the vials immediately to prevent loss. The tip of the needle should be carefully touched to the rubber in order to transfer the last drop to the rubber. Toluene and styrene may first be mixed together in suitable proportions and added together if desired. The weights of toluene and styrene added may be calculated from the volumes of the mixture added, its composition and density, or may be determined by the weight of the vials and caps prior to and after addition. Concentrations of added hydrocarbons are calculated as percent of the dry rubber weight. At least 5 standards should be prepared with the amounts of hydrocarbons added being calculated to cover the entire range possible in the unknowns. Retain two samples with no added hydrocarbons as blanks.

10.1.5 Place all the vials onto a shaker or tumbler for 24 ± 2 hours. This is essential in order for the hydrocarbons to be evenly distributed and completely absorbed into the rubber. If this is not followed the toluene and styrene will be mostly at the surface of the rubber and high results will be obtained.

10.1.6 Remove the vials from the shaker and tap them so that all the crumb settles to the bottom of the vials. Allow them to stand for 1 hour prior to analysis to allow any liquid to drain fully to the bottom.

10.2 Run the standards and blanks in the same manner as described for unknowns (section 11 of this method), starting with a blank, then in order of increasing hydrocarbon content and ending with the other blank.

10.3 Verify that the blanks are sufficiently free from toluene and styrene or any interfering hydrocarbons.

10.3.1 It is possible that trace levels may be present even in dry product. If levels are high enough that they will interfere with the calibration then the drying procedure in section 10.1.1 of this method should be reviewed and modified as needed to ensure that suitable standards can be prepared.

10.3.2 It is possible that the final blank is contaminated by the previous

standard. If this is the case review and modify the sampler parameters as needed to eliminate this problem. If necessary it is possible to run blank samples between regular samples in order to reduce this problem, though it should not be necessary if the sampler is properly set up.

10.4 Enter the amounts of toluene and styrene added to each of the samples (as calculated in section 10.1.4 of this method) into the calibration table and perform a calibration utilizing the external standard method of analysis.

10.5 At low concentrations the calibration should be close to linear. If a wide range of levels are to be determined it may be desirable to apply a nonlinear calibration to get the best fit.

11.0 Procedure

11.1 Place the vials in the tray of the headspace sampler. Enter the starting and ending positions through the console of the sampler. For unknown samples each is run in duplicate to minimize the effect of variations in crumb composition. If excessive variation is noted it may be desirable to run more than two of each sample.

11.2 Make sure the correct method is loaded on the Chemstation. Turn on the gas flows and light the FID flame.

11.3 Start the sequence on the Chemstation. Press the START button on the headspace unit. The samples will be automatically injected after equilibrating for 30 minutes in the oven. As each sample is completed the Chemstation will calculate and print out the results as percent toluene and styrene in the crumb based on the dry weight of rubber.

12.0 Data Analysis and Calculations

12.1 For each set of duplicate samples calculate the average of the measured concentration of toluene and styrene. If more than two replicates of each sample are run calculate the average over all replicates.

12.2 For each sample correct the measured amounts of toluene and styrene using the following equation:
Corrected Result = C_m/R

Where:

C_m = Average measured concentration for that compound.

R = Recovery efficiency for that compound in the same sample type (see section 9.4 of this method)

12.3 Report the recovery efficiency (R) and the corrected results of toluene and styrene for each sample.

13.0 Method Performance

13.1 This method can be very sensitive and reproducible. The actual

performance depends largely on the exact nature of the samples being analyzed. Actual performance must be determined by each laboratory for each sample type.

13.2 The main source of variation is the actual variation in the composition of non homogeneous crumb in a stripping system and the small sample sizes employed here. It therefore is the responsibility of each laboratory to determine the optimum number of replicates of each sample required to obtain accurate results.

14.0 Pollution Prevention

14.1 Samples should be kept sealed when possible in order to prevent evaporation of hydrocarbons.

14.2 When drying of samples is required it should be done in an oven which vents into a suitable device that can trap the hydrocarbons released.

14.3 Dispose of samples as described in section 15.

15.0 Waste Management

15.1 Excess stripper crumb and water as well as the contents of the used sample vials should be properly disposed of in accordance with local and federal regulations.

15.2 Preferably this will be accomplished by having a system of returning unused and spent samples to the process.

16.0 References

16.1 "HP 7694 Headspace Sampler—Operating and Service Manual", Hewlett-Packard Company, publication number G1290–90310, June 1993.

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- μ l 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 \times 0.53 mm ID with a 1.2 micron film thickness, and a Carbowax 20M (polyethylene glycol), 15 M \times 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 \times 0.53 mm SE-54 column

- to the 15 Mx0.53 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, C₉H₁₀, 99+% purity, CAS 98-83-9
- 7.2 n-Hexane, C₆H₁₄, 99+% purity, CAS 110-54-3
- 7.3 Isopropyl alcohol, C₃H₈O 99.5+% purity, reagent grade, CAS 67-63-0
- 7.4 Chloroform, CHCl₃, 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.

$$F = 1 - (\% \text{ moisture} / 100)$$

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.

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

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.

[FR Doc. 97-6506 Filed 3-14-97; 8:45 am]

BILLING CODE 6560-50-P

40 CFR Part 79

[FRL-5707-7]

Registration of Fuels and Fuel Additives: Changes in Requirements, and Applicability to Blenders of Deposit Control Gasoline Additives

AGENCY: Environmental Protection Agency.

ACTION: Final rule.

SUMMARY: This action finalizes several specific changes to existing regulations which require the registration and testing of designated motor vehicle fuels and fuel additives (F/FAs) by their manufacturers. Included are changes to the regulatory definitions of "fuel manufacturer," "additive," and "small business," as well as modifications to grouping rules for biodiesel and synthetic fuels. These changes will streamline F/FA registration and testing burdens and reduce the number of respondents, while maintaining the informational value of the program and its contributions to the public health and environmental goals of the Clean Air Act.

Another previously proposed change, to establish a *de minimis* provision for F/FAs containing certain "atypical" elements, is not addressed in this action. However, in a direct final rule also published elsewhere in this issue of the Federal Register, certain deadlines related to testing of atypical F/FAs are extended while EPA determines the most appropriate disposition of the *de minimis* proposal.

EFFECTIVE DATE: This action will be effective on May 16, 1997.

ADDRESSES: Documents related to this final rule have been placed in Public Docket No. A-90-07 located at the U.S. EPA, Air Docket Section, Room M-1500, 401 M Street S.W., Washington, DC 20460. The docket is open for public inspection from 8:00 a.m. until 5:30

p.m., Monday through Friday, except on Federal holidays. A reasonable fee may be charged for photocopying.

FOR FURTHER INFORMATION CONTACT: Jim Caldwell (202-233-9303) or Joseph Fernandes (202-233-9016), U.S. EPA, Office of Mobile Sources, Fuels and Energy Division, Mail Code 6406J, 401 M Street SW, Washington, DC 20460.

SUPPLEMENTARY INFORMATION: Electronic copies of this rule and earlier rulemaking documents related to the F/FA Registration Program are available free of charge on EPA's Technology Transfer Network Bulletin Board System (TTNBS, phone access 919-541-5742) and on the Internet (<http://www.epa.gov/omswwww>). Parties requiring assistance may call Mr. Fernandes at (202) 233-9016.

I. Regulated Entities

Regulated categories and entities potentially affected by this action include:

Category	Examples of regulated entities
Industry	Manufacturers of gasoline and diesel fuel. Manufacturers of additives for gasoline and diesel fuel.

This table is not intended to be exhaustive, but rather provides a guide for readers regarding entities likely to be regulated by this action. This table lists the types of entities that EPA is now aware could potentially be regulated by this action. Other types of entities not listed in the table could also be regulated. To determine whether your entity is regulated by this action, you should carefully examine this preamble and the changes to the regulatory text. You should also carefully examine all provisions of the registration program at 40 CFR part 79.

II. Introduction

A. Background

The F/FA registration program is authorized by section 211 of the Clean Air Act (CAA) and codified in 40 CFR part 79. In accordance with CAA sections 211(a) and (b)(1), basic registration requirements applicable to gasoline and diesel fuels and their additives were issued in 1975. These regulations require manufacturers to submit information on their F/FA products, such as the commercial identity, chemical composition, purpose-in-use, and range of concentration, in order to have such products registered by the EPA.

Additional registration requirements, implementing sections 211(b)(2) and (e), were proposed in April 1992 and