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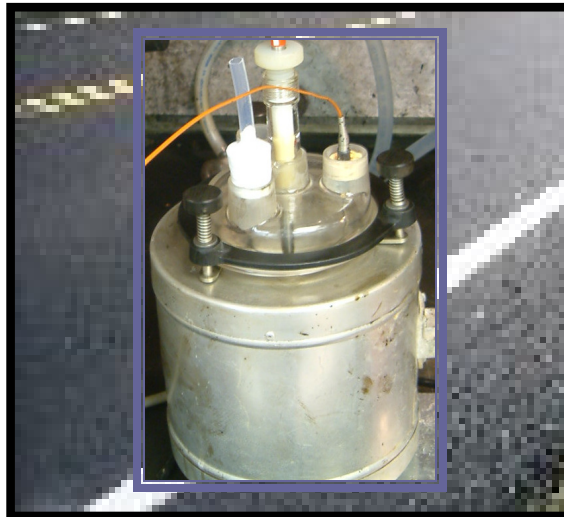
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FINAL  
FOLLOW UP STUDY SUMMARY

*CHEMICAL COMPARISON OF LABORATORY GENERATED FUMES  
CRUMB RUBBER MODIFIED BITUMENS – A LABORATORY PREPARED VERSUS  
PRODUCTION PREPARED PRODUCT*

Prepared for the  
**SWEDISH ROAD ADMINISTRATION**



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## ***1. Background and Objective***

Rubber modified bitumen generally includes a blend of crumb tire rubber, extender oils and bitumen. It is noted for reducing traffic noise, reducing maintenance costs by extending the life of fatigued roads and reducing thickness requirements for overlays by up to half. Since it uses old tires, it conserves natural resources and may be used in initial construction to extend road life. It is also noted for improving skid resistance and drainage of road surfaces when used as gap or open graded mixes (1).

Along with these benefits, however, there are concerns regarding the bitumen rubber emissions during production. Heritage Research Group has previously performed some research to this end, sponsored by the Swedish Road Administration (SRA). A report for this study was issued March 14, 2007. Basically, bitumen fumes were generated from three different samples, the parent bitumen and two modified crumb rubber blends that had been prepared in the SRA laboratories. From this study, it would appear that the modified bitumen test materials generated less fumes as compared with the unmodified bitumen based on the Total Organic Matter (TOM) parameter. Benzothiazole was present in the modified bitumen fumes at % levels, the modification process does not appear to contribute to the 4-6 ring PAC concentration in the subsequent fumes based on both the fluorescence results and individual PAC calculations.

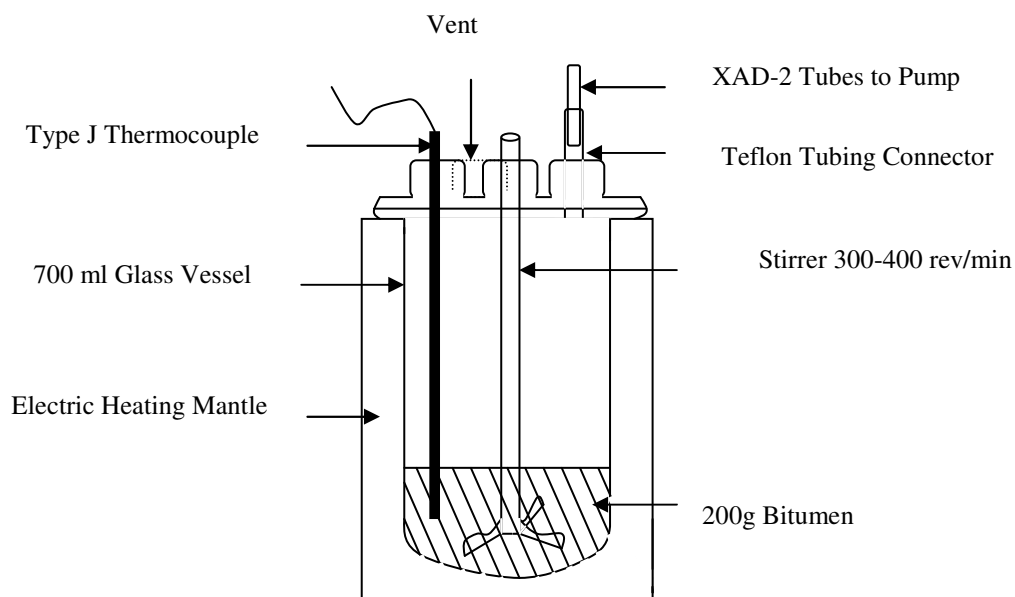
To further investigate bitumen rubber emissions, the SRA submitted another sample for investigation using the Heritage Research Group proposal dated September 21, 2007. This sample was received on October 30, 2007 and was labeled “bitumen and rubber” and is further described as D15. The purpose of this follow-up study to earlier research was to compare the chemical properties of a bitumen product produced in the field to the properties of those sent in the original research that were prepared in the laboratory.

This experiment was performed using the same protocol as that for the original studies (October 31, 2006) to allow optimal comparisons.

## 2. Fume Generation Procedure

Figure 1 shows a schematic of the modified Brandt (2) laboratory fume generation rig proposed for use in this study. The system was designed to heat the bitumen to the desired temperature (in this case 160°C) while stirring the bitumen at a controlled rate (300-400 rev/min). When the bitumen reached the desired temperature, fumes released were captured on XAD-2 resin.

A certificate of fume generation outlining specific parameters is shown in Appendix A and includes exact vessel temperature; stir rate, collection media quantities and sampling duration. Using XAD-2 tube collection systems, fumes emitted in the generator vessel were drawn through the resin with a pump calibrated to a flow rate of ~2.0 liters per minute (lpm).



**Figure 1. Modified Brandt laboratory fume generator schematic.**

### 3. Bitumen Fume Analysis & Results

#### 3 A. Gas Chromatography/ Flame Ionization Detection (GC/FID)

##### 3 A i. Total Organic Matter (TOM)

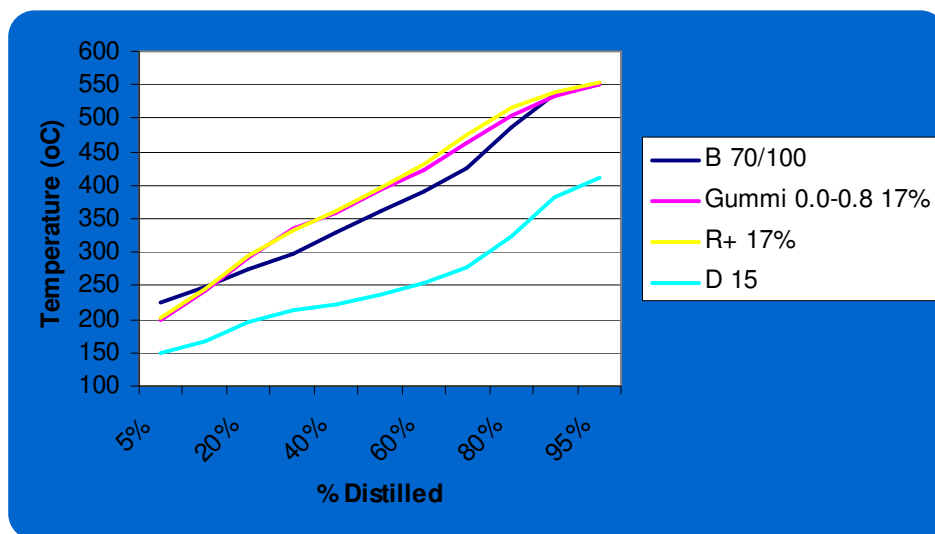
Using gas chromatography with flame ionization detection (GC/FID), the amount of fume collected was determined, referred to as total organic matter (TOM) (SW 846-8015 mod) (3). TOM results are shown in Table 1, along with the original data. GC/FID Chromatograms are presented in Appendix B.

**Table 1. TOM, Fluorescence and Sim-Dis Results on Laboratory-Generated Fumes**

	Source of Bitumen Fume	Total Organic Matter mg/m <sup>3</sup>	Fluorescence Emission Units/gram (EU/g)	10% Distilled (°C)	50% Distilled (°C)	90% Distilled (°C)
1	B 70/100	752	191	250	362	535
2	B 70/100 83%, + gummi 0.0-0.8 17%	494	190	242	393	534
3	B 70/100 83% + 17% ROAD <sup>+</sup>	451	193	244	398	540
4	Production Sample D15	320	312	168	237	381

##### 3 A ii. Simulated Distillation (Sim-Dis)

Using GC/FID, the boiling point profile of each fume was determined using a simulated distillation method ASTM D-2887 (4). Results for the 10, 50 and 90 percent distilled are shown in Table 1 and the comparative boiling point distributions are shown in Figure 2.



**Figure 2. Simulated distillation comparison of bitumen fumes. The field prepared sample is well below the laboratory prepared boiling point curves.**

### 3 B. Fluorescence

An aliquot of the fume extract was also exchanged into cyclohexane for fluorescence analysis. These analyses were performed using a Perkin Elmer Luminescence Spectrometer LS50B following the asphalt fume fluorescence (AFF) test protocol outlined in a separate publication (5). This fluorescence test method is designed to optimize response to potentially carcinogenic compounds in bitumen fumes. Results are listed in Table 1 and show approximately a 1.6 times higher fluorescence at the 385nm ex and 415 nm em wavelength pair than from the original study samples.

### 3 C. Gas Chromatography/Mass Spectroscopy (GC/MS)

Two different types of mass spectrometers were employed for analyses of these fume samples. Gas chromatography with a time of flight mass spectrometer (GC/TOFMS) was used for the speciation of polycyclic aromatic compounds (PACs). For fingerprinting various extracted ions, an Agilent GC with a quadrupole mass spectrometer was used.

### 3 C i. Polycyclic Aromatic Compounds

To investigate compounds of regulatory concern, this fume condensate was analyzed by GC/TOFMS for 35 PACs following the guidelines of EPA SW-846 8270 (6) and the method published by Heritage (7) for the Emergency Planning and Community Right to Know Act (EPCRA) list of compounds. These results are compiled in Table 2 which also includes the data from the original study. Comparing the sum of all of the detectable PACs excluding benzothiazole, the production sample D15 fumes are approximately 4 times less than the parent bitumen fumes. The benzothiazole concentration in the D15 sample is significantly less than the concentration in the laboratory prepared samples from the original study.

### 3 C ii. Extracted Ion Fingerprints

To further characterize compounds in the fumes of these three bitumen materials, GC/MS was also used to create fingerprints of extracted ions. This takes advantage of collecting the three dimensional GC/MS data. Two of these dimensions are the mass versus intensity of the normal mass spectrum; the third dimension is the GC retention time over which the mass spectral data are acquired. The original bitumen sample extract was reanalyzed on the same run with the new sample to provide the best comparison.

Examination of these extracted ion fingerprints (listed in Table 3), provided additional means of comparing the fume composition between these three materials. Recommended by Dr. Larry Olsen of NIOSH (National Institute of Occupational Safety and Health) for other studies, this list is based on work done on the original NIOSH fumes (8) and his own research. (The carbazoles and benzothiazoles were added to this table for the crumb rubber modified bitumen). Figure 3 shows the extracted ion 85 for the field-prepared sample as compared to the straight run bitumen. This similarity was not observed in the original study. All of the ion fingerprints are

shown in Appendix C. A summary of qualitative difference after examination of all of these extracted ions is presented in Table 4.

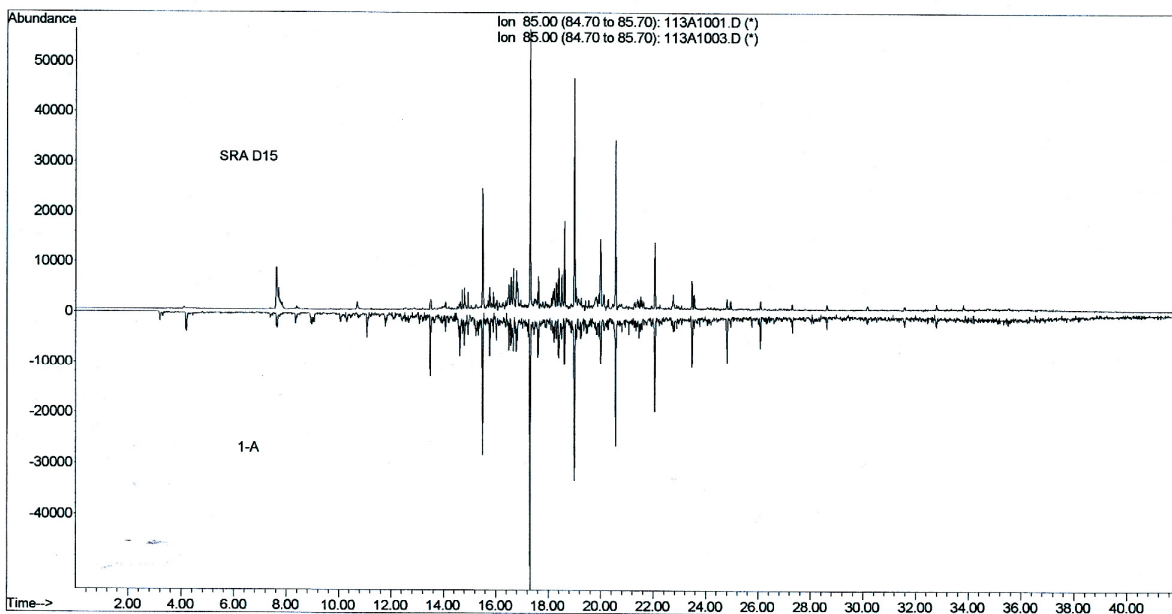
**Table 2. Polycyclic Aromatic Compounds Concentrations (mg/kg)**

	mg/kg	1	2	3	4
	Polycyclic Aromatic Compounds	70/100	70/100 + Gummi 0.0-0.8 17%	70/100 + 17% ROAD <sup>+</sup>	Field Sample D15
1	Naphthalene	350	385	178	<2
2	Acenaphthene	43.3	118	31.0	33.5
3	Acenaphthylene	≤3	52.9	14.7	13.8
4	Anthracene	12.8	≤4	≤2	4.59
5	Fluoranthene	≤3	27.0	19.2	6.97
6	Fluorene	39.1	169	38.6	23.5
7	Benzo[a]anthracene	≤3	≤4	≤2	<2
8	Chrysene	10.5	12.3	12.6	2.91
9	5-Methylchrysene	≤3	≤4	≤2	<2
10	1-Nitropyrene	≤3	≤4	≤2	<2
11	Pyrene	23.8	66.4	52.3	13.3
12	Phenanthrene	84.9	325	94.6	36.6
13	Benzo[b]fluoranthene	≤3	4.7	3.8	<2
14	Benzo[j]fluoranthene	≤3	≤4	≤2	<2
15	Benzo[k]fluoranthene	≤3	≤4	≤2	<2
16	7,12-Dimethylbenz[a]anthrene	≤3	≤4	≤2	<2
17	Benzo[a]pyrene	≤3	≤4	≤2	<2
18	Benzo[e]pyrene	≤3	6.0	4.7	<2
19	3-Methylcholanthrene	≤3	≤4	≤2	<2
20	Dibenz[a,h]acridine	≤3	≤4	≤2	<2
21	Dibenz[a,j]acridine	≤3	≤4	≤2	<2
22	Indeno[1,2,3-cd]pyrene	≤3	≤4	≤2	<2
23	Dibenz[a,h]anthracene	≤3	≤4	≤2	<2
24	7H-Dibenzo[c,g]carbazole	≤3	≤4	≤2	<2
25	Benzo[g,h,i]perylene	4.8	8.0	4.2	<2
26	Dibenzo[a,e]fluoranthene	≤3	≤4	≤2	<2
27	Dibenzo[a,e]pyrene	≤3	≤4	≤2	<2
28	Benzo[r,s,t]pentaphene	≤3	≤4	≤2	<2
29	Dibenzo[a,h]pyrene	≤3	≤4	≤2	<2
30	Dibenzo[a,l]pyrene	≤3	≤4	≤2	<2
31	Benzo[b]naphtho[2,1-d]thiophene	9.3	15.8	12.2	3.17
32	Cyclopenta[cd]pyrene	≤3	≤4	≤2	<2
33	Triphenylene	≤3	≤4	≤2	<2
34	Carbazole	≤3	≤4	≤2	<2
35	Benzothiazole	≤18	254993	92413	977
	Sum (excluding Benzothiazole)	578	1190	466	138

**Table 3. List of Extracted Ions (m/z) for Validation and Characterization**

Compounds	Extracted Ions (m/z)
n-alkanes	85
Naphthalene	128
alkylated naphthalenes	142,156,170
Monocycloalkanes	69
Benzothiophene	134
alkylated benzothiophenes	148,162,176
Dibenzothiophene	184
alkylated dibenzothiophenes	198,212
Benzofuran	118
alkylated benzofurans	132,146
Dibenzofuran	168
alkylated dibenzofurans	182,196
benzothiozoles	108, 135
carbozoles	211, 139, 167

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Operator :  
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Misc Info : A758923  
Vial Number: 0



**Figure 3. Extracted Ion 85, indicative of n alkanes, for fumes generated from the parent bitumen and from the field prepared sample.**

**Table 4. Extracted Ions-Description of Differences Relative to the Parent Bitumen Fumes**

Class of Compounds	Extracted Ion	Field Sample D15
n-alkanes	85	Not exact, but very similar
naphthalene	128	small differences
alkylated naphthalenes	142	similar, 1 peak slightly higher at ~19.8 min.
alkylated naphthalenes	156	similar
alkylated naphthalenes	170	similar, 2 small peaks in front of alkylated series and slightly higher peaks at end
monocycloalkanes	69	Different profiles
benzothiophene	134	Different profiles
alkylated benzothiophenes	148	Different profiles
alkylated benzothiophenes	162	Different profiles
alkylated benzothiophenes	176	Different profiles
dibenzothiophene	184	similar but ratio variations & extraneous peaks
alkylated dibenzothiophenes	198	similar-slight ratio variations.
alkylated dibenzothiophenes	212	Similar, extra peaks
benzofuran	118	6 extra peaks at end.
alkylated benzofurans	132	Different profiles
alkylated benzofurans	146	Many variations, some overlap
dibenzofuran	168	similar except for 1 peak at ~22.5 min.
alkylated dibenzofurans	182	Some similar peaks but varying ratios
alkylated dibenzofurans	196	very different pattern
benzothiozoles	108	strong peak at ~16 min.
benzothiozoles	135	strong peak at ~16 min.
carbozoles	211	similar-some extra patterns ~23 min. + 32.5 min. strong peak
carbozoles	139	Larger pk at ~19.5, similar but varying ratios at noise levels
carbozoles	167	Some similarities, but near noise level

#### **4. Discussion**

Based on the TOM, the production sample D15 yields the least amount of fumes (320 mg/m<sup>3</sup>). From the original study, the two laboratory-prepared modified samples had concentrations of 451 mg/m<sup>3</sup> and 494 mg/m<sup>3</sup>. Finally, the un-modified B 70/100 bitumen fume produced the highest amount of TOM (752 mg/m<sup>3</sup>). This differs from the NIOSH studies on Crumb Rubber (9), which found that the personal breathing zone exposures were usually higher during crumb rubber modified asphalt paving as compared to the conventional sites. The design of the SRA study, however, allows a more direct comparison of these particular materials under controlled conditions.

For a given material source, a lower boiling point implies that the concentration of 4-6 ring PACs would also be lower, which is indeed the case as compared to the other three samples from the original SRA study.

Fluorescence results show no change in response between all three bitumen fumes in the original study, but shows a significant increase for the field-prepared sample. The increase does not appear to correspond to the individual PAC data reported.

The PAC concentrations as determined by GC/MS appear to be significantly less in the production-prepared sample as compared to the laboratory-prepared modified bitumens and the parent material. Acenaphthylene is detected in the modified bitumen fumes, but is not detected in the parent fumes. This compound is not typically seen in bitumen fumes (10).

As compared to the B 70/100 bitumen fumes, examination of the extracted ion fingerprints from the production-prepared modified bitumen fume show strong similarities for the n-alkanes, a prominent peak at ~16 minutes that show up on the 69, 134, 108 and 135 mass to charge ions which is identified as benzothiazole, many extra peaks at the benzofuran ion (118), a very different pattern for the alkylated dibenzofurans, and a strong peak at 32 minutes

corresponding to the 211 ion. It appears that the strong peak at 32 minutes may be within the benzothiazole family, but the exact identification is unknown.

Although this bitumen modified sample was prepared in the field, the fumes generated from this material were prepared in the laboratory. It is important while reviewing this data to consider that these results represent a worst case scenario under the laboratory conditions by which the condensates were generated. Because real world field conditions are complicated by many variables which can not be accounted for in a controlled laboratory setting it is recommended that industrial hygiene exposure measurements be made to obtain information about actual worker exposures.

## **5. Conclusions**

Based on the TOM data, it would appear that the field-prepared modified bitumen material generates less fumes as compared with the unmodified bitumen and modified bitumens from the original study. The quality of the fumes are also different showing a lower boiling point range and lower concentrations of individual and summed PACs.

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