SERIAL CHROMATOPYROGRAPHY-MASS SPECTROMETRY OF NATURAL RUBBER VULCANIZATES

ALFRED J. DEOME and CHRISTOPHER J. KULIG
POLYMER RESEARCH DIVISION

JACOB PATT
U.S. ARMY TANK-AUTOMOTIVE COMMAND

March 1986

Approved for public release; distribution unlimited.
The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Mention of any trade names or manufacturers in this report shall not be construed as advertising nor as an official endorsement or approval of such products or companies by the United States Government.

DISPOSITION INSTRUCTIONS

Destroy this report when it is no longer needed.
Do not return it to the originator.
**SERIAL CHROMATOGRAPHY-MASS SPECTROMETRY OF NATURAL RUBBER VULCANIZATES**

**Final Report**

**AUTHOR(s):**
Alfred J. Deome, Christopher J. Kulig, and Jacob Patt*

**PERFORMING ORGANIZATION NAME AND ADDRESS**
U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
ATTN: SLCMT-OP

**CONTROLLING OFFICE NAME AND ADDRESS**
U.S. Army Tank-Automotive Command
Warren, Michigan 48090

**REPORT DATE**
March 1986

**NUMBER OF PAGES**
20

**DISTRIBUTION STATEMENT (of this report)**
Approved for public release; distribution unlimited.

**SUPPLEMENTARY NOTES**
*U.S. Army Tank-Automotive Command, Warren, MI 48090

**KEY WORDS**
Gas chromatography
Mass spectrometry
Pyrolysis
Natural rubber

**ABSTRACT**
SEE REVERSE
ABSTRACT

Applications of serial pyrolysis-gas chromatography-mass spectrometry, developed at the U.S. Army Materials Technology Laboratory, are used to determine the qualitative organic formulation and polymer composition of two proprietary experimental natural rubber formulations.
INTRODUCTION

Previous work in the area of pyrolysis-gas chromatography-mass spectrometry1-5 has shown that this technique is a powerful analytical tool well suited for studying the complex composition of intractable materials, such as vulcanized elastomers. An interesting and particularly valuable application of the many pyrolysis techniques available is serial chromatopyrography-mass spectrometry (Ser-Py-GC-MS). This technique appears to be very applicable to separating residual vulcanize formulation components from polymer composition without the need for complicated sample manipulation procedures. Instrumental techniques employing a combination of serial pyrolysis techniques, high resolution capillary gas chromatography, and mass spectrometry have been developed at the U.S. Army Materials Technology Laboratory, Watertown, MA, in collaboration with the U.S. Tank-Automotive Command (TACOM), Warren, MI, during the last several years. The technique is used as a means of accurately accessing and reconstructing formulations of vulcanized elastomers where few, if any, straightforward analytical procedures are available for this type of work.

This report documents the application of Ser-Py-GC-MS in determining the composition of two experimental natural rubber formulations. The vulcanized tensile sheets, both of proprietary composition, are referenced in this report as Sample LG-1 (465 VI and II) and Sample LG-2 (465 X-5).

EXPERIMENTAL

Thermal gravimetric analysis (TGA) was performed on each sample using a DuPont 1090 thermal analyzer to determine temperature profiles at which the organic formulation is thermally desorbed from the polymer and inorganic component matrix of the vulcanizates. Pyrolysis experiments were performed on each sample using a Chemical Data Systems, Inc., Model 122 pyrolysis unit interfaced to a Hewlett-Packard Model 5996 gas chromatograph-mass spectrometer system under computer control (Hewlett-Packard 1000 Data System). The samples were each subjected to an initial pyrolysis temperature of 350°C followed serially by a second pyrolysis at 600°C. The pyrolyzate from each experiment was chromatographed on a 12-meter fused silica capillary column of crosslinked methyl silicone (SE 30). The gas chromatograph was programmed from 50°C for 4 minutes to 280°C for 15 minutes at 10°C/minute. Mass spectra of the chromatographic effluent were collected and stored; a mass range of 33 to 450 amu was repeatedly scanned at approximately 1.5-second intervals for the selected mass range. Reconstructed mass pyrograms and mass spectra were generated subsequent to each analysis from the stored data. Identifications were facilitated by the use of computer library search routines of the Wiley-NBS data base of reference mass spectra.

RESULTS AND DISCUSSION

The thermal gravimetric analyses of the respective samples under investigation are shown in Figures 1 and 2. Both rubber systems appear to be very similar thermally in that the organic additive portions of both vulcanizates are liberated at temperatures of less than 350°C. The temperature region where the formulation is desorbed from the polymer is critical in order to separate the additives from the polymer during the serial pyrolysis experiments. Table 1 shows the various temperature and weight loss relationships associated with the two samples under investigation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Organic Additives</th>
<th>Polymer</th>
<th>Filler</th>
<th>Residues</th>
</tr>
</thead>
<tbody>
<tr>
<td>LG-1</td>
<td>361.0°C (0.929 mg)</td>
<td>422.6C</td>
<td>618.6C</td>
<td>633.9C</td>
</tr>
<tr>
<td>LG-2</td>
<td>366.6°C (1.006 mg)</td>
<td>428.5C</td>
<td>645.8C</td>
<td>660.9C</td>
</tr>
</tbody>
</table>

In order to desorb the organic formulation from the respective samples, a pyrolysis temperature of 350°C was selected. Samples weighing approximately 5 mg were used in the pyrolysis experiments. A quartz tube probe was heated at 20°C/ms and held at the maximum temperature for 20 seconds. The gas chromatograph program and data acquisition were then started. The 350°C mass chromatopyrograms of LG-1 and LG-2 are shown in Figures 3 and 4. These components represent the major portion of the formulation added to the rubber polymer during the mixing process. It would seem that the fatty acid materials of hexadecanoic and octadecanoic acids are derived from the polymer system rather than from the formulation. The antioxidant in both LG-1 and LG-2 is N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine; the mass spectrum of this component is shown in Figure 3a. Polymer identifications were achieved through pyrolysis of each sample at 600°C subsequent to each 350°C analysis. The reconstructed mass chromatopyrograms are shown in Figures 5 and 6. Essentially, these pyrograms indicate the presence of 2-methyl-1,3-butadiene (isoprene) as shown in Figure 5a.

In addition to the serial pyrolysis experiments performed, each sample was also extracted with acetone for 16 hours (ASTM D297). The extract was evaporated and concentrated to approximately 5 ml. Two microliters of each extract were injected using the gas chromatographic-mass spectrometric parameters previously described. The mass chromatograms are shown in Figures 7 and 8, respectively. The correlation of low temperature pyrolysis with the extract chromatography is excellent. The extract showed additional compounds indicative of the sulfur accelerator used in the formulation. The representative mass spectra corresponding to the individual components used for identification purposes are shown in Figures 7a, 7b, and 8a-8c.
CONCLUSIONS

Serial chromatopyrography-mass spectrometry experiments and gas chromatography-mass spectrometry of 16-hour acetone extracts have revealed a reasonably conclusive qualitative analysis of the formulation additives in Samples LG-1 and LG-2. The polymer is identified as cis-polyisoprene (natural rubber). The formulation additives are:

a. N-cyclohexyl-2-benzothiazole-2-sulfenamide (accelerator),
b. Hydrocarbon blend of wax or oil (processing/protective), and
c. N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (antioxidant).

Both samples are identical in qualitative formulation as evidenced from the results presented in this report. No attempt was made to evaluate these samples quantitatively. The polymer composition, shown to be of polymerized 2-methyl-1,3-butadiene (m/z 68) also shows various natural products and essential oils. There is no indication of polymer blending.

ACKNOWLEDGMENT

Appreciation is extended to Ms. Jane Brousseau for the thermal gravimetric analyses performed on these samples, and to Dr. Robert E. Sacher for his helpful interpretation of the data.
Figure 1. Thermal gravimetric analysis (TGA) of Sample LG-1.
Figure 2. Thermal gravimetric analysis (TGA) of Sample LG-2.
COMPONENT IDENTIFICATION

1. Hexadecanoic Acid
2. Octadecanoic Acid (Stearic Acid)
4. N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (Antioxidant)
5-12. Hydrocarbons

Figure 3. The reconstructed mass pyrogram of Sample LG-1 pyrolyzed at 350°C.
Figure 3a. The mass spectrum of the antioxidant \([\text{N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine}]\), m/z 268, derived during the 350°C pyrolysis experiments on LG-1 (top) and LG-2 (bottom).
COMPONENT IDENTIFICATION

1. Hexadecanoic Acid
2. Octadecanoic Acid (Stearic Acid)
3. N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (Antioxidant)
4-8. Hydrocarbons

Figure 4. The reconstructed mass pyrogram of Sample LG-2 pyrolyzed at 350°C.
COMPONENT IDENTIFICATION

1. 2-Methyl-1,3-Butadiene (Isoprene)
2. Bornylene
3. Limonene
4. Natural Products

Figure 5. The reconstructed mass pyrogram of Sample LG-1 pyrolyzed at 600° C.
1. 1,3-Butadiene, 2-methyl-  
2. 1,2-Pentadiene  
3. 1,3-Pentadiene, (E)-  
4. 1,3-Pentadiene, (Z)-  
5. 1,3-Pentadiene, (Z)-  

Figure 5a. The mass spectrum of isoprene (2-methyl-1,3-butadiene), m/z 68, resulting from the 600°C pyrolysis of Sample LG-1.
COMPONENT IDENTIFICATION

1. 2-Methyl-1,3-Butadiene (Isoprene)
2. 3-Methyl-1,3,5-Hexatriene
3. 1,4-Dimethylbenzene
4. 4-Vinyl-1,4-Dimethylcyclohexene
5. 2,7-dimethyl-3-octen-5-yne
6. Limonene
7. Farnesene

Figure 6. The reconstructed mass pyrogram of Sample LG-2 pyrolyzed at 600°C.
COMPONENT IDENTIFICATION

1. 4-Hydroxy-4-methyl pentanone
2. Decane
3. N-Isopropylidene-cyclohexylamine (Accelerator Decomposition)
4. Hydrocarbon
5. Benzothiazole (Accelerator Decomposition)
6. Hexadecanoic Acid
7. Octadecanoic Acid (Stearic Acid)
8. N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (Antioxidant)

Figure 7. The reconstructed mass chromatogram of the 16-hour acetone extract of Sample LG-1.
1. N-ISOPOPYLIDENE-CYCLOHEXYLAMINE 139 C9H17N
2. N-ISOPOPYLIDENE-CYCLOHEXYLAMINE 139 C9H17N
3. Azetidine, 1-cyclohexyl- 139 C9H17N
4. Cyclohexane, cyclopropyl- 124 C9H16
5. Spiro[3.4]octan-5-one 124 C8H12O

Figure 7a. The mass spectrum of N-isopropylidene-cyclohexylamine, m/z 139, found in Sample LG-1 (16-hour acetone extraction).
1. Benzothiazole 135 C7H5NS
2. Thieno[3,2-c]pyridine 135 C7H5NS
3. 1,2-Benzisothiazole 135 C7H5NS
4. Benzothiazole 135 C7H5NS
5. Benzothiazole 135 C7H5NS

Figure 7b. The mass spectrum of benzothiazole, m/z 135, found in Sample LG-1 (16-hour acetone extraction).
COMPONENT IDENTIFICATION

1. 4-Hydroxy-4-Methylpentanone
2. Cyclohexanamine (Accelerator Decomposition)
3. 3-Methyl Pyrrolidine
4. N-Isopropylidene cyclohexylamine (Accelerator Decomposition)
5. Hydrocarbon
6. N-(1,3-Dimethylbutyl)-N¹-phenyl-p-phenylenediamine (Antioxidant)
7. Hydrocarbon
8. Hydrocarbon

Figure 8. The reconstructed mass chromatogram of the 16-hour acetone extract of Sample LG-2.
Figure 8a. The mass spectrum of cyclohexaneamine, m/z 99, found in Sample LG-2 (16-hour acetone extraction).
Figure 8b. The mass spectrum of N-isopropylidene-cyclohexylamine found in Sample LG-2 (16-hour acetone extraction).

Figure 8c. The mass spectrum of the antioxidant [N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine], m/z 268, found in Sample LG-2 (16-hour acetone extraction).
<table>
<thead>
<tr>
<th>No. of Copies</th>
<th>To</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301</td>
</tr>
<tr>
<td>Commander, U.S. Army Laboratory Command, 2800 Powder Mill Road, Adelphi, MD 20783-1197</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: Technical Library</td>
</tr>
<tr>
<td>2</td>
<td>Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 22314</td>
</tr>
<tr>
<td>Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: Information Processing Office</td>
</tr>
<tr>
<td>Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: AMCLD</td>
</tr>
<tr>
<td>Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: AMXSY-MP, H. Cohen</td>
</tr>
<tr>
<td>Commander, U.S. Army Electronics Research and Development Command, Fort Monmouth, NJ 07703</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: AMDSD-L</td>
</tr>
<tr>
<td>1</td>
<td>AMDSD-E</td>
</tr>
<tr>
<td>Commander, U.S. Army Missile Command, Redstone Arsenal, AL 35898</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: AMSMI-RKP, J. Wright, Bldg. 7574</td>
</tr>
<tr>
<td>1</td>
<td>AMSMI-TS, Redstone Scientific Information Center</td>
</tr>
<tr>
<td>1</td>
<td>AMSMI-RLM</td>
</tr>
<tr>
<td>1</td>
<td>Technical Library</td>
</tr>
<tr>
<td>Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>ATTN: Technical Library</td>
</tr>
<tr>
<td>1</td>
<td>AMDAR-SCM, J. D. Corrie</td>
</tr>
<tr>
<td>1</td>
<td>AMDAR-QAC-E</td>
</tr>
<tr>
<td>1</td>
<td>AMDAR-LCA, Mr. Harry E. Pobly, Jr., PLASTEC, Director</td>
</tr>
<tr>
<td>Commander, U.S. Army Natick Research and Development Center, Natick, MA 01760</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: Technical Library</td>
</tr>
<tr>
<td>Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: Technical Document Center</td>
</tr>
<tr>
<td>Commander, U.S. Army Tank-Automotive Command, Warren, MI 48090</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: AMSTA-ZSK</td>
</tr>
<tr>
<td>2</td>
<td>AMSTA-UL, Technical Library</td>
</tr>
<tr>
<td>Commander, White Sands Missile Range, NM 88002</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: STEWS-WS-VT</td>
</tr>
<tr>
<td>President, Airborne, Electronics and Special Warfare Board, Fort Bragg, NC 28307</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: Library</td>
</tr>
<tr>
<td>Director, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: AMDAR-TSB-S (STINFO)</td>
</tr>
<tr>
<td>Commander, Dugway Proving Ground, Dugway, UT 84022</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ATTN: Technical Library, Technical Information Division</td>
</tr>
</tbody>
</table>
No. of Copies To

1 Commander, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783
   ATTN: Technical Information Office

1 Director, Benet Weapons Laboratory, LCWSL, USA AMCOM, Watervliet, NY 12189
   ATTN: AMSMC-LCB-TL
   ATTN: AMSMC-LCB-R
   ATTN: AMSMC-LCB-RM
   ATTN: AMSMC-LCB-RP

1 Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E.,
   Charlottesville, VA 22901
   ATTN: Military Tech, Mr. Marley

1 Commander, U.S. Army Aeromedical Research Unit, P.O. Box 577, Fort Rucker,
   AL 36360
   ATTN: Technical Library

1 Director, Eustis Directorate, U.S. Army Air Mobility Research and Development
   Laboratory, Fort Eustis, VA 23604-5577
   ATTN: Mr. J. Robinson, SAVDL-E-MOS (AVSCOM)

1 U.S. Army Aviation Training Library, Fort Rucker, AL 36360
   ATTN: Building 5906-5907

1 Commander, U.S. Army Agency for Aviation Safety, Fort Rucker, AL 36362
   ATTN: Technical Library

1 Commander, USACDC Air Defense Agency, Fort Bliss, TX 79916
   ATTN: Technical Library

1 Commander, U.S. Army Engineer School, Fort Belvoir, VA 22060
   ATTN: Library

1 Commander, U.S. Army Engineer Waterways Experiment Station, P. O. Box 631,
   Vicksburg, MS 39180
   ATTN: Research Center Library

1 Technical Director, Human Engineering Laboratories, Aberdeen Proving
   Ground, MD 21005
   ATTN: Technical Reports Office

1 Commandant, U.S. Army Quartermaster School, Fort Lee, VA 23801
   ATTN: Quartermaster School Library

1 Naval Research Laboratory, Washington, DC 20375
   ATTN: Dr. C. I. Chang - Code 5830
   ATTN: Dr. G. R. Yoder - Code 6384

1 Commander, U.S. Army Radio Propagation Agency, Fort Bragg, NC 28307
   ATTN: SCCR-2

1 Chief of Naval Research, Arlington, VA 22217
   ATTN: Code 471

1 Commander, U.S. Air Force Wright Aeronautical Laboratories,
   Wright-Patterson Air Force Base, OH 45433
   ATTN: AFWAL/MLC
   ATTN: AFWAL/MLLP, M. Forney Jr.
   ATTN: AFWAL/MLBC, Mr. Stanley Schulman

1 Director, U.S. Army Materials Technology Laboratory, Watertown, MA 02172-0001
   ATTN: SLCMT-IML
   Authors
Applications of serial pyrolysis-gas chromatography-mass spectrometry, developed at the U.S. Army Materials Technology Laboratory, are used to determine the qualitative organic formulation and polymer composition of two proprietary experimental natural rubber formulations.