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HETA 94–0408–2564 Granite Construction Company Sacramento, California

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# PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, technical and consultative assistance to Federal, State, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

# **ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT**

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#### Health Hazard Evaluation Report 94–0408–2564 Granite Construction Company Sacramento, California March 1996

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## **EXECUTIVE SUMMARY**

Approximately 285 million used tires are discarded in the United States each year, posing significant health, fire, and solid waste management problems. As one means of reducing these problems, considerable attention has been focused on the use of the scrap tire rubber in highway paving materials. In 1991, Congress enacted the Intermodal Surface Transportation Efficiency Act (ISTEA), which required each state to use a minimum quantity of "crumb rubber modified" (CRM) hot-mix asphalt (HMA) paving material, beginning at 5% of the HMA used in federally funded paving in 1993, and increasing to 20% in 1997 and thereafter. Because of public concerns over the lack of available information on the environmental and human health effects resulting from the use of CRM-HMA, along with the high cost of using this paving material, a temporary legislative moratorium was passed which precluded enforcement of the penalty provisions of the ISTEA legislation. This legislation also directed the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Transportation, Federal Highway Administration (FHWA) to evaluate the potential environmental and human health effects associated with the use of CRM asphalt. The recently passed National Highway System Designation Act of 1995 has eliminated the mandate requiring the use of CRM asphalt but continues to require research concerning CRM asphalt paving.

Approximately 300,000 workers are currently employed in the asphalt paving industry in the U.S. In June 1994, the National Institute for Occupational Safety and Health (NIOSH) entered into an Interagency Agreement with the FHWA to evaluate occupational exposures among asphalt workers. A research protocol developed by NIOSH included the following objectives:

- P Characterize and compare occupational exposures to CRM asphalt and conventional asphalt.
- P Develop and field test new methods to assess asphalt fume exposures.
- P Evaluate potential health effects associated with CRM asphalt and conventional asphalt.

The protocol allows for up to eight individual site evaluations in different geographic regions of the country, enabling investigators to observe different asphalt pavement formulations, climatic conditions, and paving techniques.

One of the greatest challenges in conducting this study is the fact that asphalt is not a consistent product. Asphalt is composed of a highly complex mixture of paraffinic and aromatic hydrocarbons and heteroatomic compounds containing sulfur, nitrogen, and oxygen. The specific chemical content of asphalt products is dependent on the crude petroleum source, production techniques, and process temperatures. The addition of rubber further complicates the asphalt mixture as numerous additional substances present in tires (such as aromatic oils, accelerants, and antioxidants used during tire manufacturing) may become airborne during the asphalt heating and mixing processes. Finally, there is a lack of available air sampling methods and occupational exposure limits for most of the compounds present in asphalt and the rubber tire components.

This report presents the findings from the evaluations conducted in Sacramento and Davis, California, during asphalt pavement construction at two different sites: Interstate 80 and U.S. 99. The purpose of this report is not to draw definitive conclusions about conventional and CRM asphalt exposures, but rather to provide the site-specific information obtained from the California project.

On October 7 and 10, 1994, approximately 1,814 metric tons of conventional asphalt were applied by Granite Construction Company; 4,082 metric tons of CRM asphalt were placed October 6 and 11 by the same workers. The rubber content was approximately 20% of the asphalt binder by weight. The workplace exposure and health assessment was performed during all four paving days. The evaluation included the collection of area air samples to characterize the asphalt fume emission, personal breathing zone (PBZ) air samples to evaluate worker exposures, and a medical component that included symptom questionnaires and lung function tests.

Asphalt fume exposures have typically been measured as total particulate and the benzene soluble particulate fraction. However, since neither of these exposure markers measure exposure to a distinct chemical component or even a distinct class of chemicals, it is difficult to relate them to possible health effects. For example, many organic compounds are soluble in benzene, and any dust may contribute to total particulate levels. In an effort to address this problem, new or modified analytical methods were developed and included in this study to more definitively characterize asphalt fume exposures. For example, polycyclic aromatic compounds (PACs), which may be present in asphalt fume, were measured using a new analytical method. Some of the PACs are believed by NIOSH investigators to have irritative effects while other PACs are suspected to be carcinogenic. In addition to PACs, benzothiazole (a sulfur-containing compound present in rubber tires) along with other sulfur-containing compounds (suspected to be present as a result of the addition of rubber to the asphalt or from crude petroleum used for asphalt manufacturing) were also measured. Benzothiazole is of interest since it may be useful as a surrogate indicator for other CRM asphalt fume exposures while other sulfur-containing compounds may be associated with respiratory irritation. Samples were collected for selected organic compounds (toluene, benzene, and methyl isobutyl ketone) and total hydrocarbons (as Stoddard solvent). Elemental carbon was measured to determine if diesel exhaust could have contributed to the air contaminants measured at the paving site. The airborne particulate at the paving site was analyzed to determine the concentration of particles which were respirable. Air samples were collected for 28 different metals and minerals and direct-reading instruments were used to measure carbon monoxide, hydrogen sulfide, sulfur dioxide, and ozone. Finally, bulk air samples of asphalt fume were collected at the asphalt cement storage tank located at the hot mix asphalt plant and submitted for mutagenicity testing.

The area air sample results for total particulate, respirable particulate, and benzene soluble particulate concentrations varied between sampling locations and across survey days, but appeared to be slightly higher during the conventional asphalt paving period as compared with the CRM asphalt paving period. Total PAC concentrations above the paver screed were approximately 2.5 times higher during the conventional asphalt paving period. Whereas, benzothiazole concentrations above the paver screed were approximately the CRM asphalt paving period as compared to the conventional asphalt paving period. Whereas, benzothiazole concentrations above the paver screed were approximately ten times higher during the CRM asphalt paving period as compared to the conventional asphalt paving period. With the exception of the total PAC and benzothiazole area air measurements over the paver screed, no consistent pattern of exposure results were observed during the CRM or conventional asphalt paving periods.

Over 50 volatile organic compounds (VOCs) were detected in the asphalt emissions, but only the most significant peaks were analyzed quantitatively. The concentrations of toluene, methyl isobutyl ketone, and total "other" hydrocarbons were orders of magnitudes below their respective occupational exposure criteria. Benzene was detected in area samples near the paver hopper at concentrations as high as 0.24 parts per million (ppm). While these benzene concentrations do not represent personal exposures, they do suggest the potential for employee exposure. NIOSH considers benzene to be an occupational carcinogen and recommends that occupational exposures be reduced to the lowest feasible level. Extremely low or trace concentrations of the following metals were detected: aluminum, calcium, iron, magnesium, manganese, and titanium.

Short-term instantaneous CO concentrations as high as 1000 ppm in the middle of the paver deck and up to 300 ppm near the operators seat were measured. The use of gasoline powered electric generators for providing light on the paver was the source of the CO. The NIOSH Recommended Exposure Limit (REL) for CO is an 8-hour time-weighted average (TWA) of 35 ppm and a ceiling limit (never to be exceeded even momentarily) of 200 ppm. After the generators were repositioned to direct the exhaust off of the paver, the CO levels were reduced substantially. Concentrations of hydrogen sulfide (H<sub>2</sub>S), sulfur dioxide (SO<sub>2</sub>), and ozone (O<sub>3</sub>) were well below their respective occupational exposure criteria.

Personal breathing-zone air samples were collected on six to nine workers during each of the four days of sampling. The PBZ samples were analyzed for total particulates, and for some workers, a second sample was analyzed for total PACs, benzothiazole and other sulfur compounds, or for benzene soluble particulate fractions. The PBZ exposures for total particulates ranged up to 0.7 milligrams per cubic meter (mg/m<sup>3</sup>) during CRM asphalt paving and 1.3 mg/m<sup>3</sup> during conventional asphalt paving. All of the PBZ concentrations were well below the current NIOSH REL for asphalt fume of 5 mg/m<sup>3</sup> (measured as total particulate).

Seven of the nine workers with exposure to the asphalt paving operation (pavers) were included in a health assessment. Additionally, seven workers (five workers performing jobs associated with road construction at another construction site and two workers performing traffic control duties at the paving site) not typically exposed to hot asphalt fume (non-pavers) were included for comparison. Serial symptom questionnaires were administered to obtain information concerning the prevalence of acute symptoms (i.e., respiratory, eye, nose, throat, and skin symptoms) in relation to worksite exposures. Serial measurements of peak expiratory flow rate (PEFR) were conducted to evaluate acute changes in lung function in relation to worksite exposures. Among pavers the number of occurrences of reported health symptoms and the rate of symptoms per completed questionnaire were 100% higher during the CRM asphalt paving period than during the conventional asphalt paving. Also, the rate of symptoms per hour of estimated exposure to asphalt paving was about 60% higher among pavers during the CRM asphalt paving. Most notable was the increased reporting of eye, throat, and skin irritation during CRM asphalt paving. Acute irritant symptoms, including lower airway symptoms, were reported by a number of workers in association with work exposures, however, none of the reported symptoms were accompanied by significant bronchial lability. The PEFR results at this study site did not show an association between measurable bronchospastic responses and asphalt paving.

This study showed that asphalt fume emissions, as well as other exposure measurements, were below current NIOSH RELs or other relevant exposure limits for those substances with established occupational exposure criteria. With the exception of higher PAC measurements over the screed during the conventional asphalt paving period and higher benzothiazole measurements over the screed during the CRM asphalt paving period, no consistent differences in source exposures were observed between the CRM and conventional asphalt paving periods. Acute symptoms were reported by workers in association with asphalt paving exposures, with higher reporting of symptoms during the CRM asphalt paving period. Interpretation of the higher symptom rates associated with CRM asphalt paving, in view of the exposure results, is unclear. Data provided from this evaluation are based on a very small sample size and may reflect production and weather conditions specific to this site. Additional site evaluations may enable more definitive conclusions to be drawn.

**Keywords:** SIC 1611 (Highway and Street Construction), asphalt fume, bitumen, crumb rubber modifier, CRM, recycled tires, paving, interstate highways, polycyclic aromatic compounds, PACs, polynuclear aromatic hydrocarbons, PAH, total particulate, respirable particulate, benzene soluble particulate, volatile organic compounds, hydrocarbons, elemental carbon, eye irritation, respiratory irritation.

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# **PROCESS OVERVIEW**

There are three basic steps in constructing an asphalt pavement - manufacture of the hot mix asphalt (HMA), placement of the mix onto the ground, and compaction. The asphalt mix contains two primary ingredients, a binder which is typically an asphalt cement, and an aggregate which is usually a mixture of coarse and fine stones, gravel, sand, and other mineral fillers. The mix design establishes the proportions of the aggregate materials and sizes to the amount of asphalt cement to obtain the appropriate pavement properties (flexibility, drainage, durability, etc.).

The purpose of an HMA plant is to blend the aggregate and asphalt cement to produce a homogenous paving mixture at a hot temperature so that it can be easily applied and compacted. Asphalt cement is typically received from a refinery by tractor trailer tankers and is transferred into heated storage tanks. Aggregate of different materials and sizes is blended through a series of belt conveyors and a dryer (a heated drum mixer). Once the aggregate is sufficiently blended and dried, asphalt cement is applied so that a continuous thin film of cement covers the aggregate evenly. The finished HMA is then placed in a storage silo until it can be dispensed into trucks that haul the material to the paving site. At the paving site the following equipment is typically used:

P Tack truck: A vehicle which precedes the paver and applies a low viscosity asphalt ("tack" coat) to the roadway to improve adhesion prior to the HMA placement.

P **Paver**: A motorized vehicle which receives the HMA from the delivery trucks and distributes it on the road in the desired width and depth. The HMA may be directly transferred from the delivery truck to the paver by: (1) directly pouring HMA into a hopper located in the front of the paver; (2) dumping HMA in a line onto the road where it is picked up by a windrow conveyor and loaded into the paver hopper; or (3) conveying the mix with a material transfer vehicle.

P **Screed**: Located at the rear of the paver, the screed distributes the HMA onto the road to a preselected width and depth and grades the HMA mix to the appropriate slope as the paving vehicle moves forward.

P **Rollers**: Typically two or three roller vehicles follow the paver to compact the asphalt.

Paving crews normally consist of eight to ten workers. Job activities include a foreman who supervises the crew; a truck dumper (or "dumpman") who coordinates the arrival (and operates the hatches) of the bottom-dump trucks, a paver operator who drives the paver; one or two screed operators who control and monitor the depth and width of the HMA placement; one or two rakers who shovel excess HMA, fill in voids and prepare joints; laborers who perform miscellaneous tasks; roller operators who drive the rollers; and a tackman who applies the tackcoat. The paver operators and roller operators do not usually perform different jobs, while the screed operators, rakers, and laborers may perform a variety of tasks throughout the workday.

For purposes of this report, workers associated with the asphalt paving operation (i.e., workers with potential exposure to HMA fume) will be referred to as "pavers." This definition may include workers not specifically employed by the paving contractor (i.e., state highway inspectors) but who are associated with the paving operation and could be exposed to HMA fume during paving. Additionally, some workers who performed jobs associated with road construction, but not exposed to HMA fume (i.e., foremen, laborers, heavy equipment operators, and road surveyors), participated as a control group for the pavers and will be referred to as "nonpavers."

# SITE DESCRIPTION

On October 6 - 12, 1994, NIOSH investigators conducted a study in Sacramento and Davis, California, during asphalt pavement construction on Interstate 80 and US 99 by the Granite Construction Company. The same paving crew was evaluated throughout the survey and consisted of a foreman, a paver operator, a screed operator, two rakers, a laborer, two truck dumpers, two roller operators, and a tackman.

During this survey, both the conventional hot mix asphalt (hereafter referred to as "conventional asphalt") and crumb rubber modified hot mix asphalt (subsequently referred to as "CRM asphalt") were manufactured at the same plant from the same petroleum crude source. The conventional asphalt was placed on October 7 and 10 while the CRM asphalt was used on October 6 and 11. All of the paving occurred on traffic lanes or shoulders with the traffic diverted to adjacent lanes.

A summary of the paving activities and equipment used at the I-80 and US 99 sites is contained in Table 1. Both of the projects used AR 4000, type "G" asphalt cement binder manufactured by Conoco Oil. The conventional asphalt mix was a 1.9 centimeter (3/4") maximum, medium grade type "A" asphalt concrete; the CRM asphalt mix was a 1.3 centimeter  $(\frac{1}{2}")$  maximum, gap graded type "G" asphalt concrete. The granulated rubber was manufactured by the Baker Rubber Company. The rubber content of the CRM asphalt was approximately 20% by weight of the asphalt cement.

The HMA plant for this construction project was located approximately 45-60 minutes away from the I-80 paving site and approximately 20 to 30 minutes away from the US 99 site. During the conventional asphalt paving, the HMA was hauled to the paving site by 7 belly dump double trailer trucks (each trailer contained approximately 10 metric tons [13 short tons]); 18 of these trucks were used during the CRM asphalt paving on I-80.

The conventional asphalt was used to construct a superelevation grade correction whereas the CRM asphalt was used to construct the mainline traffic lanes and shoulders. Approximately 1,814 metric tons of conventional asphalt were applied on October 7 and 10, compared to 4,082 metric tons of CRM asphalt placed during October 6 and 11. The mean temperatures for the asphalt mix as it was applied was 138°C (280°F), 142°C (288°F), 143°C (289°F), and 142°C (287°F) for days 1 through 4. The depth of both the conventional asphalt and CRM asphalt overlays was approximately 61 millimeters; the width of the paving was typically about 3.7 meters (about 12 feet).

The bottom dump trailers placed the hot asphalt material onto the road in a windrow channel approximately 1.5 meters (5 ft.) wide and 0.6 meters (2 ft.) high. The paver, following behind the trucks, used a windrow conveyor to pick-up the asphalt from the road, load it into its hopper, and then placed the asphalt with a screed attachment.

# INDUSTRIAL HYGIENE EVALUATION DESIGN

Previous research efforts by NIOSH investigators and other researchers have attempted to characterize asphalt fume exposures among road paving workers. Asphalt fume exposures have typically been measured as total particulates and benzene soluble particulate fraction. Correspondingly, occupational exposure criteria for asphalt fume have been expressed in terms of total particulates and the benzene soluble fraction of the particulates. However, since neither of these exposure markers measure exposure to a distinct chemical component or even a distinct class of chemicals, it is difficult to relate them to possible health effects. For example, many organic compounds are soluble in benzene, and any dust may contribute to total particulate levels. In an effort to address this situation, new or modified sampling and analytical methods were developed and included in this study. For example, polycyclic aromatic compounds (PACs) which may be present in asphalt fume were measured using a new analytical method. Some of the PACs are believed to have irritative effects while other PACs are suspected to be carcinogenic. In addition to PACs, benzothiazole (a sulfur-containing compound present in rubber tires) along with other sulfurcontaining compounds (suspected to be present as a result of the addition of rubber to the asphalt or from high sulfur crude petroleum used for asphalt manufacturing) were also measured. Benzothiazole is of interest since it may be useful as a surrogate indicator for other CRM asphalt fume exposures while other sulfur-containing compounds may be associated with respiratory irritation. Samples were collected for selected organic compounds (toluene, benzene, and methyl isobutyl ketone) and total hydrocarbons (as Stoddard solvent). Elemental carbon was measured to determine if diesel exhaust could have contributed to the air contaminants measured at the paving site. The airborne particulate at the paving site was analyzed to determine the concentration of particles which were respirable. Air samples were collected for 28 different metals and minerals and direct-reading instruments were used to measure carbon monoxide, hydrogen sulfide, sulfur dioxide, and ozone. Bulk air samples of asphalt fume were collected at the asphalt cement storage tank located at the hot mix asphalt plant and submitted for mutagenicity testing.

## Weather Information

Meteorological conditions were recorded at regular intervals to allow comparison among survey days. The meteorological data included dry bulb and wet bulb temperatures (for subsequent calculation of relative humidity), wind speed and direction, and wet bulb globe temperature (WBGT). Wind speed and direction were measured with a Climatronics<sup>®</sup> cup anemometer equipped with a strip chart recorder. Environmental measurements were obtained at 15minute intervals using a Reuter Stokes RSS 214 Wibget<sup>®</sup> heat stress meter.

## **Process Information**

Process information and operational details were recorded daily by FHWA, State Department of Transportation (DOT), contractors, or NIOSH investigators. This information included the asphalt grade, type of application, crude source, percent rubber, additives, production quantities, application temperature, paving depth, average application rate, site description, and traffic density.

## **Area Air Samples**

To evaluate worst-case conditions and characterize the asphalt fume, area air samples were collected above the screed auger of the paving vehicle and adjacent to the paver hopper. Background area air samples were collected in the construction trailer yard and in the highway median to evaluate the ambient air and possible impact from vehicle emissions. Area samples were collected for total and respirable particulate, PACs, sulfur-containing compounds (including benzothiazole), benzene soluble particulate fraction (BSF), aromatic and aliphatic solvents (based on the qualitative identification of volatile organic compounds via mass spectroscopy), elemental and organic carbon, and elemental metals. Direct reading instruments were used to measure carbon monoxide, hydrogen sulfide, sulfur dioxide, and ozone.

Except for the samples obtained with direct-reading instruments, air samples were collected using calibrated battery-operated sampling pumps with the appropriate sorbent tube or filter media connected via Tygon<sup>®</sup> tubing. The area and personal breathingzone (PBZ) sample concentrations were calculated based on the actual monitoring time (time-weighted average [TWA-actual] concentrations) instead of calculating an 8-hour TWA concentration so that the sampling data could be compared between days that had unequal monitoring durations. Calibration of the air sampling pumps with the appropriate sampling media was performed daily, before and after each monitoring period. Field blanks were collected and submitted to the laboratory for each analytical method.

High volume air samples of the asphalt fume were collected above an open hatch on the asphalt cement storage tank at the HMA plant and are being evaluated at various concentrations for mutagenic activity via a modified Ames testing protocol. The basic analytical procedure has been described by Maron and Ames [1983], except a spiral plater device described by Houk et al. [1989, 1991] is used. The results from these modified Ames tests of asphalt fume will be discussed in a future NIOSH report.

# Personal Breathing-Zone Air Samples

Personal breathing-zone monitoring was conducted on nine members of the paving crew. Total particulate samples were collected on all workers. Air samples for PACs, sulfur-containing compounds (including benzothiazole), or for benzene soluble particulates, were also collected on some workers.

## **Air Sampling Methods**

Table 2 summarizes all of the air sampling methods used in this evaluation. Since sampling for PACs involved a new analytical technique, Appendix A is included to provide additional detail on this method. Appendix B is the draft NIOSH Sampling and Analytical Method No. 5040 for elemental carbon.

# MEDICAL EVALUATION DESIGN

On October 5, NIOSH investigators began recruiting workers to participate in the health assessment, which included a general health and occupational history questionnaire, serial acute symptom questionnaires, and serial peak expiratory flow rate (PEFR) testing. PEFR testing was conducted to evaluate acute changes in lung function. Peak flow refers to the amount of air in liters per minute that can be exhaled through the flow meter in one complete breath.

All nine pavers were asked to participate in the study. Seven pavers volunteered and were included in the health assessment. Additionally, seven workers (five workers performing jobs associated with road construction at another construction site and two workers performing traffic control duties at the paving site) not typically exposed to hot asphalt fume (non-pavers), were included in the health assessment for comparison purposes.

A general health questionnaire was privately administered once to each health assessment participant during the study. Each worker was asked about the presence of chronic respiratory, eye, nose, throat, and skin symptoms. Additionally, information concerning smoking history and work history was solicited.

Acute symptom questionnaires were periodically administered to all study participants during their work shift to determine if eye, nose, throat, skin, or respiratory symptoms (including cough, chest tightness, or wheezing) were associated with their job. Whenever possible, the acute symptom questionnaires were administered before and after each work shift and three times during the work shift, at approximately two-hour intervals during each survey day.

PEFR measurements were made using Wrights portable peak flow meters just prior to the administration of the acute symptom questionnaire. Three exhalations were recorded each time, and the highest of the three recordings was accepted as the PEFR determination. Participants were considered to have significant bronchial lability if the difference between the minimum and the maximum PEFR on at least one day exceeded 20% of that day's maximum PEFR.

# **EVALUATION CRITERIA**

To assess the hazards posed by workplace exposures, NIOSH investigators use a variety of environmental evaluation criteria. These criteria are exposure limits to which most workers may be exposed for a working lifetime without experiencing adverse health effects. However, because of the wide variation in individual susceptibility, some workers may experience occupational illness even if exposures are maintained below these limits. The evaluation criteria do not take into account individual sensitivity, preexisting medical conditions, medicines taken by the worker, possible interactions with other workplace agents, or environmental conditions.

The primary sources of evaluation criteria for the workplace are NIOSH criteria documents and recommended exposure limits (RELs) [NIOSH 1994], the Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) [OSHA 1993], and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs®) [ACGIH 1995]. These occupational health criteria are based on the available scientific information provided by industrial experience, animal or human experiments, or epidemiologic studies. It should be noted that RELs and TLVs are guidelines, whereas PELs are legally enforceable standards. The NIOSH RELs are primarily based upon the prevention of occupational disease without assessing the economic feasibility of the affected industries and, as such, tend to be conservative. The OSHA PELs are required to take into account the technical and economical feasibility of controlling exposures in various industries where the agents are present. A Court of Appeals decision vacated the OSHA 1989 Air Contaminants Standard in AFL-CIO v OSHA, 965F.2d 962 (11th cir., 1992); and OSHA is now enforcing the previous standards (listed as Transitional Limits in 29 CFR 1910.1000, Table Z-1-A), which were originally promulgated in 1971. However, some states with OSHA-approved state plans continue to enforce the more protective ("final rule") limits promulgated in 1989. For

exposures with evaluation criteria, NIOSH encourages employers to use the 1989 OSHA PEL or the NIOSH REL, whichever is lower.

Evaluation criteria for chemical substances are usually based on the average PBZ exposure to the airborne substance over an entire 8- to 10-hour workday, expressed as a time-weighted average (TWA). Personal exposures can be expressed in parts per million (ppm), milligrams per cubic meter  $(mg/m^3)$ , or micrograms per cubic meter ( $\mu g/m^3$ ). To supplement the TWA where adverse effects from short-term exposures are recognized, some substances have a short-term exposure limit (STEL) for 15-minute periods; or a ceiling limit, which is not to be exceeded at any time. Additionally, some chemicals have a "skin" notation to indicate that the substance may be appreciably absorbed through direct contact of the material or its vapor with the skin and mucous membranes.

It is important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these occupational health exposure criteria. A small percentage may experience adverse health effects because of individual susceptibility, preexisting medical conditions, previous exposures, or hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, or with medications or personal habits of the worker (such as smoking) to produce health effects even if the occupational exposures are controlled to the limit set by the evaluation criterion. These combined effects are often not considered by the chemical-specific evaluation criteria. Furthermore, many substances are appreciably absorbed by direct contact with the skin and thus potentially increase the overall exposure and biologic response beyond that expected from inhalation alone. Finally, evaluation criteria may change over time as new information on the toxic effects of an agent becomes available. Because of these reasons, it is prudent for an employer to maintain worker exposures well below established occupational health criteria.

## Asphalt Fumes (Petroleum)

Asphalt, produced from refining crude petroleum, is commercially valuable for pavement construction because of its adhesive properties, flexibility, durability, water and acid resistance, and its ability to form strong cohesive mixtures with mineral aggregates. Asphalt pavement is the major paving product in commercial use and accounts for 85% of the total asphalt usage (and over 90% of the roadway paving) in the United States [AI 1990]. About 4,000 HMA facilities and 7,000 paving contractors employ nearly 300,000 workers in the United States [AI 1990].

The specific chemical content of asphalt, a brown or black solid or viscous liquid at room temperature, is difficult to characterize because it is extremely complex and variable. In general, asphalt primarily contains high molecular weight cyclic hydrocarbon compounds as well as saturated organics. The chemical composition and physical properties of the asphalt products are influenced by the original crude petroleum and the manufacturing processes. The basic chemical components of asphalt include paraffinic, naphthenic, cyclic, and aromatic hydrocarbons as well as heteroatomic molecules containing sulfur, oxygen, and nitrogen [AI 1990].

Petroleum based asphalt and coal tar pitch are often considered to be equivalent materials because of their similar physical appearance and construction applications. However, these materials are quite different chemically as a result of raw material origin and manufacturing processes. Approximately 80% of the carbon in coal tar is associated with the aromatic ring structures, whereas less than 40% of the carbon in asphalt is present in aromatic rings [Puzinauskas 1978]. Furthermore, analysis by nuclear magnetic resonance indicated that an asphalt fume condensate was <1% aromatic and >99% aliphatic, whereas a coal tar pitch condensate was>90% aromatic [Niemeier et al. 1988]. Coal tar has a greater reported carcinogenic activity than asphalt and is considered an occupational carcinogen by NIOSH [1992] and ACGIH [1995].

In a 1977 criteria document, NIOSH established a REL of 5 mg/m<sup>3</sup> (as a 15-minute ceiling limit ) for asphalt fumes, measured as a total particulate. This level was intended to protect against acute effects, including irritation of the serous membranes of the conjunctivae and the mucous membranes of the respiratory tract [NIOSH 1977a]. Asphalt fumes can be absorbed through the lungs or the skin. Hansen [1991] and Maizlish et al. [1988] indicated that nonmalignant lung diseases such as bronchitis, emphysema, and asthma were also among the toxic effects of exposure to asphalt fumes. Norseth et al. [1991] reported that during road repair and construction, three groups of asphalt workers experienced abnormal fatigue, reduced appetite, eye irritation, and laryngeal/pharyngeal irritation.

Since publication of the criteria document [NIOSH 1977a], data have become available indicating that exposure to roofing asphalt fume condensates, raw roofing asphalt, and asphalt-based paints may pose a risk of cancer to workers occupationally exposed. In 1988, NIOSH recommended that asphalt fumes be considered a potential occupational carcinogen [NIOSH 1988]. This recommendation was based on information presented in the 1977 criteria document [NIOSH 1977a] and a study by Niemeier et al. [1988] showing that exposure to condensates of asphalt fumes caused skin tumors in mice. Several epidemiologic studies concerning workers exposed to asphalt fumes have indicated a potential excess in mortality from cancer [Hansen 1989a,b, 1991; Maizlish et al. 1988; Engholm et al. 1991; Wilson 1984; Bender et al. 1989; Mommsen et al. 1983; Risch et al. 1988; Bonassi et al. 1989].

Currently there is no OSHA PEL for asphalt fume. In 1992, OSHA published a proposed rule for asphalt fumes that included a PEL of 5 mg/m<sup>3</sup> (total particulate) for general industry as well as for the maritime, construction, and agricultural industries [OSHA 1992]. OSHA is presently reviewing public comments. The current ACGIH TLV® for asphalt fumes is 5 mg/m<sup>3</sup> as an 8-hour TWA [ACGIH 1995]. This TLV was recommended to "maintain good housekeeping conditions and reduce the risk of possible carcinogenicity" [ACGIH 1992]. Table 3 summarizes the toxicity and exposure criteria information for asphalt fume and the other contaminants evaluated during this study, including total particulate, respirable particulate, benzene soluble particulate fraction, PACs, elemental carbon, and selected organic solvents.

# INDUSTRIAL HYGIENE RESULTS

### Weather

A daily description of the weather is extremely important since the outdoor conditions directly impact the construction process and air sampling results. Table 4 summarizes the weather data recorded for each survey day. The weather on both the conventional and CRM asphalt paving days was cool. The high temperatures recorded for all 4 days ranged from 14°C to 18°C (58 to 64°F).

Wind speed and direction are particularly important factors that may influence the air sampling results. As shown in Table 4, the wind velocity and direction pattern differed each day. The strongest winds were observed October 6. For three of the four sampling days, the wind direction was variable throughout the workshift. Since many workers on the paving crew were located behind or near the rear of the paver, their potential for asphalt fume exposure increases with low or no wind conditions, or with low "headon" winds relative to the paver direction.

## **Process Information**

When reviewing these industrial hygiene results, it is important to note that main traffic lanes and shoulders were paved using CRM asphalt, whereas conventional asphalt was used for a smaller construction project to provide an elevation (grade) correction. This resulted in shorter work shift durations and lower production quantities for the conventional asphalt projects.

## Area Air Samples

# Total Particulate and Respirable Particulate

Tables 5 and 6 provide the results for the total and respirable particulate concentrations, respectively. Most of the total particulate concentrations were well below 5 mg/m<sup>3</sup>. Total particulate concentrations at emission locations ranged from 1.3 to 6.2 mg/m<sup>3</sup> and from 1.4 to 4.1 mg/m<sup>3</sup>, for conventional and CRM asphalt paving, respectively. The highest total particulate concentrations for both asphalt mixes were observed near the paver hopper. The total particulate *background* concentrations measured during this survey ranged from ND to 0.19 mg/m<sup>3</sup>; all but one of these background samples were  $\leq .0.09$  mg/m<sup>3</sup>.

The highest respirable particulate concentration  $(3.1 \text{ mg/m}^3)$  was obtained over the screed during conventional asphalt paving. All of the remaining respirable particulate concentrations collected near asphalt fume emission areas ranged from 0.48 to 1.0 mg/m<sup>3</sup>. All of the background respirable particulate concentrations were either non-detectable or <0.08 mg/m<sup>3</sup>.

### Benzene Soluble Particulate Fraction

As summarized in Table 7, the highest BSF concentrations (regardless of the hot mix asphalt composition) were measured adjacent to the hopper. Benzene soluble particulate concentrations at emission locations ranged from 1.1 to 4.7 mg/m<sup>3</sup> during conventional paving and from 1.4 to 2.0 mg/m<sup>3</sup> during CRM asphalt paving. Overall, the highest BSF concentrations were measured on October 10, during conventional asphalt paving. Presently, there are no occupational exposure criteria for the benzene soluble particulate fraction of asphalt fume from NIOSH or OSHA.

#### Polycyclic Aromatic Compounds (PACs), Sulfur-containing Compounds, and Benzothiazole

A number of asphalt fume source samples from this study were analyzed by high pressure liquid chromatography (HPLC). The chromatograms obtained from these samples demonstrated the typical pattern associated with asphalt fume which prevented quantitation of individual PAHs. Hence, NIOSH method 5506 was modified to quantitate total PACs, as a class, via a flow injection technique with spectrofluorometric detection using emission wavelengths of 370 and 400 nanometers (nm). The 370 nm emission wavelength provides greater sensitivity to 2-3 ring PACs and the 400 nm wavelength is more sensitive to 4-7 ring PACs.

Table 8 summarizes the total PAC area concentrations collected at emission and background locations. The concentration for the total  $PAC_{370}$  at emission sources ranged from 29 to 264 micrograms per cubic meter ( $\mu g/m^3$ ) for conventional and from 45 to 117  $\mu$ g/m<sup>3</sup> for CRM asphalts. The total PAC<sub>400</sub> concentrations from these same samples ranged from 19 to 62 and from 10 to 21  $\mu$ g/m<sup>3</sup>, respectively, for conventional and CRM asphalt paving. In every sample except for one, the  $PAC_{370}$  concentrations were greater than the  $PAC_{400}$  concentration implying that the 2-3 ring PACs may be more abundant. The smaller ring number PACs are believed to be associated with more irritative effects, whereas more concern exists for suspect carcinogenicity of the 4-7 ring PACs. Occupational exposure criteria for total PACs, as a class, are presently unavailable from either NIOSH, OSHA, or ACGIH.

Table 8 also presents the sulfur compounds and benzothiazole concentrations obtained from hexane extracts of PAC samples which were analyzed by gas chromatography with sulfur chemiluminescence detection. Benzothiazole, an additive used in tire manufacturing, was detected on conventional asphalt projects at concentrations which ranged from 3.1 to 21  $\mu$ g/m<sup>3</sup>. Benzothiazole concentrations during CRM asphalt paving ranged from 2.3 to 121  $\mu$ g/m<sup>3</sup>.

The background benzothiazole levels ranged from ND to  $24 \ \mu g/m^3$ ; every benzothiazole concentration detected at emission locations during conventional asphalt paving was less than the highest background sample. Based on this information, the CRM asphalt formulation appears to be more important for generating benzothiazole.

The highest concentration of sulfur compounds  $(784 \ \mu g/m^3)$  was measured near the paver hopper during conventional asphalt paving. The highest concentrations detected for sulfur compounds at the screed for conventional and CRM asphalt days were 93 and 178  $\mu g/m^3$ , respectively. The sulfur compounds levels varied widely between area locations and asphalt types.

### Elemental and Organic Carbon

Elemental and organic carbon analytical results are provided in Table 9. In general, a high elemental carbon (EC) to total carbon (TC) ratio and EC concentrations above background levels suggest that diesel engine exhaust may be contributing to other exposure measurements made in this study (such as the PAC results). All of the EC concentrations collected on the paver vehicle were above the background concentrations, suggesting that some diesel exhaust was present. The EC:TC ratio ranged from 0.01 to 0.03 near the hopper (which is adjacent to the paver engine) and from 0.04 to 0.06 above the screed. Since diesel exhaust has been reported to contain EC levels between 0.6 to 0.8 of the TC [Blade 1989], these ratios imply that diesel exhaust was not excessively contributing to these air sampling results.

# *Volatile Organic Compounds (VOCs) and Elements*

Table 10 summarizes the predominant VOC concentrations detected during both the conventional asphalt and CRM asphalt paving periods. The qualitative GC/MS analysis identified over 50 VOCs. However, only the most significant peaks (benzene, toluene, xylene, methyl isobutyl ketone

[MIBK], and total hydrocarbons) were quantitatively analyzed by GC/FID. The quantities of VOCs (except benzene) detected at emission sources were orders of magnitudes below their respective occupational exposure criteria published by NIOSH, OSHA, or ACGIH.

Benzene was detected at the hopper as high as 0.24 ppm and 0.11 ppm on conventional and CRM asphalt days, respectively. Although these samples were collected at the source of emission and employees are not at these locations for long durations, this does suggest that the potential exists for employee exposure to benzene. NIOSH regards benzene as an occupational carcinogen and recommends that exposure be reduced to the lowest feasible level. The OSHA PEL for benzene is an 8-hour TWA of 1 ppm.

Extremely low or trace concentrations were observed for aluminum, calcium, iron, magnesium, manganese, and titanium. All other elemental metals were not detected.

### Hydrogen Sulfide ( $H_2$ S), Sulfur Dioxide (SO<sub>2</sub>), Carbon Monoxide (CO), and Ozone

Hydrogen sulfide,  $SO_2$ , and  $O_3$  were screened using direct reading instrumentation. All of these compounds were present in very low concentrations and were well below their respective occupational exposure criteria. Hydrogen sulfide concentrations were not detected and  $SO_2$  concentrations near the screed were usually ND (with a few readings of 2 ppm). Background  $O_3$  concentrations were typically 0.01 ppm.

On October 7, short-term instantaneous carbon monoxide concentrations were detected as high as 1000 ppm in the middle of the paver deck and as high as 300 ppm near the operator's seat. The use of two gasoline powered electric generators for providing light on the paver was the source of the excessive CO concentrations due to wind conditions and the generators orientations. The NIOSH REL for carbon monoxide is an 8-hour TWA of 35 ppm with a ceiling limit of 200 ppm, never to be exceeded, even momentarily. After the generators were repositioned to aim the exhaust off of the paver, the CO levels were reduced substantially.

# Personal Breathing Zone Air Samples

Table 11 presents the PBZ monitoring results for total particulate collected during conventional and CRM paving operations. All of the PBZ exposures were well below the criteria of 5 mg/m<sup>3</sup> currently The TWA-actual PBZ proposed by NIOSH. exposure to total particulate ranged from 0.09 to 1.3 mg/m<sup>3</sup> and from 0.11 to 0.71 mg/m<sup>3</sup> during conventional and CRM asphalt paving, respectively. Total particulate PBZ exposure of the truck dumper, paver operator, and screed operator (jobs in close proximity to asphalt fume emissions) ranged from 0.28 to 1.3 mg/m<sup>3</sup> on conventional asphalt days and from 0.11 to 0.71 mg/m<sup>3</sup> on CRM asphalt paving days. Although the conventional asphalt exposures were slightly higher than the CRM asphalt exposures, a conclusion regarding this difference cannot be determined due to the limited number of PBZ samples.

Table 12 contains the PBZ results for PACs, benzothiazole, and sulfur compounds for six different jobs. Excluding the roller operators' and laborers' samples, the PBZ concentrations of PAC<sub>370</sub> and PAC<sub>400</sub> ranged from 8.4 to 24  $\mu$ g/m<sup>3</sup> and from 1.3 to 4.9  $\mu$ g/m<sup>3</sup>, respectively. The PBZ exposures to benzothiazole ranged from ND - 68  $\mu$ g/m<sup>3</sup>, while exposures to sulfur compounds ranged from ND - 14  $\mu$ g/m<sup>3</sup>. Most of these samples were collected during the CRM asphalt paving on a day when the concurrent biomonitoring study was not being conducted.

Two PBZ samples were collected on rakers for BSF particulate during this survey. Benzene soluble particulate was detected from only one of these samples, at a concentration equal to 0.23 mg/m<sup>3</sup>.

# **MEDICAL RESULTS**

The seven pavers in the health assessment included one paver operator, one screed operator, one roller operator, two rakers, one dumpman, and one paving foreman. The crew foreman also performed work on the paver on occasion. The paving crew worked night-shifts, from about 7:00 p.m. to 7:00 a.m., during the survey period. Five of the pavers participated in the study for all four days, the roller operator left the study after three days, and the foreman was absent on the second day. The seven non-pavers in the health assessment included one crew supervisor, two traffic controllers, one heavy equipment operator, one engineer, one water truck driver, and one road surveyor. Five of the nonpavers worked at a different work site from the pavers, and worked day-time hours (6:30 a.m. - 3:00 p.m.). The two traffic controllers, included in the non-paver group, worked at the same work site and time as the pavers but typically were not exposed to hot asphalt fume. Six of the non-pavers participated in the study for all four days; one traffic controller was absent on the second day.

All of the pavers were male, and the average age of this group was 43 years (range 33-55 years). Six of the seven non-pavers were male, and the average age of this group was 37 years (range 24-56 years). None of the pavers currently smoked cigarettes (two never smoked, and five were former smokers). Two of the non-pavers currently smoked cigarettes (both smoked during work), two were former smokers, and three never smoked.

The number of acute symptom questionnaires completed (i.e., the number of opportunities a worker had to report a health symptom) varied somewhat between survey days and among the pavers and nonpavers (Table 13). For each survey day, a maximum of 35 (seven workers times five questionnaires/day) questionnaires could have been completed for each group (pavers and non-pavers). Both the pavers and non-pavers completed about 8% more acute symptom questionnaires during the first and fourth study days (the CRM asphalt paving period), as compared to the second and third study days (the conventional asphalt paving period).

Responses to the acute health questionnaires were evaluated for symptoms potentially associated with worker tasks and exposures. A worker could report seven different types of symptoms during each survey time (including eye, nose, throat, and skin irritation, cough, shortness of breath, and wheezing); each such symptom report will be referred to as a "symptom occurrence." Thus, if a worker completed all five daily acute health questionnaires and reported all seven symptoms during each survey, he/she would have 35 symptom occurrences for that survey day.

Table 14 shows the number of workers reporting a health symptom at any time during a survey day. Also shown are the number of symptom occurrences reported during the survey day. Among non-pavers, the number of reported symptom occurrences was similar between the conventional paving period (13 symptom occurrences) and the CRM asphalt paving period (15 symptom occurrences). The number of reported symptom occurrences among pavers, however, was approximately twice as high during the CRM paving period (52 symptom occurrences) compared to the conventional paving period (24 symptom occurrences). Eighty-nine percent (68/76)of the symptoms reported by pavers were during ongoing or recent exposure to the asphalt paving Ninety-two percent (70/76) of the operation. symptoms reported by the pavers were rated as "mild" in severity (the choices were "mild," "moderate," or "severe").

During the CRM paving period the number of symptom occurrences among non-pavers of eye and nose irritation was higher, throat irritation was lower, and other symptoms did not appreciably change. Among pavers, the number of symptom occurrences of eye, throat, and, skin irritation and shortness of breath, were higher during the CRM asphalt paving period, with no appreciable change in other symptoms. Among pavers, the most frequently reported symptoms (as a percentage of occurrences over all four days) were throat irritation (33%), eye irritation (25%), and nasal irritation (22%).

Because of differences in the number of completed questionnaires, the number of symptom occurrences may not be the best measure for comparing health effects between conventional and CRM asphalt paving exposures. A more appropriate measure is the rate of symptom occurrences per completed questionnaire (defined as the number of symptom occurrences divided by the number of completed questionnaires). The rates of reported symptom occurrences among pavers by survey day and by period of exposure are presented in Table 15. The symptom reporting rate was about 100% higher during the CRM paving period (0.81 symptoms per completed questionnaire) as compared to the conventional paving period (0.41 symptoms per completed questionnaire).

The number of hours the road crew performed paving operations, and thus, were potentially exposed to asphalt fumes, varied between survey days and across jobs. Each paver estimated his or her own exposure time to the paving operation (typically in 15-minute increments) and this information was collected with each acute symptom questionnaire. Table 16 shows each pavers' estimated exposure time to asphalt paving for each The average estimated hours of survey day. exposure to asphalt paving noticeably increased over the survey period. Workers had a combined average of 6.0 hours of exposure/day to the paving operation during the conventional paving period, compared to a combined average exposure of 8.2 hours/day during the CRM asphalt paving period. All five offsite non-pavers denied any exposure to asphalt paving throughout the survey period. The two onsite non-pavers (traffic controllers) reported 0.5 hours and 1.75 hours, respectively, of exposure to asphalt fume during the entire survey period. These workers did not report any symptom occurrences associated with their asphalt paving exposures.

The *rate* of reported symptom occurrences per hour of estimated exposure to asphalt fume (defined as the *number of symptom occurrences* divided by the *number of hours of estimated exposure*) was calculated for the pavers for each survey day (Table 17). The rate of symptom occurrences per hour of exposure was approximately 60% higher during the CRM paving period (0.49 symptom occurrences per hour of exposure), as compared to the conventional paving period (0.31 symptom occurrences per hour of exposure).

Study participants occasionally reported cough and shortness of breath during the survey period. However, the PEFR measurements did not reveal any workers with significant bronchial lability (i.e., difference between a day's minimum and maximum PEFR exceeding 20% of the day's maximum PEFR) on any survey day.

# DISCUSSION

## Weather

The weather, especially wind conditions, could affect air sampling measurements obtained outdoors during this construction project. Based on observations of the paver and the movement of the asphalt plume, it appears that the wind could impact the area air samples collected near the paver hopper more than those collected above the screed auger. (The paver hopper was more open and emissions were more prone to effects from wind speed and direction than at the more enclosed screed auger area). Therefore, the screed sample results may be more useful than the hopper sample results for comparison between conventional and CRM asphalt paving.

## **Process Information**

The most significant difference between conventional and CRM asphalt paving construction projects during this survey was the scope of each project. For example, paving main traffic lanes and shoulders on I-80 with CRM asphalt involved greater quantities of asphalt and longer work shifts than the conventional asphalt project on US 99. Because of the greater HMA quantities and the farther distance from the hot mix plant to the I-80 site, eighteen bottom dump trucks were dispatched to haul the material to the CRM project, compared to seven trucks for transporting the conventional asphalt to the US 99 location. Furthermore, the CRM asphalt project used an additional truck dumpman to unloaded many of the HMA deliveries well ahead of the paver vehicle; the conventional asphalt project needed only one truck dumpman who worked very near the paver. This caused much of the CRM asphalt to be present on the roadway for longer durations before it was loaded into the paver which could alter the fume emission.

## **Air Sampling**

The current occupational criterion for asphalt fume is  $5 \text{ mg/m}^3$ , measured as total particulate. All of the PBZ and all but one of the area samples collected adjacent to emission sources were below this However, exposure criteria are concentration. presently unavailable for several groups of compounds (such as total PACs, sulfur compounds, and benzothiazole) which are present in asphalt fume. Concentrations of other compounds that were detected above the screed (i.e, toluene, xylene, MIBK, petroleum distillates, etc.) were also well below any existing occupational exposure criteria. Benzene was detected in area samples collected near the hopper and screed; NIOSH considers benzene to be an occupational carcinogen and recommends that exposure be reduced to the lowest feasible level.

Jobs that cause the worker to be in closer proximity to HMA for prolonged durations (and thus have greater exposure to asphalt fume) were also jobs that were less likely involved in activities that generated dust. In this regard, the truck dumpman, paver and screed operators' PBZ exposure probably represents the highest asphalt fume exposure among workers on the paving crew. The total particulate PBZ exposure of these workers showed a similar pattern as the area screed samples; PBZ exposure during the conventional asphalt paving period was slightly higher than the CRM asphalt paving period (0.3 to 1.3 mg/m<sup>3</sup> versus 0.1 to 0.7 mg/m<sup>3</sup>, respectively).

Table 18 contains the results from the area air

samples, arranged by location. Although there were many inconsistent factors that could affect results, the following descriptive observations are presented:

P The highest total particulate, respirable particulate, and BSF concentrations were lower during CRM asphalt paving, despite the higher production quantities.

P Two detector emission wavelengths were used to provide greater sensitivity either to 2-3 ring PACs (370 nanometers [nm]) or to 4+ ring PACs (400 nm). Greater PAC concentrations were detected using the 370 nm wavelength, implying that the 2-3 ring PACs may be more abundant.

P Total PAC concentrations above the screed were slightly lower on CRM asphalt paving days than on conventional paving days. Furthermore, the CRM asphalt paving appeared to generate more benzothiazole than the conventional paving.

## Medical

The results of the acute symptom survey revealed that the number of reported health symptoms and rate of symptom occurrences per completed questionnaire was approximately 100% higher during the CRM asphalt paving period as compared to the conventional asphalt paving period. Also, the rate of symptom occurrences per average hour of asphalt paving exposure was approximately 60% higher during the CRM asphalt paving period as compared to the conventional asphalt paving period. The observed increase in symptom occurrences was primarily due to increased reporting of mild eye, throat, and skin irritation during the CRM asphalt paving period. Additionally, one of the pavers reported experiencing increased symptoms of shortness of breath during the CRM asphalt paving period.

Evaluation of acute symptoms in combination with peak flow testing was performed to determine whether acute irritant effects of the airways (as measured by symptom reporting) were associated with intermittent or reversible bronchospastic responses. While acute irritant symptoms, including lower airway symptoms, were reported by a number of workers in association with work site exposures, none of the reported symptoms were accompanied by significant bronchial lability. The inability to detect an association, if truly present, between reported symptoms or exposures and PEFR results at this study site may be due to the small number of workers tested and/or variability between worker exposures and individual responses to those exposures. Also, the two-hour PEFR testing interval may not be of sufficient frequency to detect intermittently occurring transient bronchospastic effects.

# CONCLUSIONS

Results presented here only apply to this survey and cannot be generalized to indicate the exposures or health effects associated with CRM asphalt paving. This study showed that asphalt fume emissions, as well as other exposures, were below current NIOSH RELs or other relevant exposure limits (for those substances with established occupational exposure criteria). The industrial hygiene data suggest that there were no consistent differences in source exposures between the CRM and conventional asphalt paving periods, with the possible exception of the PAC measurements (higher over the screed during the conventional asphalt paving period) and benzothiazole measurements (higher over the screed during the CRM asphalt paving period). Acute symptoms were reported by workers in association with asphalt paving exposures, with higher reporting of symptoms during the CRM asphalt paying period. Interpretation of the higher symptom rates associated with CRM asphalt paving, in view of the exposure Data provided from this results, is unclear. evaluation are based on a very small sample size and may reflect production and weather conditions specific to this site. Additional site evaluations may increase our ability to understand and interpret observations made at this site and should lead to more definitive conclusions.

## RECOMMENDATIONS

The following recommendations are based on observations made during the survey and are intended to help ensure the safety and health of paving crew workers. These recommendations stem from our present understanding of the workers' occupational exposures and potential health effects associated with these exposures.

1. To minimize asphalt fume generation, the hot mix should be applied at the lowest temperature possible that can maintain quality control specifications.

2. To avoid contamination and possible ingestion of potentially harmful substances, workers should be prohibited from consuming food and beverages and from using tobacco products in close proximity to asphalt fume emissions.

3. Workers should be provided with adequate washing facilities for use prior to eating and leaving the work site.

4. To reduce potential contamination of workers' cars and homes, workers should be encouraged to change clothing prior to leaving the work site and should be provided with adequate facilities for changing.

5. All workers should wear protective clothing or appropriate sunscreen to shield exposed skin surfaces from the harmful ultraviolet component of sunlight.

6. Over the course of this survey workers were observed performing a number of job tasks which could potentially lead to musculoskeletal injury. Employees performing manual lifting and shoveling should be taught appropriate lifting techniques and be provided with the appropriate equipment to minimize musculoskeletal strain.

# **ABBREVIATIONS AND TERMS**

ACGIH	American Conference of Governmental Industrial Hygienists			
BSF	Benzene soluble (particulate) fraction	]		
С	Ceiling, an exposure that shall not be exceeded during any part of the workday	I		
CFR	Code of Federal Regulations	I		
cm <sup>2</sup>	Square centimeters			
CO	Carbon monoxide	I		
Control	A person working in road construction but not exposed to hot asphalt fume.	ז ו		
CRM	Crumb rubber modifier			
DOT	Department of Transportation			
EC	Elemental carbon			
EPA	Environmental Protection Agency	I		
FHWA	Federal Highway Administration	I		
FID	Flame ionization detector	1		
GC-MS	Gas chromatography-Mass Spectrometry	I		
$H_2S$	Hydrogen sulfide	1		
HHE	Health hazard evaluation			
HMA	Hot mix asphalt			
IARC	International Agency for Research on Cancer	1		
ICP-AES	Inductively coupled (argon) plasma- atomic emission spectroscopy	1		

IH	Industrial hygiene		
ISTEA	Intermodal Surface Transportation Efficiency Act		
LC	Liquid chromatography		
LOD	Limit of detection (analytical method)		
LOQ	Limit of quantitation (analytical method)		
Lpm	Liters per minute		
MCE	Mixed cellulose-ester filter		
MDC	Minimum <i>detectable</i> concentration (the smallest amount of a material which can be reliably detected). The MDC is calculated by dividing the analytical LOD by a representative air volume.		
mg	Milligrams		
mg mg/m <sup>3</sup>	Milligrams Milligrams per cubic meter of air		
-	-		
mg/m <sup>3</sup>	Milligrams per cubic meter of air		
mg/m <sup>3</sup> MIBK	Milligrams per cubic meter of air Methyl isobutyl ketone		
mg/m <sup>3</sup> MIBK mL	Milligrams per cubic meter of air Methyl isobutyl ketone Milliliter		
mg/m <sup>3</sup> MIBK mL mm	Milligrams per cubic meter of air Methyl isobutyl ketone Milliliter Millimeter Minimum <i>quantifiable</i> concentration (the smallest amount of a material which can be reliably measured). The MQC is calculated by dividing the analytical LOQ by a representative air		

nm	Nanometer		
OC	Organic carbon		
OSHA	U.S. Occupational Safety and Health Administration		
PAC <sub>370</sub>	PACs monitored at an emission wavelength of 370 nanometers (representative of 2-ring and 3-ring compounds)		
PAC <sub>400</sub>	PACs monitored at an emission wavelength of 400 nanometers (representative of 4-ring and higher compounds)		
PACs	Polycyclic aromatic compounds		
PAHs	Polynuclear aromatic hydrocarbons		
PBZ	Personal breathing-zone air sample		
PEFR	Peak expiratory flow rate		
PEL	Permissible exposure limit (OSHA)		
ppm	Parts (of a contaminant) per million parts of air		
REL	Recommended exposure limit (NIOSH exposure criteria)		
RP	Respirable particulate		
SCLD	Sulfur chemiluminescent detector		
Screed	During road paving, the screed levels the hot-mix asphalt to the desired thickness and slope as the paving vehicle moves forward		
$SO_2$	Sulfur dioxide		
STEL	Short-term exposure limit		
TC	Total carbon (elemental + organic)		

TLV®	Threshold limit value (ACGIH exposure criteria)
TWA	Time-weighted average
VOCs	Volatile organic compounds
WBGT	Wet bulb globe temperature
°C &°F	Degrees Celsius and Degrees Fahrenheit
μg	Microgram (10 <sup>-6</sup> ), a unit of weight
$\mu g/m^3$	Micrograms of contaminant per cubic meter of air (a unit of concentration)

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# **APPENDIX A**

#### MODIFIED ANALYTICAL METHOD FOR POLYCYCLIC AROMATIC COMPOUNDS

Historically, attempts to characterize asphalt fume have focused on the analysis of 16 standard unsubstituted polynuclear aromatic hydrocarbons (parent PAHs). This approach has been successful in most of the other matrices where PAH exposure occurs; however, asphalt fume is composed of a multitude of aliphatic and alkylated PAC compounds that is so complex that the mixture cannot be separated into discrete compounds. The analytical results obtained from analyzing asphalt fume samples by simply monitoring the 16 parent PAHs typically does not yield useful information regarding worker exposure.

Individual PACs typically are not quantifiable from asphalt fume if the current NIOSH liquid chromatography (LC) and gas chromatography (GC) methods (NIOSH methods 5506 and 5515) for PACs are used. This is due to the enormous number of substituted PACs in asphalt fume that are present in minute quantities which create signal interference from compounds that chromatographically co-elute at the same retention time. This has been previously shown in conventional asphalt fume studies when only the standard 16 unsubstituted PACs were evaluated.

Furthermore, the current method for detecting PACs does not evaluate the asphalt fumes for the compounds believed to be the most likely human health hazards. The health hazards associated with asphalt fume exposure are usually attributed to polycyclic aromatic compounds (PACs) that contain three to seven annulated rings with side chains of one to two carbons in length (with a maximum of four saturated carbons), or to PACs containing nitrogen, oxygen, and sulfur. For these reasons, a new method has been developed to separate the asphalt fume samples into aliphatic, aromatic, and polar fractions.

Since the published NIOSH methods do not account for all of these different compound types, the current methods were modified to provide a better indication of the total PAC content of the asphalt fumes. A new liquid chromatographic method was developed to give a better indication of the total PAC content in asphalt fume. This was achieved by adapting existing methods, reported in the literature, to initially remove the saturated compounds and the highly polar organic compounds. The remaining PACs can then be analyzed by LC with fluorescence detection. This modification should not only allow for the detection of the standard 16 PACs, that are usually analyzed, but should also allow measurement of the total PAC content present in each sample (i.e. sum of the peak areas). The total PAC content in the sample can then be compared to a PAH reference standard mixture to determine which fume samples have the most PACs. The total PAC content of the crumb rubber modified (CRM) asphalt fume can be compared to the total PAC content of the conventional asphalt collected from each sample location.

A commercially available standard mixture of 16 PACs was used in a recovery study to show that these compounds are not lost during sample preparation and that the remaining materials can be analyzed. Asphalt fume collected from an earlier pilot investigation has been used to test the possible methods. The sample preparation used solid phase extraction columns and solvent extraction steps. The material remaining after the sample preparation (PACs) was analyzed by means of a reversed-phase high performance liquid chromatographic column with fluorescence detection. After this study was successfully accomplished, the asphalt fume samples collected from paving construction sites were analyzed.

The air sampling collection methods for PACs are very similar to those published in NIOSH method 5506, Polynuclear Aromatic Hydrocarbons. The sampling train consisted of 37-mm,  $2 \mu m$  pore size, Teflon® filter to

collect particulate PACs, connected in series with an ORBO 43 sorbent tube to collect volatile or semi-volatile PACs. Air was sampled at a pump flow rate of 2 liters per minute (lpm). Opaque filter cassettes and sorbent tube holders were used to prevent the degradation of PACs by ultraviolet light.

After collection, the asphalt fume sample was extracted from the sampling filter with hexane. The hexane extract was then eluted through a cyano solid phase extraction column. The polar material will be retained on the column, and the aliphatic and the aromatic compounds will elute with hexane. Dimethyl sulfoxide (DMSO) is added to the hexane solution; the aromatic compounds will partition into the DMSO layer while the aliphatics will remain in the hexane layer. Next, the polar compounds are eluted from the column with methanol. The aromatic compounds in the DMSO fraction are analyzed by means of reversed-phase liquid chromatography with fluorescence detection. Since the excitation and emission wavelengths are not the same for all PACs, two sets of excitation and emission wavelengths is more sensitive for the 2-ring and 3-ring compounds (254 nm excitation, 370 nm emission), and the other set of wavelengths is more sensitive for the 4-ring and higher compounds (254 nm excitation, 400 nm emission). Finally, the total fluorescent response was normalized with a commercially available standard of 16 unsubstituted PAHs.

This methodology was applied to a representative number of CRM and conventional asphalt samples that were obtained from emission locations. The results obtained from this procedure confirmed that the chromatograms were due to widespread signal responses, elapsing over 20 minutes of column retention time indicative of coelution interference. Upon completion of the chromatography, the samples were analyzed with a flow injection (FI) technique where the LC column was bypassed; an aliquot of the DMSO/asphalt fume extract was injected directly into the fluorescence detection system. The advantage of this modification is that it is a much quicker procedure and the signal response is a single, reproducible peak due to all PAC compounds that fluoresce at the selected wavelength producing a more sensitive and precise signal. The total fluorescent response was also normalized with the same commercially available standard of 16 unsubstituted PAHs that was used in the chromatography methods.

Furthermore, an investigation of the compounds that contain sulfur was conducted. If a significant difference exists between conventional and CRM asphalt, it may be evident in the number and type of sulfur compounds in each asphalt formulation because of the vulcanizing process used during rubber tire production. Preliminary analyses by GC/MS have indicated that the CRM asphalt does contain more sulfur-containing compounds than the conventional asphalt mix. Additionally, higher levels of benzothiazole was present in the CRM asphalt samples. To exploit this potential difference in the asphalt compounds, a sulfur chemiluminescent detector (SCLD) was used in conjunction with a gas chromatograph (GC). This detector is sulfur specific and enables the analysis of sulfur in the low picogram range. The GC/SCLD system was used to analyze hexane extracted sample aliquots prepared from each asphalt fume sample.

## **APPENDIX B**

#### ELEMENTAL CARBON (DIESEL EXHAUST)

ELEMENTAL CARBON	(DIESEL EXH	AUST) 504	0
C MW: 12.01 CA	S: none	RTECS: none	
METHOD: 5040, Issue 1 EVALUATION	N: PARTIAL	Issue 1: 15 March 1996	
OSHA : NIOSH: see APPENDIX A ACGIH:	PROPERTIES:	nonvolatile solid; MP >350 °C	
SYNONYMS (related terms): soot, black carbon, diesel emissions,	diesel exhaust particle	es, diesel particulate matter	
SAMPLING		MEASUREMENT	
SAMPLER: FILTER (quartz fiber, 37-mm; size-selective impactor may be required, see INTERFERENCES)	TECHNIQUE: ANALYTE: elem	EVOLVED GAS ANALYSIS (EGA) by therm optical analyzer ental carbon (EC)	nal-
FLOW RATE:         1 to 4 L/min           VOL-MIN:         106 L @ 40 μg/m³           -MAX:         4300 L (for filter load ~ 20 μg/cm²)	FILTER PUNCH SIZE: CALIBRATION:	1.54 cm <sup>2</sup> methane injection [1]	
SHIPMENT: routine	RANGE:	0.76 to 54 $\mu$ g per filter portion	
SAMPLE         STABILITY:       stable         BLANKS:       2 to 10 field blanks per set	ESTIMATED LOD: PRECISION (\$,):	0.2 μg per filter portion 0.10 @ 1 μg C, 0.01 @ 10 - 72 μg C	
ACCURACY			
RANGE STUDIED: 4.0 mg/m <sup>3</sup> (60-L sample) [1]			
BIAS: none [1]			
OVERALL PRECISION (Ŝ <sub>rt</sub> ): see EVALUATION OF METHOD			
ACCURACY: see EVALUATION OF METHOD			
<b>APPLICABILITY:</b> The working range is 4.4 to 312 $\mu$ g/m <sup>3</sup> with an L a 1.54 cm <sup>2</sup> punch from the sample filter. If a lower LOD is desired			

sample on 25-mm filter gives an LOD of 0.3 µg/m³) [1]. The split between organic-based carbon (OC) and EC may be affected at higher EC loadings (e.g., >30 µg/cm<sup>2</sup> of filter), depending on type and amount of OC present. If pyrolysis correction is not required, an upper limit of ~800 µg/m³ (90 µg/cm²) can be determined, but post-analysis designation of OC-EC split may be necessary [1].

INTERFERENCES: As defined by the thermal-optical method, EC is the carbon determined during the second stage of the analysis (after pyrolytic correction). If the sample contains no pyrolyzable material, all the carbon evolved during this stage is considered elemental. Carbonate and cigarette smoke do not interfere. Various EC sources (diesel engines, carbon black, coal dust, and humic acid) may be present [1]. For measurement of diesel-source EC in coal mines, an impactor with submicrometer cutpoint [2,3] must be used to minimize collection of coal dust.

OTHER METHODS: Other methods for determination of EC and OC are described in the literature [4].

#### **REAGENTS:**

- 1. Aqueous organic carbon solutions (e.g., sucrose), 0.10 to 2.4 mg C per mL solution.
- 2. Helium, prepurified.
- 3. Hydrogen, purified.
- 4. Oxygen (10%) in helium, premixed, purified.
- 5. Methane (5%) in helium, premixed, purified.

#### EQUIPMENT:

- Sampler: Quartz fiber filter, precleaned (clean in low temperature asher 2 to 3 h, or muffle furnace at ~ 800 °C), 37-mm, in a 3-piece, 37-mm cassette with support pad (stainless steel or cellulose).
- 2. Personal sampling pump, 1 to 4 L/min, with flexible tubing.
- 3. Thermal-optical analyzer, or other analyzer capable of EC speciation (see APPENDIX B).
- 4. Punch (e.g., cork borer) for removal of filter sample portion.

NOTE: Portion  $\ge 0.5 \text{ cm}^2$  with diameter or width of  $\le 1 \text{ cm}$  is recommended.

5. Syringe, 10-µL

#### SPECIAL PRECAUTIONS: None

#### SAMPLING:

- 1. Calibrate each personal sampling pump with a representative sampler in line.
  - NOTE: Sampler should be used in open-face configuration.
- 2. Attach sampler outlet to personal sampling pump with flexible tubing. Remove top piece of cassette.
- 3. Sample at an accurately known flow rate between 1 and 4 L/min.
- 4. After sampling, replace top piece of cassette and pack securely for shipment to laboratory.
  - NOTE: If the EC in the sample is more difficult to oxidize (e.g., graphite) than typical black carbon (e.g., soot), notify the laboratory of this fact.

#### SAMPLE PREPARATION:

5. Use punch to cut out a representative portion of the sample filter for analysis. Take care not to disturb deposited material and avoid hand contact with sample.

#### CALIBRATION AND QUALITY CONTROL:

- 6. Perform CH<sub>4</sub> calibration injection at end of each sample analysis.
- 7. If a particular sample filter deposit appears uneven, take a duplicate portion (step 5) for analysis to check evenness of deposition. Analyze at least one duplicate and others as required to replicate 10% of the samples for sets of up to 50 samples and 5% of the samples over 50.
  NOTE: Description in duplicate act as fitter in unuplicate and others as required to replicate 20%.
  - NOTE: Precision in duplicate analyses of a filter is usually better than 2%.
- 8. Analyze three quality control blind spikes and three analyst spikes to ensure that instrument calibration is in control. Prepare spike as follows:
  - a. Using a microliter syringe, apply known volume of OC standard solution directly onto portion taken (step 5) from a precleaned blank filter.
  - b.. Allow H<sub>2</sub>O to evaporate and analyze with samples and blanks (steps 10 and 11).
- 9. Determine instrument blank (results of analysis with no sample present) for each sample set.

#### **MEASUREMENT:**

- 10. Set analyzer according to manufacturer's recommendations (see APPENDIX B). Place sample portion into sample oven.
  - NOTE: Forms of carbon that are difficult to oxidize (e.g., graphite) may require increased analysis time to ensure that all EC in the sample is quantified.
- Determine EC (and OC) mass, μg, as provided by analyzer and divide by sample punch area, cm<sup>2</sup>, to report result in terms of μg C per cm<sup>2</sup> of filter.

#### CALCULATIONS:

- 12. Multiply the reported EC value by filter deposit area, cm<sup>2</sup>, (typically 8.55 cm<sup>2</sup> for a 37-mm filter) to calculate total mass, μg, of EC on each sample (W<sub>EC</sub>). Do the same for the blanks and calculate the mass found in the average field blank (W<sub>b</sub>). (OC masses may be calculated similarly.)
- 13. Calculate EC concentration ( $C_{EC}$ ) in the air volume sampled, V (L):

$$C_{EC} = \frac{W_{EC} - W_{b}}{V}, mg/m^{3}$$

#### EVALUATION OF METHOD:

Currently, a suitable EC standard reference material is not available for verification of the accuracy of the method in the determination of EC. For this reason, only the accuracy of the method in the analysis of various OC standards and carbonaceous dusts for total carbon could be examined [1]. A commercial instrument was used for method evaluation [5]. No discernable differences in the responses of five different compounds were noted. Linear regression of the data for all five compounds gave a slope and correlation coefficient near unity [ $\mathbf{m} = 0.99 (\pm 0.01)$ ,  $r^2 = 0.999$ , n = 43]. Based on results for individual compounds, reported carbon values are expected to be from 98 to 100% of the actual amount present. In addition, results (total carbon) of analysis of different carbonaceous materials were in good agreement with those reported by two other independent laboratories. These findings indicate that instrumental response appears to be compound- and matrix-independent (i.e., carbon is accurately quantified irrespective of compound and matrix type). Such a response is required for accurate carbon determination.

To calculate the estimated LOD of the method (i.e.,  $\approx 0.24 \ \mu g \ C \ or \ 0.15 \ \mu g \ C/cm^2$ ), ethylenediaminetetraacetic acid (EDTA) calibration standards covering a range from 0.23 to 2.82  $\mu g \ C$  (or from 0.15 to 1.83  $\mu g \ C$  per cm<sup>2</sup> of filter) were analyzed. Results of linear regression of the low-level calibration data (i.e.,  $\mu g \ C$  reported vs. actual) were then used to calculate the LOD as 3  $\sigma_y/m$  (where  $\sigma_y$  is the standard error of the regression and **m** is the slope of the regression line). The calculated LOD shows good agreement with that estimated as LOD = (blank +  $3\sigma_{blank}$ ), which gives a value of  $\approx 0.22 \ \mu g \ C$ . The mean (*n* = 40) instrumental blank was  $\approx .02 \ (\pm 0.07) \ \mu g \ C$ .

Because the split between EC and OC is method-dependent [1,4], and no suitable EC standard exists for assessment of a particular method's accuracy, various methods can be compared on a relative basis only. At present, the thermal-optical method is considered unbiased (i.e., it is the reference method), and the overall precision reflects the method accuracy. The S<sub>r</sub> of the mean EC concentration (4 mg/m<sup>3</sup>) found using fourteen samplers (two each of seven types) for collection of diesel exhaust was 5.6%. Although pumps were used for sample collection, a 5% pump error was added in the calculation of the overall precision of the method because of the relatively small sample taken (0.5 h, 60 L). Based on the 95% confidence limit (19%; 13 degrees of freedom, n = 14) on the accuracy, results of this experiment indicate that the NIOSH accuracy criterion [6] is fulfilled. The amount of EC collected (240 µg per sample) would be equivalent to sampling an EC level of 250 µg/m<sup>3</sup> for 8 h at 2 L/min.

The thermal-optical method is applicable to nonvolatile, carbon-containing species only. The method is not appropriate for volatile or semivolatiles, which require sorbents for efficient collection. A complete discussion on the evaluation of this method for monitoring occupational exposures to particulate diesel exhaust in general industry can be found in the literature [1]. Application of the method for monitoring exposures to diesel particulate matter in the mining industry may require use of a size-selective sampling strategy in some

situations [11]. In coal mines, a specialized impactor [2,3] with a sub-µm cutpoint is required to minimize the contribution of coal-source EC [2].

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#### METHOD WRITTEN BY:

M. Eileen Birch, Ph.D., NIOSH/DPSE.

#### APPENDIX A.

Diesel exhaust has been classified by IARC as a probable human carcinogen [8]. NIOSH has recommended "...that whole diesel exhaust be regarded as a potential occupational carcinogen..." and that workers' exposures be reduced[9,10]. The American Conference of Governmental Hygienists (ACGIH) has proposed a TWA of 0.15 mg/m<sup>3</sup> for diesel particulate (see Notice of Intended Changes for 1995-1996) [12]. The TLV applies to submicrometer particulate matter, which includes the solid carbon particle core and particulate-adsorbed components. A submicrometer size fraction was selected so that interference of other larger dusts is minimized. If other submicrometer particulate (e.g., cigarette smoke, fumes, oil mists) is present, it will interfere in the gravimetric determination of diesel particulate.

#### APPENDIX B. THERMAL-OPTICAL ANALYZER DESIGN AND OPERATION:

In the thermal-optical analysis of carbonaceous aerosols, speciation of various carbon types (organic, carbonate, and elemental) is accomplished through temperature and atmosphere control, and by continuous monitoring of filter transmittance. A schematic of the instrument is given below. The instrument is a modified version of a design previously described in the literature [11]. An optical feature corrects for pyrolytically generated elemental carbon (EC), or "char," which is formed during the analysis of some materials (e.g., cigarette smoke, pollen). He-Ne laser light passed through the filter allows continuous monitoring of filter transmittance. Because temperatures in excess of  $850^{\circ}$ C are employed during the analysis, quartz-fiber filters are required for sample collection. A punch from the sample filter is taken for analysis, and organic carbon (OC) and elemental carbon are reported in terms of  $\mu g/cm^2$  of filter area. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. In this approach, a homogeneous sample deposit is assumed. At the end of the analysis (after the EC is evolved), calibration is achieved through injection of a known volume of methane into the sample oven.

Thermal-optical analysis proceeds essentially in two stages. In the first, organic and carbonate carbon (if present) are evolved in an inert helium atmosphere as the temperature is raised (stepped) to about 850 °C. Evolved carbon is catalytically oxidized to  $CO_2$  in a bed of granular  $MnO_2$  (at 950°C),  $CO_2$  is reduced to  $CH_4$  in a Ni/firebrick methanator (at 450°C), and  $CH_4$  is quantified by an FID. In the second stage of the analysis, the oven temperature is reduced, an oxygen-helium mix (2%  $O_2$  in He) is introduced into the sample oven, and the oven temperature is again raised to about 850°C. As oxygen enters the oven, pyrolytically generated EC is oxidized and a concurrent increase in filter transmittance occurs. The point at which the filter transmittance reaches its initial value is defined as the "split" between EC and OC. Carbon evolved prior to the split is considered OC (or carbonate), and carbon volatilized after the split (excluding that from the  $CH_4$  standard) is considered elemental. The presence of carbonate can be verified through analysis of a second portion (punch) of the filter after its exposure to HCl vapor. In the second analysis, the absence of the suspect peak is indicative of carbonate carbon in the original sample.

Currently, only one commercial laboratory (Sunset Laboratory) performs thermal-optical analyses. To support the new method, a collaborative effort between NIOSH researchers and the instrument's developer is underway. During 1996, a thermal-optical instrument will be constructed and evaluated. This effort will assist in the transfer of this technology to other interested parties.

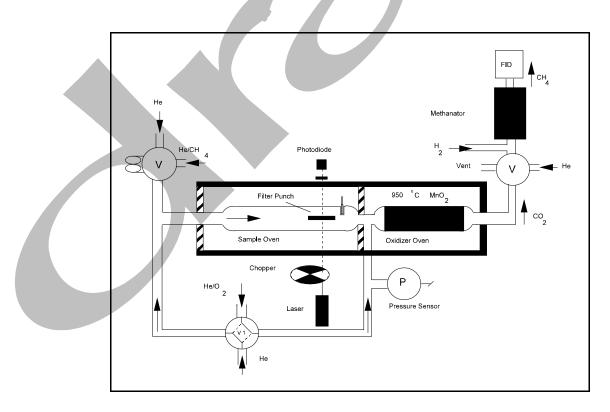


Figure 1. Schematic of Thermal-Optical Analyzer.

		npany, Sacramento and	, .	,
Description	10/7/94 Conventional	10/10/94 Conventional	10/6/94 Crumb Rubber	10/11/94 Crumb Rubber
Pavement Function	Traffic Lane and Shoulder Elevation correction	Traffic Lane and Shoulder Elevation correction	Traffic Lanes and Shoulders Surface overlay	Traffic Lanes and Shoulders Surface overlay
Hot Mix Asphalt Type	Conventional 1.9 cm (3/4") maximum (medium grade)	Conventional 1.9 cm (3/4") maximum (medium grade)	Rubber 1.3 cm (½") maximum (gap grade)	Rubber 1.3 cm (½") maximum (gap grade)
Crude Supplier	Conoco Oil	Conoco Oil	Conoco Oil	Conoco Oil
AC Grade†	AR 4000, type G	AR 4000, type G	AR 4000, type G	AR 4000, type G
% Rubber (by weight)‡	0	0	20	20
<b>Production</b> (metric tons)	907 (1000 short tons)	907 (1000 short tons)	2041 (2250 short tons)	2040 (2250 short tons)
Average Application Temperature	142°C (288°F)	143°C (289°F)	138°C (280°F)	142°C (288°F)
Laydown Depth	61mm	61mm	61mm	61mm
Laydown Width	3.7 meters (12')	3.7 meters (12')	3.7 meters (12')	3.7 meters (12')
Hot Mix Asphalt Conveyance	Bottom dump trailers; windrow pick–up into hopper	Bottom dump trailers; windrow pick–up into hopper	Bottom dump trailers; windrow pick–up into hopper	Bottom dump trailers; windrow pick–up into hopper
Job Duration	5.5 hours	8.0 hours	8.5 hours	9.0 hours
Transport	7 Bottom dump double trailers (25 ton capacity per truck)	7 Bottom dump double trailers (25 ton capacity per truck)	18 Bottom dump double trailers (25 ton capacity per truck)	18 Bottom dump double trailers (25 ton capacity per truck)
Windrower Pick-up	yes	yes	yes	yes
Paver	l (w/windrow elevator and w/screed)	1 (w/windrow elevator and w/screed)	1 (w/windrow elevator and w/screed)	1 (w/windrow elevator and w/screed)
Roller (joint pinch)	No	No	No	No
Roller (breakdown)	yes	yes	yes	yes
Roller (finishing)	yes	yes	yes	yes

 Table 1

 Production and Equipment Information for I–96 Project

 Paving Site: Granite Construction Company, Sacramento and Davis, California (HETA 94–0408)

Average1111111111165111111111125240 metric tons/hr227 metric tons/hrProduction Ratemetric tons/hrmetric tons/hr240 metric tons/hr227 metric tons/hr
---

= Crumb rubber modified hot mix asphalt = Conventional hot mix asphalt Crumb Rubber Conventional = millimeters mm

† Asphalt cement

‡ By weight of asphalt cement



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Table 2 Summary of Sampling and Analytical Methods Paving Site: Granite Construction Company, Sacramento and Davis, California (HETA 94–0408)				
Substance	Flow Rate (Lpm)	Sample Media	Analytical Method	Comments
Total Particulate	2.0	Tared PVC filter (37 mm diameter, 0.8µm pore size)	NIOSH Method No. 0500, Gravimetric analysis	Both personal breathing-zone and area samples collected
Respirable Particulate	1.7	Tared PVC filter (37 mm diameter, 0.8μm pore size)	NIOSH Method No. 0600, Gravimetric analysis	Dorr-Oliver nylon cyclone used as particle size selector
Polycyclic Aromatic Compounds (PACs) and Sulfur Compounds	2.0	Zefluor filter (37 mm diameter, 2µm pore size), followed by an ORBO 43 sorbent tube (Note: an ORBO 42 sorbent tube was used in subsequent evaluations to reduce the pressure drop and pump failures.	NIOSH 5506, modified to quantitate PACs via HPLC and a flow injection technique with spectrofluorometric detection. Two detector emission wavelengths were used: 370 nm (more sensitive to 2-3 ring PACs); and 400 nm (more sensitive to 4+ ring PACs). Sulfur compounds were analyzed by gas chromatography with sulfur chemiluminescence detection. This method may be found in Appendix A.	The collection method is similar to NIOSH method 5506, Polynuclear Aromatic Hydrocarbons. Opaque filter cassettes and sorbent tube holders were used to prevent the degradation of PACs by ultraviolet light. A detailed description of this method may be found in Appendix A.
Benzene Soluble Particulate	2.0	Glass fiber filter (37 mm diameter)	OSHA Method No. 58. The filters were rinsed with benzene, the leachate collected and evaporated, and the residue weighed to report the <i>benzene soluble fraction</i> . Organic compounds are generally soluble in benzene, whereas inorganic compounds are not benzene soluble. This method has been applied as an indirect measure of exposure to polynuclear aromatic hydrocarbons (PAHs) to evaluate a variety of exposure matrices including asphalt fume.	Because the method is nonspecific, the results are not necessarily due to PAH compounds. This method was used since it has been reported in many asphalt investigations and will also allow comparison of the conventional and CRM asphalt paving operations.
Elemental/Organic Carbon	2.0	Quartz-fiber filters (37 mm diameter, open face)	A rectangular punch (1.54 cm <sup>2</sup> ) is taken from the quartz filter for a three stage thermal-optical analysis.	A draft copy of NIOSH Method 5040 is provided as Appendix B.
Metals	2.5	Mixed cellulose ester (MCE) membrane filters (37 mm diameter)	NIOSH Method No. 7300. The samples were wet-ashed with concentrated nitric and perchloric acids. The residues were dissolved in a dilute solution of the same acids and the resulting solutions were analyzed for metals and minerals via Inductively Coupled Argon Plasma, Atomic Emission Spectroscopy (ICP-AES).	Analyses included silver, aluminum, arsenic, barium, beryllium calcium, cadmium, cobalt, chromium, copper, iron, lithium, magnesium, manganese, molybdenum, sodium, nickel, phosphorous, lead, platinum, selenium, tellurium, thallium, titanium, vanadium, yttrium, zinc, and zirconium.

Table 2         Summary of Sampling and Analytical Methods         Paving Site: Granite Construction Company, Sacramento and Davis, California (HETA 94–0408)				
Substance	Flow Rate (Lpm)	Sample Media	Analytical Method	Comments
Qualitative Volatile Organic Compound (VOC) Screen	0.02	Thermal desorption tubes	Samples analyzed using the Tekmar thermal desorber interfaced directly to a gas chromatograph and a mass spectrometry detector (GC/MS).	Each thermal desorption (TD) tube contains three beds of sorbent materials: (1) a front layer of Carbotrap C; (2) a middle layer of Carbotrap; and (3) a back section of Carbosieve S-III.
Quantitative Analysis for Selected Solvents	0.2	Activated charcoal sorbent tubes (100 milligram front section/50 milligram back section)	Currently existing NIOSH methods were merged and modified (i.e. NIOSH Methods 1300 and 1301 for ketones, 1501 for aromatic hydrocarbons, and 1550 for petroleum distillates.) The activated charcoal was desorbed with carbon disulfide; an aliquot of this solution was analyzed using GC-FID.	SpecificVOCs that were quantified included benzene, toluene, MIBK, and petroleum distillates (other hydrocarbons with retention times greater than toluene).
H <sub>2</sub> S, SO <sub>2</sub> , CO, and Ozone	Diffusion	Toxilog® diffusion monitors for H <sub>2</sub> S, SO <sub>2</sub> , CO. CEA® TG-KA Portable Toxic Gas Detector for ozone	Toxilog® diffusion monitors use individual electrochemical sensors specific for H <sub>2</sub> S, SO <sub>2</sub> , CO. The CEA® TG-KA Portable Toxic Gas Detector for ozone uses an electrochemical galvanic cell method.	Spot measurements were made throughout the work day around the paving site.
Mutagenic Potential	≈10	Zefluor filter (37 mm diameter)	Mutagenic activity evaluated via a modified Ames testing protocol. The basic analytical procedure used has been described by Maron and Ames except it was to be conducted using a spiral plater device as described by Houk et al. ( <u>Environ. Mol. Mut.</u> 1991, <u>17</u> , 112-121; and <u>Mut. Res.</u> 1989, <u>223</u> , 49-64).	Area samples were collected in the plume over an open port of a heated asphalt cement storage tank at the hot mix plant. The results of this modified Ames testing will be discussed in a separate NIOSH report.
The following are abbreviations which were not spelled out in the table.				
PVC = mm = μm = GC-FID = H <sub>2</sub> S = HPLC =	millimeter micrometer Gas chrom Hydrogen s	atography-flame ionization detector	SO <sub>2</sub> = Sulfur dioxide CO = Carbon monoxide lpm = Liters per minute MIBK = Methyl isobutyl keto Zefluor = Teflon® sampling fil nm = Nanometer	

### Table 3 Toxicity and Exposure Criteria Information Paving Site: Granite Construction Company, Sacramento and Davis, California (HETA 94–0408)

	g Site: Granite Construction Company, Sacramento and Davis, California (H	121A ) <del>1</del> 0400)
Compound	Toxicity Review	Exposure Criteria
Asphalt Fume (As Total Particulate)	Although the composition of asphalt fume cannot be easily characterized, one evaluation technique has been to sample total particulate. Total particulate is a measure of all airborne particulate which was collected on the sample filter. Current occupational exposure criteria from NIOSH and ACGIH for asphalt fume are expressed as total particulate. Asphalt fume has also been measured as the benzene soluble particulate fraction (BSF), a surrogate of exposure to polynuclear aromatic hydrocarbons (PAHs, see discussion below). Asphalt consists primarily of polycyclic aromatic compounds (PACs), many of which are soluble in benzene. These substances are of concern due to their irritancy and cancer-causing potential.	The NIOSH REL is 5 mg/m <sup>3</sup> for a 15-minute ceiling exposure. There is no current OSHA PEL for asphalt fume. The ACGIH TLV® is 5 mg/m <sup>3</sup> as an 8-hour TWA to total particulate.
Respirable Particulate	In contrast to total particulate, a respirable particulate sample uses a selection device to obtain the fraction of the airborne particulate that is small enough to be retained in the respiratory system once inhaled. Any conclusions based on respirable (or total) particulate concentrations may be misleading since other potentially toxic substances may be present. These particulate concentrations, along with the results obtained from tests for individual components (such as polycyclic aromatic compounds [PACs], benzene solubles, and selected solvents) should be considered together when determining the degree of hazard.	No NIOSH REL The OSHA PEL is 5 mg/m <sup>3</sup> , 8-hour TWA. The ACGIH TLV® for particulates not otherwise classified is 10 mg/m <sup>3</sup> for inhalable particulate and 3 mg/m <sup>3</sup> for respirable particulate. Both are 8-hour TWAs.
Benzene Soluble Particulate	<ul> <li>The benzene soluble particulate fraction (BSF) is that portion of the total particulate that is soluble in benzene. Organic compounds are generally soluble in benzene, whereas inorganic compounds are not benzene soluble.</li> <li>Historically, the BSF concentrations were measured in asphalt studies in an attempt to differentiate exposure between the asphalt fume and dirt or other dust present at asphalt construction operations. However, this method is non-specific and the BSF results are not necessarily due to polycyclic aromatic compounds (PACs) or polynuclear aromatic hydrocarbons (PAHs).</li> </ul>	None established for BSF associated with asphalt fume
Polynuclear Aromatic Hydrocarbons and Polycyclic Aromatic Compounds	<ul> <li>Analysis for unsubstituted PAHs has been applied to evaluate asphalt fume exposure. However, this approach provides limited information because asphalt fume contains numerous alkylated PACs that coelute, causing chromatographic interference, which prevents quantitation of specific compounds.</li> <li>Polycyclic aromatic compounds refer to a set of cyclic organic compounds that includes PAHs and also includes compounds that may have sulfur, nitrogen, or oxygen in the ring structure and alkyl substituted cyclics. Hundreds of PACs with varying degrees of alkyl substitutions are typically associated with asphalt materials [Lunsford et al. 1989]. PAHs have received considerable attention since some have been shown to be carcinogenic in experimental animals.</li> <li>NIOSH investigators have hypothesized that PACs with 2 to 3 rings (referred to in this report as PAC<sub>370</sub>) are associated with more irritative effects, while the 4 to 7 ring PACs (termed PAC<sub>400</sub>) may have more carcinogenic and/or mutagenic effects. It is not currently posssible to definitively distinguish between these two PAC groups analytically; however, using two different spectrofluorometric detector wavelengths (370 nanometer [nm] and 400 nm) allows the detector to be more sensitive to PACs based on ring number. A more complete discussion of the NIOSH analytical method for PACs may be found in Appendix A.</li> </ul>	None established for PAHs and PACs as a class.
Benzothiazole	In its pure form, benzothiazole is a yellow liquid with an unpleasant odor [Sax 1987]. It is used as a rubber vulcanization accelerator [ILO 1971], as an antimicrobial agent [ITO 1978], and in dyes [Kirk-Othmer 1978]. Benzothiazole was identified in the air during rubber vulcanization [Rappaport 1977]. Reports also indicate that benzothiazole is present in tires and CRM asphalt. Benzothiazole was selected for study since it may be useful as an indicator to represent the complex exposures resulting from CRM asphalt paving. It is not known if there are any health effects associated with benzothiazole at the air concentrations measured in this study.	None established

Pavir	Table 3 Toxicity and Exposure Criteria Information ng Site: Granite Construction Company, Sacramento and Davis, California (H	HETA 94-0408)
Compound	Toxicity Review	Exposure Criteria
Other Sulfur- Containing Compounds	The addition of tire rubber may increase sulfur compounds in asphalt. In this report "other sulfur-containing compounds" refer to aliphatic and aromatic organic compounds that contain sulfur. Although no specific occupational exposure limits exist for this group of sulfur compounds, it was hypothesized by NIOSH investigators that some of them may cause respiratory irritation.	None established
Organic and Elemental Carbon	Measuring organic, elemental, and total carbon concentrations (and determining a ratio between elemental and total carbon) provides an indication of diesel exhaust exposure. Any elemental carbon above background will most likely be from diesel exhaust. Unfortunately, this method cannot be used to specifically differentiate carbon sources (i.e., asphalt fume, diesel exhaust, cigarette smoke). There are no occupational exposure criteria for either elemental or organic carbon. This method was employed previously in several NIOSH trucking industry studies [Zaebst et al. 1991, Blade 1989]. A copy of the draft NIOSH Method 5040 is provided in Appendix B.	None established
МІВК	Tire rubber may be a source for methyl isobutyl ketone (MIBK) since this organic compound can be used as an antioxident in the tire manufacturing process. In its pure form, MIBK is a colorless, flammable organic solvent that is typically used as a solvent in the surface coating and synthetic resin industries [ACGIH 1992]. This solvent is absorbed primarily through inhalation and causes irritation of the eyes, mucous membranes, and skin [Proctor 1989]. At air concentrations much higher than were measured in this asphalt study, MIBK has caused central nervous system depression [Proctor 1989]. Continued or prolonged skin contact with the liquid can cause dermatitis [Proctor 1989].	The NIOSH REL and ACGIH TLV are 50 ppm, 8 hour TWA; and 75 ppm, 15 minute STEL. OSHA PEL is 100 ppm for an 8-hour TWA.
Benzene	Acute benzene overexposure can cause central nervous system depression with symptoms such as headache, nausea, and drowsiness. Chronic exposure to benzene has been associated with the depression of the hematopoietic system and is associated with an increased incidence of leukemia and possibly multiple myeloma [ACGIH 1992]. NIOSH classifies benzene as a human carcinogen [NIOSH 1992]. *Note: ACGIH has proposed to lower its TLV® for benzene to 0.3 ppm with a skin notation (indicating that skin exposure contributes to the overall absorbed inhalation dose and potential effects), and classify it as a proven human carcinogen [ACGIH 1995].	NIOSH REL is to reduce exposures to the lowest feasible level. OSHA PEL is 1 ppm for an 8-hour TWA. ACGIH TLV is 10 ppm* for an 8-hour TWA.
Toluene	Toluene can cause acute initation of the eyes, respiratory tract, and skin. Since it is a defatting solvent, repeated or prolonged skin contact will remove the natural lipids from the skin which can cause drying, fissuring, and dermatitis [Proctor 1989, NIOSH 1973]. Studies have shown that subjects exposed to 100 ppm of toluene for six hours complained of eye and nose irritation, and in some cases, headache, dizziness, and a feeling of intoxication (narcosis) [WHO 1981]. No symptoms were noted below 100 ppm in other studies [Bruckner 1981a,b]. The ACGIH TLV® carries a skin notation, indicating that skin exposure contributes to the overall absorbed inhalation dose and potential effects [ACGIH 1995].	NIOSH REL is 100 ppm, 8 hour TWA (15-minute STEL of 150 ppm). OSHA PEL is 200 ppm, 8- hour TWA; 300 ppm for a ceiling limit (not to be exceeded at any time). ACGIH TLV is 50 ppm, 8-
		hour TWA (skin).
Xylene	Structurally similar to toluene, xylene can also cause acute irritation of the eyes, respiratory tract, and skin [Proctor 1989]. In previous studies, humans exposed to concentrations ranging from 60 to 350 ppm (concentrations much higher than were measured in this asphalt study) experienced giddiness, anorexia (loss of appetite), and vomiting [Proctor 1989].	NIOSH REL is 100 ppm, 8 hour TWA. OSHA PEL is 100 ppm, 8- hour TWA. ACGIH TLV is 100 ppm
		for an 8-hour TWA and 15 ppm for a 15-minute STEL

Pavin	Table 3 Toxicity and Exposure Criteria Information g Site: Granite Construction Company, Sacramento and Davis, California (I	HETA 94-0408)
Compound	Toxicity Review	Exposure Criteria
Total Hydrocarbons (as Stoddard Solvent)	In this study, total hydrocarbons (HC) refer to Stoddard solvent, a petroleum distillate mixture. Effects from exposure to Stoddard solvent are primarily acute, unless significant amounts of substances that have chronic toxicity are present, such as benzene or glycol ethers. Epidemiologic studies have shown that exposure to similarly refined petroleum solvents (i.e.,Stoddard solvent, mineral spirits) can cause dry throat, burning or tearing of the eyes, mild headaches, dizziness, central nervous system depression, respiratory irritation, and dermatitis [NIOSH 1977b]. The evaluation criteria are based upon the similarity of the mixture composition in relation to the most commonly available products (in this case Stoddard solvent).	NIOSH REL is 350 mg/m <sup>3</sup> , 10-hour TWA (for all petroleum distillate mixtures, including Stoddard solvent). The a NIOSH ceiling limit is 1800 mg/m <sup>3</sup> , 15 minutes. OSHA PEL for Stoddard solvent is 2,900 mg/m <sup>3</sup> , 8- hour TWA.
		ACGIH TLV for Stoddard solvent is 525 mg/m <sup>3</sup> , 8- hour TWA.
Abbreviations:		
TLV = Threshold	d Limit Value (ACGIH) m exposure limit TWA = Time-weight ppm = parts per mi	llion

Description	10/7/94 Conventional	10/10/94 Conventional	10/6/94 Crumb Rubber	10/11/94 Crumb Rubber	
Summary	Cool	Cool	Cool	Cool	
Minimum Temp.	13°C (55°F)	13°C (55°F)	14°C (57°F)	10°C (50°F)	
Maximum Temp.	18°C (64°F)	18°C (64°F)	16°C (60°F)	14°C (58°F)	
Average Humidity	60-70%	75-80%	80-85%	75-80%	
Minimum WBGT	n.a.	51°F	n.a.	48°F	
Maximum WBGT	n.a.	55°F	n.a.	54°F	
Wind Speed	slight breeze	moderate breeze	windy	moderate breeze	
Wind Direction	Highly variable, N-E	Variable SW	Variable N	S–SW	
Traffic Density	Low-Moderate	Low-Moderate	Low-Moderate	Low-Moderate	

Crumb Rubber =Crumb rubber modified hot mix asphalt

ampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m <sup>3</sup> )
	Paver Hopper	267	534	2.3
Conventional	Screed	273	547	1.3
Asphalt	Ambient Background	314	644	0.05
10/7/94	Highway Background	A.	Sample Lost	
	Paver Hopper	85†	169	6.2
Conventional	Screed	451	905	3.2
Asphalt	Ambient Background	522	1044	0.06
10/10/94	Highway Background	447	897	0.04
	Paver Hopper	501	972	1.5
Crumb Rubber	Screed	498	995	1.5
Asphalt	Ambient Background	496	964	0.05
10/6/94	Highway Background	479	961	0.09
	Paver Hopper	99†	198	4.1
Crumb Rubber	Screed	496	992	1.4
Asphalt	Ambient Background	589	1181	0.04
10/11/94	Highway Background	528	1059	0.19

Due to special circumstances at this construction site, it was not possible to collect air samples on two consecutive days during either conventional or crumb rubber paving activities

Ambient background refers to area air samples collected in the construction and equipment yard

Highway background refers to area air samples collected in the highway median

Paving	Respirable Part g Site: Granite Construction	iculate Concentrations: Company, Sacramento		94-0408)
Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m <sup>3</sup> )
	Paver Hopper	267	440	0.94
Conventional	Screed	193	321	0.76
Asphalt	Ambient Background	314	532	0.08
10/7/94	Highway Background	272	463	ND (<0.04)
	Paver Hopper	465	760	0.75
Conventional	Screed	467	797	3.1
Asphalt	Ambient Background	522	883	0.07
10/10/94	Highway Background	447	764	0.06
	Paver Hopper	501	854	0.48
Crumb Rubber	Screed	498	848	0.81
Asphalt	Ambient Background	495	842	0.03
10/6/94	Highway Background	479	814	ND (<0.02)
	Paver Hopper	496	808	1.0
Crumb Rubber	Screed	496	844	0.61
Asphalt	Ambient Background	589	1027	0.03
10/11/94	Highway Background	528	903	ND (<0.02)

ND = Not Detected (below the Minimum Detectable Concentration)

 $mg/m^3$  = Concentration, milligrams per cubic meter () = The value which is shown in brackets is the

The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a less than (<) value.</p>

1. Due to special circumstances at this construction site, it was not possible to collect air samples on two consectutive days during either non-rubber or rubber paving activities.

2. Ambient background refers to area air samples collected in the construction and equipment yard.

3. Highway background refers to area air samples collected in the highway median.

		Area Air Samples				
ampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	e Concentration (mg/m <sup>3</sup> )		
	Paver Hopper	267	534	1.1		
Conventional	Screed	273	547	1.3		
Asphalt	Ambient Background	314	630	ND (<0.2)		
10/7/94	Highway Background	272	544	Trace		
	Paver Hopper	214	428	4.7		
Conventional	Screed	467	935	3.0		
Asphalt	Ambient Background	522	1073	ND (<0.1)		
10/10/94	Highway Background	447	891	ND (<0.1)		
Crumb Rubber	Paver Hopper	501	1002	1.4		
	Screed		Sample Lost			
Asphalt	Ambient Background	193	404	ND (<0.3)		
10/6/94	Highway Background	479	984	ND (<0.1)		
C. J.	Paver Hopper	496	992	2.0		
Crumb Rubber	Screed	496	990	1.5		
Asphalt	Ambient Background	589	1218	Trace		
10/11/94	Highway Background	Sampling Pump Malfunctioned - Sample Voided				
	Per	sonal Breathing-Zone Air San	ples			
Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m <sup>3</sup> )		
Crumb Rubber	Raker	529	1057	Trace		
Asphalt 10/6/94	Raker	557	1085	ND (<0.1)		

		Sampling	Sample	Concentration, micrograms per cubic meter				
Sampling Date	Area	Time (minutes)	Volume (Liters)	PACs @ 370 nm	PACs @ 400 nm	Other SulCom†	Benzothiazole	
	Paver Hopper	267	531	29	62	784	17	
Conventional	Screed	273	547	102	19	79	15	
Asphalt	Ambient Background	314	629	0.45	0.09	ND (<0.5)	24	
10/7/94	Highway Background	272	543	0.40	0.14	ND (<0.6)	14	
	D II	200	<i></i>	222		69	21	
Conventional	Paver Hopper Screed	390 467	655 929	233 264	56 59	68 93	3.1	
Asphalt	Ambient Background	522	1016	0.18	0.03	ND (<0.3)	ND (<0.3)	
10/10/94	Highway Background	447	867	0.14	0.02	ND (<0.3)	ND (<0.3)	
	Paver Hopper	501	1002	117	21	186	104	
Crumb Rubber Asphalt	Screed	498	832	85	17	178	121	
-	Ambient Background	340	735	0.20	0.05	ND (<0.4)	ND (<0.4)	
10/6/94	Highway Background	479	591	0.18	0.03	ND (<0.5)	ND (<0.5)	
	Paver Hopper	496	958	104	21	118	2.3	
Crumb	Screed	496	995	45	10	20	81	
Rubber Asphalt	Ambient Background	589	1174	0.09	0.02	ND (<0.3)	1.2	
10/11/94	Highway Background	528	1051	Trace	ND (<0.01)	ND (<0.3)	ND (<0.3)	

Polycycuc

†SulCom = Other sulfur-containing compounds 370 nm =

370 nanometers, spectrofluorometric detector wavelength (includes both vapor and particulate phase) 400 nm

400 nanometers, spectrofluorometric detector wavelength (includes both vapor and particulate phase) =

Concentration is between the Minimum Detectable and Minimum Quantifiable Concentrations

Not Detected (below the Minimum Detectable Concentration)

The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a less than (<) value.

Other Comments:

Trace

ND

()

Air samples were collected using 37 millimeter Zefluor® filters followed by an ORBO 43 sorbent tube.

				Concentrati	on, micrograms per	cubic meter			
Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Organic Carbon (OC)	Elemental Carbon (EC)	Total Carbon (TC)	EC/TO		
	Paver Hopper	267	533	2050	29	2079	0.01		
Conventional	Screed	273	545	1191	49	1240	0.04		
Asphalt	Ambient Background	314	538	45	32	77	0.42		
10/7/94	Highway Background	272	544	17	ND (<3.1)	NA	NA		
Conventional	Paver Hopper	465	465         933         3254         95         3349         0						
	Screed	Sample Lost							
Asphalt 10/10/94	Ambient Background	522	1074	ND (<1.6)	ND (<1.6)	NA	NA		
10/10/94	Highway Background	447	890	14	Trace	NA	NA		
	D 11	501	1000	12.50	24	1202	0.00		
<b>a</b> 1	Paver Hopper	501	1000	1268	24	1292	0.02		
Crumb Rubber	Screed	498	994	1237	51	1288	0.04		
Asphalt 10/6/94	Ambient Background	493	1030	1.0	ND (<1.7)	NA	NA		
10/0/94	Highway Background	479	962	5.0	Trace	NA	NA		
	Paver Hopper	496	995	2648	69	2717	0.03		
Crumb	Screed	496	987	1292	85	1377	0.05		
Rubber Asphalt	Ambient Background	589	1181	ND (<1.4)	ND (<1.4)	NA	NA		
10/11/94	Highway Background	528	1056	6.8	Trace	NA	NA		

EC/TC NA ND ( )

=

Ratio of Elemental Carbon to Total Carbon Not applicable since one or both analytes were not detected. Not Detected (below the Minimum Detectable Concentration) The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a less than (<) value.

Other Comments:

=

Ambient background refers to area air samples collected in the construction and equipment yard

Highway background refers to area air samples collected in the highway median

G. P. D. (	•	Sampling	Sample Volume	Conce	ntration, expres	sed in parts per	million	Concentration, ex	xpressed in mg/m <sup>3</sup>
Sampling Date	Area	Time (minutes)	(Liters)	Benzene	Toluene	Xylene	MIBK	Total HC< Toluene†	Total HC > Toluene
	Paver Hopper	267	52	Trace	Trace	Trace	ND	18	3.3
Conventional	Screed	267	53	0.06	0.08	0.06	ND	2.1	6.6
Paving 10/7/94	Ambient Background	314	63	ND	ND	ND	ND	Trace	Trace
10/7/94	Highway Background	272	54	ND	ND	ND	ND	ND	ND
	Paver Hopper	465	93	0.24	0.63	0.40	Trace	16	7.6
Conventional Paving 10/10/94	Screed	467	95	0.02	Trace	Trace	ND	0.65	9.0
	Ambient Background	522	103	ND	ND	ND	ND	ND	ND
	Highway Background	447	90	ND	ND	ND	ND	ND	ND
	Paver Hopper	501	97	0.09	0.13	0.14	0.10	3.8	7.3
Crumb	Screed	498	99	0.09	0.09	0.10	0.12	2.7	9.7
Rubber Paving	Screed	498	99	0.09	0.08	0.10	0.13	2.8	10
10/6/94	Ambient Background	499	100	ND	ND	ND	ND	Trace	Trace
	Highway Background	479	94	ND	ND	ND	ND	ND	Trace
	Paver Hopper	496	100	0.11	0.11	0.10	Trace	3.4	2.8
Crumb Rubber Paving	Screed	496	99	Trace	ND	Trace	Trace	0.51	2.5
10/11/94	Ambient Background	589	118	ND	ND	ND	ND	ND	ND
	Highway Background	528	106	ND	ND	ND	ND	ND	ND

() = The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a less than (<) value.

Pavin	g Site: Granite Construction	i Company, Sacramento a	nd Davis, CA (HETA	94-0408)	
Sampling Date	Activity	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m <sup>3</sup> )	
	Paver Operator†	260	520	0.56	
Conventional	Screed Operator	337	675	0.30	
Asphalt	Raker	347	692	0.38	
10/7/04	Raker	339	678	0.22	
10/7/94	Roller Operator (Front)	343	665	0.09	
	Truck Dumper	511	1025	0.28	
	Paver Operator <sup>+</sup>	87	174	1.3	
	Screed Operator	476	952	0.31	
Conventional	Raker	512	1028	0.29	
Asphalt	Raker	513	1026	0.28	
10/10/94	Roller Operator (Front)	470	969	0.35	
	Traffic Control	468	935	0.24	
	Traffic Control	478	954	0.22	
	Foreman	526	1054	0.23	
	Truck Dumper	502	1002	0.34	
	Paver Operator	428	849	0.71	
Crumb	Screed Operator	559	1114	0.25	
Rubber	Raker	554	1120	0.30	
Asphalt	Raker	316	1152	0.27	
10/6/94	Roller Operator (Front)	509	1001	0.13	
	Foreman	536	1079	0.17	
	Truck Dumper	539	1080	0.59	
	Paver Operator	546	1059	0.11	
	Screed Operator	555	1071	0.38	
Crumb Rubber	Raker	549	912	0.17	
Asphalt	Raker	553	1105	0.16	
- 10/11/94	Laborer	545	1088	0.18	
10/11/94	Traffic Control	385	747	0.27	
	Traffic Control	473	942	0.31	

mg/m<sup>3</sup>

Concentration, milligrams per cubic meter At the request of the employee, the sample was positioned near the seat used by the operator to approximate the = breathing zone exposure of this employee.

Other Comments:

Due to special circumstances at this construction site, it was not possible to collect air samples on two consectutive days during either conventional or crumb rubber paving activities

		Sampling	Sample	Sample Conc		centration, micrograms per cubic meter		
Sampling Date	Work Activity	Time (minutes)	Volume (Liters)	PACs @ 370 nm	PACs @ 400 nm	Other SulCom†	Benzothiazole	
Conventional Asphalt 10/7/94	Roller Operator	343	686	0.82	0.14	ND (<0,4)	ND (<0.4)	
Conventional Asphalt 10/10/94	Roller Operator	302	588	2.4	0.43	ND (<0.5)	ND (<0.5)	
	Truck Dumper	572	1145	8.4	1.3	ND (<0.3)	18	
<b>a</b> 1	Paver Operator†	507	985	24	4.9	14	68	
Crumb Rubber	Screed Operator	482	962	8.9	1.8	ND (<0.3)	24	
Asphalt	Raker	525	663	11	1.4	1.8	15	
	Roller Operator	557	1113	0.6	0.14	ND (<0.3)	2.8	
Crumb Rubber Asphalt 10/11/94	Laborer	475	948	2.5	0.50	ND (<0.3)	ND (<0.3)	
370  nm = 370 $400  nm = 400$ $ND = Nc$ $() = Th$ $cal$ $† = At$ $zon$ Other Comments: Air samples were c	her sulfur-containing con O nanometers, spectrofluc O nanometers, spectrofluc t Detected (below the M culated by dividing the a the request of the employ the exposure of this employ collected using 37 millim rations reported in this ta	prometric detector prometric detector inimum Detectabl n brackets is the n nalytical Limit of yee, the sample w byee.	r wavelength ( le Concentration ninimum detect Detection by the as positioned the ers followed b	includes both v. on) table concentra the air sample v near the seat use y an ORBO 43	apor and particulation (MDC) for to olume and is reported by the operator sorbent tube.	ate phase) his sample. The orted as a less that to approximate	an (<) value. the breathing	

# Table 13 Number of Acute Symptom Questionnaires Completed by Workers Paving Site: Granite Construction Company, Sacramento and Davis, CA (HETA 94-0408)

		Acute Questionnaires Completed				
Work Group		Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Rubber Asphalt	Day 4 CRM Rubber Asphalt	
Pavers (n= 7)		24/35‡	34/35	34/35 30/35		
	-pavers n= 7)	29/35	34/35	35/35	33/35	
Paving	Paving Period TotalsPavers58/70Non-pavers63/70		64/70			
			68/70			
‡ = Number of completed questionnaires/potential number of questionnaires						

## Table 14

Number of Workers Reporting Symptoms and Number of Symptom Occurrences by Survey Day Paving Site: Granite Construction Company, Sacramento and Davis, CA (HETA 94-0408)

	Work groups	Number of workers reporting symptoms (Number of symptom occurrences reported)				
Symptoms		Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Rubber Asphalt	Day 4 CRM Rubber Asphalt	
Dry, itching, or irritated eyes	Pavers Non-pavers	2 (3) 1 (1)	1 (2) 0	3 (8) 1 (1)	2 (6) 1 (2)	
Stuffy, burning, or irritated nose	Pavers Non-pavers	1 (3) 2 (2)	1 (3) 1 (4)	0 2 (2)	1 (5) 3 (9)	
Sore, dry, scratchy, or irritated throat	Pavers Non-pavers	2 (4) 1 (2)	2 (4) 1 (4)	5 (9) 0	2 (8) 0	
Skin burning, rash, itching, or irritated	Pavers Non-pavers	0 0	0 0	1 (2) 0	1 (4) 0	
Bothered by coughing	Pavers Non-pavers	1 (2) 0	1 (1) 0	0 0	1 (2) 1 (1)	
Chest tightness or shortness of breath	Pavers Non- pavers	0 0	1 (2) 0	1 (3) 0	1 (5) 0	
Wheezing or whistling in chest	Pavers Non- pavers	0 0	0 0	0 0	0 0	

Totals	Pavers Non- pavers	2/6 (12) 2/7 (5)	3/7 (12) 1/6 (8)	5/7 (22) 2/7 (3)	2/6 (30) 3/7 (12)
			$\wedge$		
			9		

# Table 15 Rate of Symptoms Occurrence Per Questionnaire Among Pavers by Survey Day Paving Site: Granite Construction Company, Sacramento and Davis, CA (HETA 94-0408)

Pavers (n=7)	Day 1Day 2ConventionalConventionalAsphaltAsphalt		Day 3 CRM Rubber Asphalt	Day 4 CRMRubber Asphalt
Completed Questionnaires	24	34	34	30
Symptom Occurrences	12	12	22	30
	0.5	0.35	0.65	1.0
Rate symptom occurrence per questionnaire		0.41		).81

 Table 16

 Estimated Hours of Exposure to Asphalt Fume Among Pavers by Job Title and Survey Day Paving Site: Granite Construction Company, Sacramento and Davis, CA (HETA 94-0408)

	Estimated hours exposure to asphalt fume				
Job Title (n=7)	Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Rubber Asphalt	Day 4 CRM Rubber Asphalt	
Paver Operator	5.25	7.5	6.0	11.5	
Screedman	5.25	7.5	7.5	12.0	
Raker	5.0	7.5	7.5	12.0	
Roller	5.0	7.5	7.5	11.5	
Roller	4.75	7.5	7.5	12.0	
Laborer	5.5	6.0	7.5	absent	
Tack truck/raker	absent	3.75	2.0	1.5	
Daily Total Hours (Average)	30.75 (5.1)	47.25 (6.8)	45.5 (6.5)	60.5 (10.1)	
Total Hours by Asphalt Paving Material (Average)	78.0 (6.0)		106	(8.2)	

# Table 17 Rate of Symptoms Per Hour of Exposure Among Pavers by Survey Day Paving Site: Granite Construction Company, Sacramento and Davis, CA (HETA 94-0408)

	Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Rubber Asphalt	Day 4 CRM Rubber Asphalt
Estimated Exposure to Asphalt (total hours)	30.75	47.25	45.5	60.5
Number Symptom Occurrences	12	12	22	30
Rate (symptom	0.39	0.25	0.48	0.50
occurrence/hr exposure)	0.	31		0.49

Pav	Summary of Area ving Site: Granite Construction	Table 18 Concentrations o Company, Sacra	of Air Contamina amento, Califorr	ants iia (HETA 94–04	08)	
a		TWA Concentration, micrograms per cubic meter				
Sampling Location	Analyte	10/7/94 Conventional	10/10/94 Conventional	10/6/94 Rubber	10/11/94 Rubber	
	Total Particulate	2300	6200	1500	4100	
	Respirable Particulate	940	750	480	1000	
	Benzene Soluble Particulate Fraction	1100	4700	1400	2000	
	PACs <sub>370</sub> (vapor and particulate)	29	233	117	104	
Paver	PACs <sub>400</sub> (vapor and particulate)	62	56	21	21	
Hopper	Benzothiazole	17	21	104	2.3	
	Other Sulfur Compounds	784	68	186	118	
Γ	Total Hydrocarbons with a retention time < toluene	18000	16000	3800	3400	
	Total Hydrocarbons with a retention time > toluene	3300	7600	7300	2800	
	Total Particulate	1300	3200	1500	1400	
	Respirable Particulate	760	3100	810	610	
	Benzene Soluble Particulate Fraction	1340	3000	Sample Lost	1500	
	PACs <sub>370</sub> (vapor and particulate)	102	264	85	45	
Paver Screed	PACs <sub>400</sub> (vapor and particulate)	19	59	17	10	
Screed	Benzothiazole	15	3.1	121	81	
	Other Sulfur Compounds	79	93	178	20	
	Total Hydrocarbons with a retention time < toluene	2100	650	2800	510	
	Total Hydrocarbons with a retention time > toluene	6600	9000	10000	2500	
Ambient Backgrou	Total Particulate	50	60	50	40	
nď	Respirable Particulate	80	70	30	30	

IEah	Total Particulate	Sample Lost	40	90	190		
Highway Backgrou nd							
	Respirable Particulate	ND (<40)	60	ND (<20)	ND (<20)		
PAC <sub>370</sub>	Polycyclic aromatic compound measured with 370 nanometer wavelength detector						
$PAC_{400}$	cerector Polycyclic aromatic compound measured with 400 nanometer wavelength detector						
ND	= Not Detected (below the Minimum Detectable						
()	Concentration) The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a less than (<) value.						
Note	less than (<) value.	Highway back soluble fractio reported in this	ground concentrations n, PAC370 and PAC4( s summary table. Pleas for these concentrations	s for benzene 30 are not se refer to the ins.			