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EFFECTS OF MODE OF GENERATION ON THE COMPOSITION OF ASPHALT FUMES

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Abstract.
Asphalt is used as the binder (cement) in road paving, and in the manufacture and application of roofing materials. At the elevated temperatures used in these industries, asphalt emits fumes. Concerns about the possible presence of carcinogenic PACs in asphalt fumes prompted the National Institute of Occupational Safety and Health (NIOSH) to sponsor two mouse skin-painting bioassays [1,2] of roofing asphalt fumes generated at 232º and 316ºC using a laboratory apparatus. The studies showed that the whole fume condensates and two of five HPLC subfractions of the higher temperature fume were carcinogenic. The present investigation was designed to determine the extent to which NIOSH's mode of fume generation affected their composition, and hence biological activity. The results show that minor changes in generation mode produce marked differences in fume composition, and that relative to field fumes, the laboratory-generated fumes were significantly enriched in the higher molecular weight PACs which have been associated with carcinogenicity in animal studies.

***Key Words**:* Asphalt, Fumes, Polycyclic Aromatic Compounds, Sulfur Heterocycles, Simulated Distillation

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INTRODUCTION
Asphalt is one of the most widely used industrial products. More than 90% of the roads in the U.S. are paved with asphalt, and most buildings are roofed with asphalt-containing materials. Of these two principal uses, which account for 99% of asphalt production, paving operations consume approximately 85% of the total tonnage. Approximately 400,000 workers are employed in asphalt-related industries in the U.S. -- 300,000 of them in the paving industry. When one considers worldwide use of asphalt, the total number of workers in the industry is very large indeed.

Asphalt is a solid to semi-solid material at ambient temperatures. To reduce its viscosity and achieve the required workability, it must either be dissolved in a suitable solvent or emulsified in water, as is done in waterproofing and certain paving operations. Alternatively, it must be heated, as is the case in hot mix asphalt paving and virtually all roofing operations. When asphalt, or asphalt-containing materials are heated, they release fumes. The fumes, for the purpose of this paper, are comprised of aerosol droplets as well as volatile gases which may contain irritants and small amounts of polycyclic aromatic compounds (PACs). Considerable research in recent years has been directed toward better understanding the extent to which exposure to asphalt fumes may pose a risk of adverse health effects in workers.

Two carcinogenicity evaluations conducted in the 1980s by NIOSH [1,2] are among the most comprehensive on asphalt fumes. In the first study, fume condensates generated from a roofing asphalt at temperatures of 232º and 316ºC using a laboratory apparatus (see Figure 1) were tested in the standard mouse skin-painting bioassay, a method widely used for determination of the carcinogenic potential of oils and other petroleum-derived materials. In the second study, only fumes generated at 316ºC were used and the fume condensate was separated by High Performance Liquid Chromatography (HPLC) into a series of five fractions designated A through E. Whole fume and various combinations of the fractions were then tested in the skin-painting assay.

Because of the large quantity of fume condensate required for this work, the primary consideration in the design of the laboratory apparatus and the generation method was the maximization of condensate yield. This was accomplished by employing high temperatures, long generation times (6-10 hrs), rapid stirring, and a high velocity sweep of heated air across the asphalt surface. While the method achieved the desired end -- yielding more than 8 kg of product, the extreme conditions have raised questions about whether the fume condensates studied are representative, chemically and toxicologically, of fumes typically encountered in the asphalt workplace.

In light of recent reports [3,4,5] that mode of generation can have a significant effect on the composition, and therefore toxicology, of asphalt fumes, the present studies were designed to determine the extent to which the NIOSH fumes resemble those to which asphalt workers are exposed. Fume condensates from paving asphalts were collected above asphalt storage tanks (Figure 2); those from roofing asphalts were collected above roofing kettles. These were compared to the NIOSH fumes and, to the extent possible, to those collected on worker monitoring cassettes.

The results of these studies show that there are significant quantitative and qualitative differences between NIOSH fumes and those typically found in the workplace. Since toxicology is dictated by composition, these differences suggest that any proper evaluation of hazard from exposure to workplace fumes must be conducted using fumes or fume condensates collected in the field or, at the very least, fumes generated in a laboratory apparatus proven effective at mimicking field fume composition.

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MATERIALS AND METHODS

Laboratory Fume Generation

Laboratory fume generation was conducted as described by Sivak et al. [2] using the apparatus and conditions depicted in Figure 1. Several variations on the basic method were also evaluated: (a) asphalts other than the NIOSH roofing asphalt were fumed; (b) fume generation temperature was varied; (c) the asphalt was not stirred during fuming; and (d) air was pushed rather than pulled across the hot asphalt surface.

Collection of Fume Condensates from Asphalt Storage Tanks and Roofing Kettles

The same pumps and traps from the laboratory study were used to collect fume condensates from paving and roofing asphalts. Figure 2 shows schematic representations of the collection equipment. The atmosphere above the heated asphalt was sampled at a rate of 10 L/min.

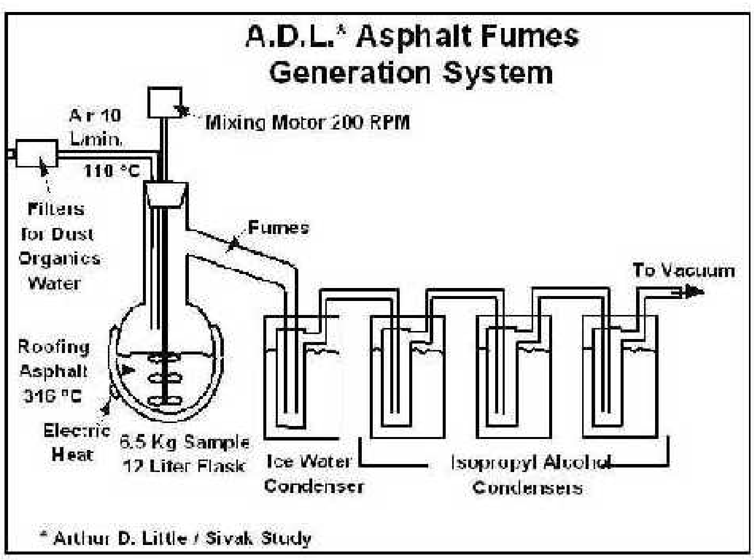

FIGURE 1 Apparatus for collection for collection of laboratory-generated fumes

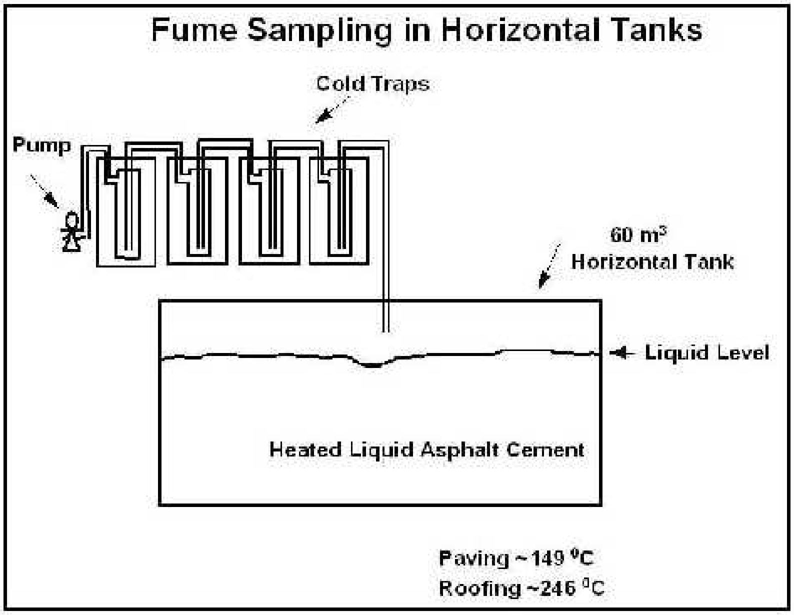

FIGURE 2 Apparatus for collection of field fumes

Personnel Sampling

NIOSH Method 5506 [7] was modified to circumvent anomalies observed in a previous exposure study. A closed face cassette containing a silver membrane backed by a glass fiber filter was used rather than the Teflon support described in the NIOSH method. Both filters were pre-extracted with benzene to remove any benzene-soluble material not associated with fume collection. At the outlet of the cassettes, an SKC tube containing XAD-2 resin was added to capture volatiles. A checklist was reviewed with workers at each monitoring site to ensure that exposures to cigarette smoke, diesel fuel, and solvent were avoided during fume collection.

Sampling of Asphalt Cement

One hundred kg samples of asphalt cement were taken from storage tanks prior to initiation of cold trap collection of condensates. These samples were later used for laboratory fume generation using the apparatus shown in Figure 1.

Analysis of Total Particulate Material on Personnel Cassettes

NIOSH Method 0500 [8] was used for determination of total particulate.

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Carbon Disulfide Soluble Material on Personnel Cassettes

NIOSH method 5023 [9] was followed, except that carbon disulfide was substituted for benzene as the extraction solvent. Cassettes from each team of four workers at a given site were combined to provide enough material for subsequent analysis. Carbon disulfide-soluble material on the filters and XAD-2 resins were combined to better simulate total organic exposure in the breathing zone air.

High Resolution Gas Chromatography/Mass Spectrometry (HRGC/MS)

Fume condensates were analyzed on a Hewlett-Packard mass spectrometer interfaced with a Hewlett Packard 5790 gas chromatograph. One microliter of sample dissolved in a suitable solvent was injected on a 30 m DB-1 capillary column in splitless mode. The injector and transfer line temperature were 280ºC, the oven was heated at 80ºC for 2 min and programmed to rise to 320ºC at 10ºC/min, and then hold for 20 min. The mass spectrometer was scanned from mass 40 to 800 in approximately one second. One sample was derivatized to form the trimethylsilyl derivative by using a commercially available prepared cocktail.

Gas Chromatography with Flame Photometric Detection (GC/FPD)
Sulfur heterocycles were determined using the following procedure. Samples were dissolved in iso-octane and partitioned between iso-octane and dimethylsulfoxide. The DMSO extract was then diluted with water and back-extracted into iso-octane. The resulting solution was analyzed using a Hewlett-Packard Model 5890 Series II gas chromatograph equipped with a 30 m x 0.54 mm DB-624 GLPC column and a flame photometric detector. External calibration standards contained 1.0, 5.0 and 10 mg/L each of benzothiophene, dibenzothiophene, thianthrene, and naphthobenzothiophene.

Sulfur-containing compounds were arbitrarily divided into two groups: those eluting between the solvent peak and dibenzothiophene (<3-ring) SH(L), and those eluting at or after the retention time of dibenzothiophene (≥3-ring) SH(H). Quantification was based on the assumption that all responses were similar to that of dibenzothiophene.

Simulated Distillation
Simulated distillation of the fume condensates was performed using ASTM Method D-2887 [10].

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RESULTS

Effects of Laboratory Generation Mode on Fume Composition of Roofing Asphalt
Figure 3 shows a comparison of four preparations of fume condensates generated at 316ºC using the NIOSH apparatus (Figure 1). Two asphalts were studied: that used in the original NIOSH investigation and a similar grade commercial roofing asphalt designated CRA. Three generation methods were evaluated: Method 1 was that reported by Sivak et al [2]. Method 2 was identical to 1 except that air was pushed across the surface of the heated asphalt rather than pulled with a vacuum pump. Method 3 was the same as 2 except that the liquid asphalt was not stirred during fume generation.

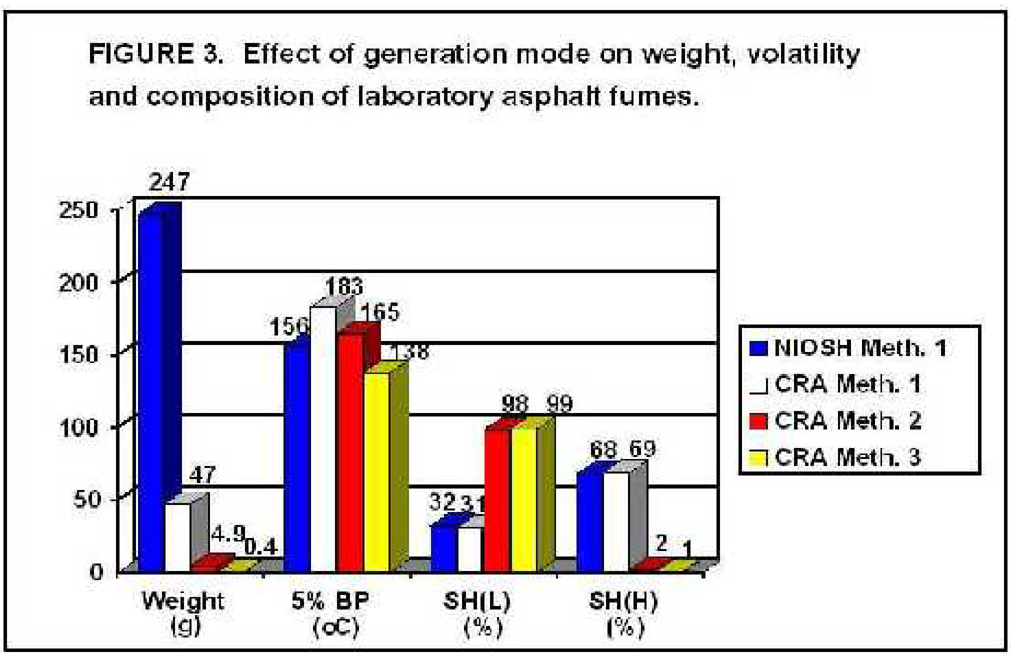

Figure 3. Effect of Generation Mode on Weight, Volatility and Composition of Laboratory Asphalt Fumes.

The columns in Figure 3 (left to right within groups) represent (a) the total weight of fume condensate produced, (b) the boiling point at which 5% of the condensate distilled, and (c) the concentration of low molecular weight (2-ring) and high molecular weight (3-5-ring) sulfur heterocycles.

The first two sets of columns represent fume condensates collected using the standard NIOSH protocol (Method 1) as applied to the original NIOSH asphalt and asphalt CRA. The total amount of fume from the NIOSH asphalt was substantially higher than that from CRA, in part owing to the longer generation time used (6-8 hrs rather than 5.5 with CRA). The other three compositional parameters are quite comparable, as might be expected given the same generation method was employed. Comparison of Method 1 fumes for asphalt CRA with those produced by Methods 2 and 3 show some striking differences. First, the amount of fume produced by Method 1, which involved an air pull and rapid stirring, is ten-fold higher than that from 2 and more than 100-fold higher than with Method 3. The ratio of low to high molecular weight sulfur heterocycle contents increased from 30.9/69.1 for Method 1 to 98.2/1.8 and 99/1 for Methods 2 and 3 respectively. Correspondingly, 5% boiling points declined from 183ºC (1) to 165ºC (2) and 138ºC (3). These pronounced changes in weight of fume, composition, and volatility indicate a much lower release into the fume of higher molecular weight compounds using Methods 2 and 3.

Comparison of Laboratory and Field Fume Condensates from Roofing Asphalt
Figure 4 and Figure 5 show a comparison of the same parameters examined in the Figure 3 data for fumes from two roofing asphalts ("Indiana" and "Ohio") collected at approximately 250ºC (typical roofing kettle temperature) (a) in the laboratory using the NIOSH apparatus, (b) over roofing kettles using the apparatus in Figure 2, and (c) in the workplace on personnel cassettes as described in MATERIALS AND METHODS.

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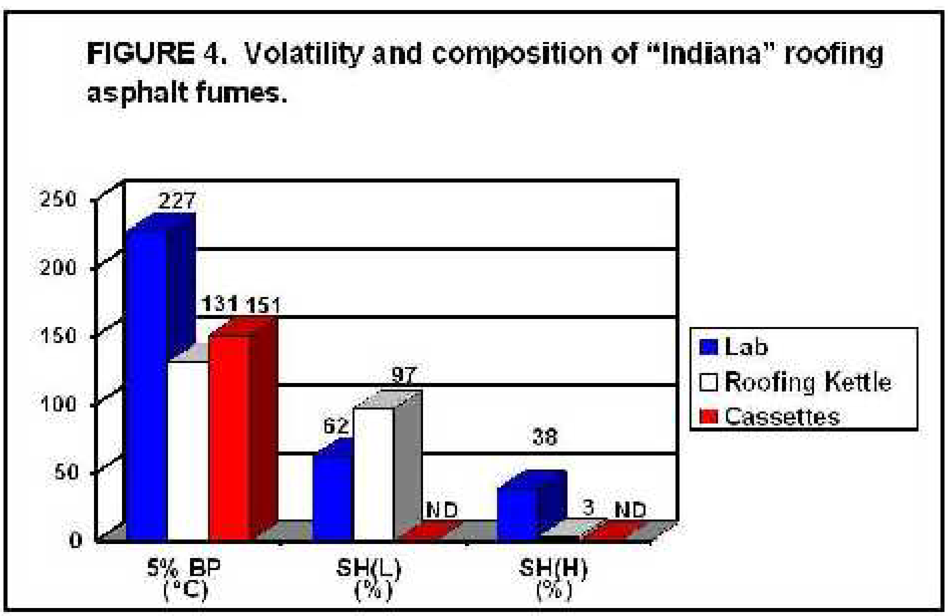

Figure 4. Volatility and Composition of "Indiana" Roofing Asphalt Fumes

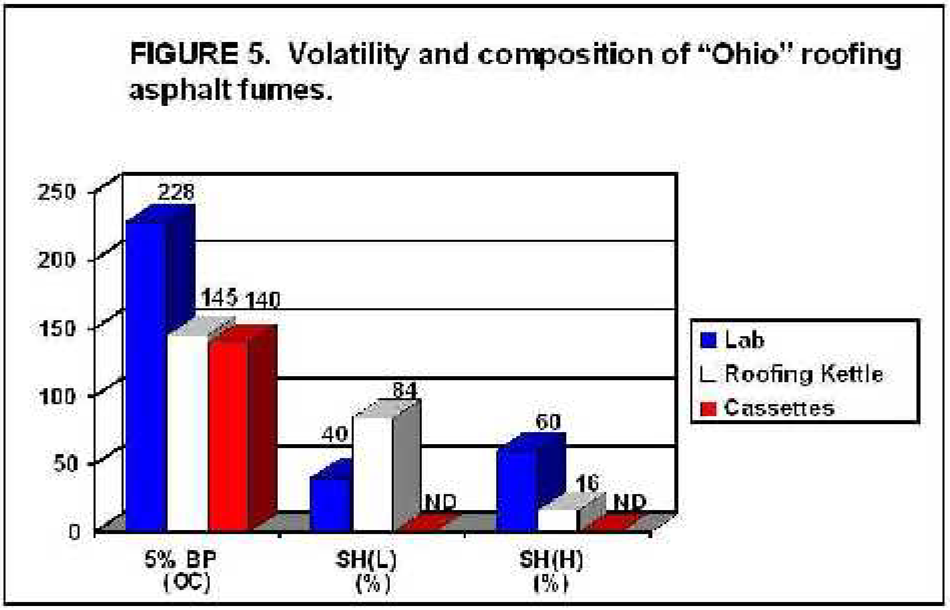

Figure 5. Volatility and Composition of "Ohio" Roofing Asphalt Fumes.

The data comparing laboratory and field condensates show that all three compositional parameters are markedly affected by the method of fume generation. The 5% boiling points of field fumes are about 80ºC lower than those of the corresponding laboratory-generated fumes. The ratios of low to high molecular weight sulfur-heterocycles were 61.7/38.3 (Indiana) and 40.1/59.9 (Ohio) for the laboratory-generated fumes, but 97.4/2.6 and 84.4/15.6 respectively for those collected over roofing kettles.

The fumes collected on personnel cassettes had boiling ranges similar to those of fume condensates collected by cold-trapping over the kettle, but markedly lower (70-80ºC) than those of laboratory fumes. The amount of fume collected on cassettes was too low to permit detection of sulfur heterocycles at the limits of the method used (equivalent to 10 µg/m3 in the workplace air), but the similarity of 5% boiling points between field condensates and the cassette samples suggests that the concentrations of these species are likely to be comparable.

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Comparison of Laboratory and Field Fume Condensates from Paving Asphalt

Paving asphalt fumes were generated at 163ºC (somewhat above normal paving temperature) using the NIOSH apparatus. Their volatility and composition were compared to fumes collected at the same temperature over asphalt storage tanks. Figure 6 shows that the 5% boiling point of field fumes is approximately 75ºC lower than that of the lab fumes. The ratios of low to high molecular weight sulfur heterocycles are consistent with the pronounced boiling range difference between the two condensates (32.9/67.1 for laboratory fumes vs. 97.2/2.8 for field fumes).

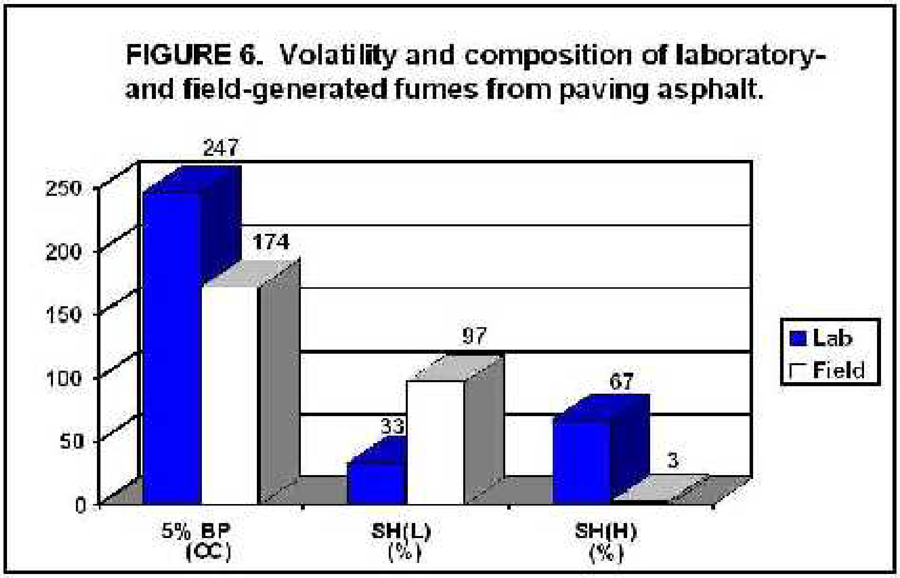

Figure 6. Voatility and Composition of Laboratory and Field-Generated Fumes from Asphalt Paving.

Aromatic Hydrocarbon/Sulfur Heterocycle Composition of Paving Asphalt Fumes
Figure 7 and Figure 8 show the aromatic hydrocarbon and sulfur heterocycle composition of paving asphalt fumes (lab and field) subdivided by ring number class. Compositions were determined using HRGC/MS.

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Figure 7 shows that laboratory-generated paving fumes are quite comparable to those from the NIOSH roofing asphalt in terms of polynuclear aromatic hydrocarbon (PAH) ring-number classes. This includes alkylated and non-alkylated PAHs. Field fumes, however, are quite distinct, showing three- to four-times the alkyl benzene content and a preponderance of two-ring compounds (67%). Three-ring compounds were twenty-five- to thirty-times lower in field fumes, and no four-ring compounds were detected.

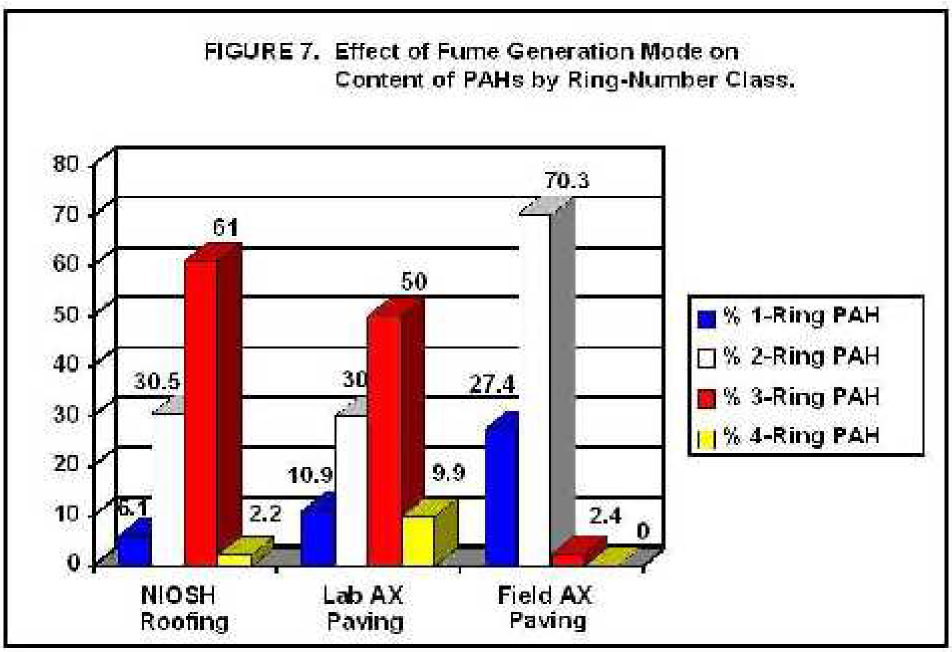

Figure 7. Effect of Fume Generation on Content of PAHs by Ring-Number Class.

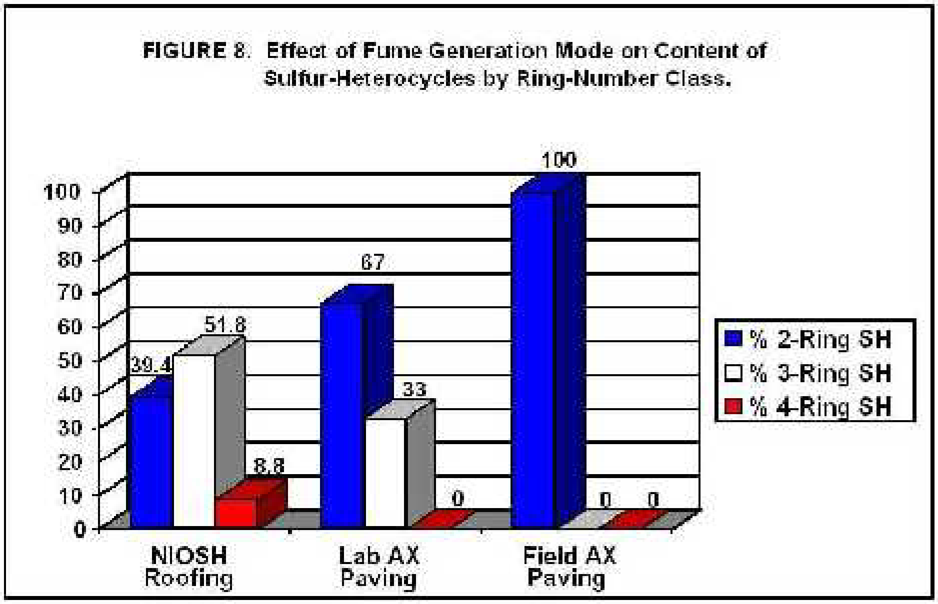

Figure 8. Effect of Fume Generation on Mode of Content Sulfur-Heterocycles by Ring-Number Class.

In terms of sulfur heterocycles (Figure 8), field fumes contained *only* two ring compounds, whereas lab fumes from paving asphalt contained 33% 3-ring species. No four-ring compounds were detected in either lab or field fumes from the paving asphalt. In the NIOSH fume, 8.8% of the sulfur heterocycles detected were four-ring compounds, 51.8% three-ring, and 39.4% two-ring.

DISCUSSION

The purpose of this study was to investigate the relationship between asphalt fume composition and the mode of fume generation. The findings from the study could then be used to help establish the relevance of the NIOSH mouse skin-painting bioassays [1,2] to any assessment of the carcinogenic potential of workplace asphalt fumes.

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Effects of Generation Conditions on the Quantity of Fume Produced

This study showed that relatively minor modifications to the NIOSH laboratory fume-generation protocol had profound effects on the weight of fume produced. Simply changing the airflow through the generation flask by introducing the stream under slight pressure, rather than drawing it through under vacuum (push vs. pull) resulted in a ten-fold reduction in the amount of fume produced. This effect presumably resulted from a higher probability that newly vaporized components would leave the liquid surface and be swept into the air stream rather than reenter the liquid under the reduced-pressure (pull) conditions.

When an air push was combined with a cessation of the 200 rpm stirring used in the NIOSH protocol, fume yield dropped by a factor of 100. The pronounced reduction in fume mass in the absence of stirring is probably best explained by the reduced formation of droplets at the edge of the agitated stirring apparatus. The energy imparted at the liquid vapor interface promoted formation of aerosols. In the absence of stirring, fume was primarily produced by release of volatiles from the liquid surface.

In field asphalt operations, whether roofing or paving, the dynamics of fume generation are substantially different from those seen in the NIOSH laboratory method. The asphalt cement is not subjected to continuous agitation or to a significant reduction in air pressure over the liquid surface -- circumstances which increase the amount of fume and its content of high molecular weight (i.e. low vapor pressure) PAC.

Time at temperature is also markedly different in the two situations. In the laboratory, the asphalt is maintained at the predetermined temperature throughout fuming; in the field, it begins cooling as soon as it is applied to the roof or road surface, and it cools to the point of solidification within minutes of application.

Effects of Generation Conditions on the Composition of Fume Produced: Implications from the Simulated Distillation Studies

In these studies complete distillation curves were obtained, but for convenience, 5% boiling point has been used to characterize asphalt fumes from various sources. As discussed above, the reductions in condensate yield seen for Methods 2 and 3 relative to Method 1 are consistent with the lower likelihood that high molecular weight (lower vapor pressure) compounds will enter the fume in the modified procedures.

Similarly, the 30 to 40% reduction in 5% boiling points of field fumes relative to those produced at the same temperature using the NIOSH apparatus, and their similarity to the values obtained using Method 3, indicate that the original NIOSH protocol produced fume condensates with a significant over-representation of high molecular weight compounds. The implications of this finding for fume carcinogenicity are discussed below.

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The similarity in 5% boiling points of fumes collected on personnel monitoring cassettes to those collected over roofing kettles and storage tanks suggests that the latter condensates, obtainable in relatively large quantities, might be good surrogates for field fumes in future studies.

Effects of Generation Conditions on the Composition of Fume Produced: Implications from Analytical Characterization Studies

Two classes of aromatic compounds were assayed in the characterization of fume condensates: aromatic hydrocarbons and sulfur-heterocycles. The latter class was further subdivided into low (< 3-ring) and high (≥ 3-ring) molecular weight groups. Detailed analytical characterization by HR GC/MS of fumes from paving asphalt was also carried out.

The rationale for selection of sulfur heterocycles as one of the endpoints was the speculation by NIOSH that the carcinogenicity seen in their skin-painting assays may have been mediated in large part by these compounds. The subdivision into low and high molecular weight groups reflects the knowledge [11] that one- and two-ring sulfur heterocycles are not carcinogenic, while some three-, and especially four- and five-ring species are known to be active in the mouse skin-painting bioassay. Similar considerations apply to the analysis of the GC/MS data on distribution of aromatic hydrocarbons and sulfur heterocycles by ring-number.

Taken as a whole, the analytical data confirm the conclusions drawn from the gravimetric and boiling range assays: (a) the original NIOSH fume condensates have significant levels of high molecular weight aromatic hydrocarbons (PAH) and sulfur heterocycles (PASH); (b) modification of the NIOSH procedure, as in Methods 2 and 3, dramatically reduces the content of these species; (c) the ratio of low to high molecular weight aromatics in field fumes is much higher than in NIOSH laboratory fumes; and (d) the concentrations of four-ring compounds, which are the lower end of the molecular weight range for likely carcinogens in the NIOSH studies, are extremely low in field fumes from roofing asphalt and undetectable in paving fumes.

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