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The Sim J. Harris Company
San Diego, 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.

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This report was prepared by Gregory Kinnes, Aubrey Miller, and Gregory Burr of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Michael Barsan and Mimi Nguyen. Analytical methods were developed by Larry Jaycox, Charles Neumeister, and Larry Olsen. Laboratory analysis provided by Ardith Grote, Robert Kurimo, Stephanie Pendergrass, Leroy May, Charles Neumeister, and Rosa Key-Schwartz. Desktop publishing by Ellen Blythe.

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Health Hazard Evaluation Report 96-0130-2619
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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 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 higher initial 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:

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

The protocol allows for up to eight individual site evaluations in different 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 a field survey conducted near Ramona, California, during asphalt pavement construction along several rural/residential San Diego County roads. 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 April 24–25, 1996, approximately 2926 metric tons of conventional asphalt were applied by the Sim J. Harris Company; on April 29–30, 1996, approximately 3474 metric tons of CRM asphalt were placed by the same workers. The rubber content was approximately 20% of the asphalt binder by weight. The workplace exposure and health assessment were 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 (TP) and the benzene soluble particulate fraction (BSF). 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 TP 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. Polycyclic aromatic compounds (PACs), which may be present in asphalt fume, were measured using a new analytical method. Some of the PACs may 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, xylene, benzene, methyl isobutyl ketone [MIBK]), and total hydrocarbons (as either n-hexane or 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 respirable particles. Direct-reading instruments were used to measure carbon monoxide (CO) and hydrogen sulfide (H₂S). 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 concentrations of TP, BSF, and respirable particulate varied between sampling locations and across survey days, but generally were higher during the CRM asphalt paving periods than during the conventional asphalt paving periods. At the paver screed area sample locations, concentrations of total PACs were approximately two times higher during CRM asphalt paving as compared to conventional asphalt paving. The concentrations of sulfur-containing compounds (except benzothiazole) were similar during the two days of CRM asphalt paving and the second day of conventional asphalt paving. However, the concentrations of sulfur-containing compounds during the first day of conventional paving were almost three times higher than the concentrations measured during the other three paving days. With the exception of one area sample, benzothiazole was only detected during CRM asphalt paving.

Over 50 volatile organic compounds (VOCs) were detected in the asphalt emissions, but only the most significant peaks were analyzed quantitatively. Toluene, benzene, xylene, and MIBK were all present at detectable concentrations which were less than 0.2 parts per million (ppm). Total hydrocarbons, quantified as either n-hexane or Stoddard solvent, ranged from 0.27 to 34 milligrams per cubic meter (mg/m³). All of these concentrations are orders of magnitudes below their respective occupational exposure limits. Concentrations of benzene ranged from not detected to 0.02 ppm. NIOSH classifies benzene as an occupational carcinogen and recommends that occupational exposures be reduced to the lowest feasible concentration.

Short-term CO concentrations as high as approximately 40 ppm were measured on the paver deck. 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. Detectable concentrations of H₂S were not observed.

Personal breathing-zone air samples were collected daily on eight workers during the four sampling days. The PBZ samples were analyzed for TP, BSF, total PACs, benzothiazole, and other sulfur-containing compounds. The PBZ exposures for TP ranged from 0.14 to 1.0 mg/m³ during conventional asphalt paving and 0.19 to 1.4 mg/m³ during CRM asphalt paving. The PBZ concentrations for TP were slightly higher during CRM asphalt paving than during conventional asphalt paving. All of the PBZ concentrations, however, were well below the current NIOSH REL for asphalt fume of 5 mg/m³ (measured as TP). The BSF concentrations for these samples were also typically higher during CRM asphalt paving than during conventional asphalt paving.

Personal breathing-zone concentrations of PACs (at analytical emission wavelengths of 370 and 400 nanometers) were generally higher during CRM asphalt paving when compared to conventional asphalt paving. The PBZ concentrations of PAC₃₇₀ during conventional and CRM asphalt paving ranged up to 26 and 58 µg/m³, respectively. In PBZ samples, benzothiazole was only detected during CRM asphalt paving operations, ranging up to 94 µg/m³.

Seven workers with exposure to the asphalt paving operation (pavers) were recruited for the health assessment. Additionally, eight workers not typically exposed to hot asphalt fume (non-pavers) were recruited for comparison. Serial symptom questionnaires were administered to obtain information concerning the prevalence of acute 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 the eight non-pavers, the most frequently reported symptoms (as a percentage of occurrences over all four days) were nasal irritation (35%); burning, itching, or irritated skin (21%); eye irritation (21%); and throat irritation (15%). The most frequently reported symptoms for the seven pavers were throat irritation (33%), eye irritation (24%), nasal irritation (24%), and cough (15%). Non-pavers reported higher percentages of skin irritation (none reported by pavers) and nasal irritation, while pavers reported higher percentages of throat irritation and cough. Eighty-seven percent of the pavers' symptoms were reported during ongoing or recent exposure to asphalt fumes and were rated as "mild" in severity (the choices were "mild," "moderate," or "severe").

This study showed that PBZ exposures to asphalt fume emissions, as well as other exposure measurements, were below current NIOSH RELs and other relevant exposure limits for those substances that have criteria. For the area samples, concentrations of TP, respirable particulate, BSF, and PACs were higher during CRM asphalt paving than during conventional paving. In contrast, the differences in PBZ concentrations between the two asphalt types for TP, BSF, and total PACs were not as large as with the area samples. However, generally higher concentrations were measured during CRM asphalt paving than during conventional asphalt paving periods for all analytes with the exception of other sulfur-containing compounds (except benzothiazole). Area samples collected on the first day of conventional asphalt paving had concentrations of other sulfur-containing compounds which were almost three times higher than the similar concentrations measured during both types of paving on the latter three days.

For the pavers, the symptom survey revealed a higher rate of symptom occurrences per completed questionnaire during the CRM asphalt paving period as compared to the conventional asphalt paving period. Two workers (both pavers) demonstrated PEFR changes consistent with significant bronchial lability (i.e., the difference between the minimum and the maximum PEFR on at least one survey day exceeded 20% of the day's maximum PEFR). In each case, the PEFR decrease was temporally associated with respiratory symptoms on at least one day. The occupational contribution to this finding is unclear at this time, however. Although the higher symptom rates associated with CRM asphalt paving are consistent with the higher air concentrations measured during the CRM asphalt paving periods, the limited number of both area and PBZ air samples obtained from this one evaluation

makes further interpretation of this association difficult. Presently, NIOSH investigators feel it is premature to draw definitive conclusions from this single site evaluation since the data provided are from a very small sample size and may reflect production and weather conditions specific to this site. Data from additional site evaluations may enable more definitive conclusions to be drawn. A final composite report will be issued after these additional site evaluations are completed.

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.

TABLE OF CONTENTS

Preface	ii
Acknowledgments and Availability of Report	ii
Executive Summary	iii
Process Overview	3
Site Description	3
Industrial Hygiene Evaluation Design	4
Weather Information	5
Process Information	5
Area Air Samples	5
Personal Breathing–Zone Air Samples	6
Air Sampling Methods	6
Medical Evaluation Design	6
Evaluation Criteria	6
Asphalt Fumes (Petroleum)	7
Industrial Hygiene Results	8
Weather	8
Process Information	9
Area Air Samples	10
Total Particulate and Respirable Particulate	10
Benzene Soluble Particulate Fraction	10
Polycyclic Aromatic Compounds (PACs), Sulfur–containing Compounds, and Benzothiazole	10
Elemental and Organic Carbon	11
Volatile Organic Compounds (VOCs)	11
Hydrogen Sulfide (H ₂ S) and Carbon Monoxide (CO)	11
Personal Breathing Zone Air Samples	12
Medical Results	12
Discussion	14
Weather	14
Process Information	15
Air Sampling	15
Medical	16
Conclusions	16
Recommendations	17
Abbreviations and Terms	18

References	20
Appendix A	23
Appendix B	25

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 and sizes of the aggregate materials to the amount of asphalt cement to obtain the appropriate pavement properties (flexibility, drainage, durability, etc.).

The purpose of a 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 delivered directly to trucks or 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:

- **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.
- **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.

- **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.
- **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 "dumppman") 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, roller operators, and the tackman 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 "non-pavers."

SITE DESCRIPTION

On April 24–25, and continuing on April 29–30, 1996, NIOSH investigators conducted a study near Ramona, California, during asphalt pavement construction on rural/residential San Diego County

roads by the Sim J. Harris Company. The same paving crew was evaluated throughout the survey and consisted of a foreman, two truck dumpers, a paver operator, two screed operators, two traffic control persons, and two roller operators.

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 April 24–25 while the CRM asphalt was used on April 29–30. 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 Ramona site is contained in Table 1. The conventional paving projects used a 13 millimeter (mm) medium gap grade hot mix asphalt while the CRM paving projects used a 13 mm maximum gap grade hot mix. The crude supplier was Paramount and the granulated rubber was manufactured by the Baker Rubber Company. An asphalt cement grade AR 4000 was used for both the conventional and CRM asphalt paving. Although the CRM asphalt design mix allowed up to 22% rubber (total weight of rubber by the total weight of the asphalt/rubber blend), the actual rubber content on April 29–30 was approximately 20%.

The HMA plant used for this construction project was located near San Marcos, California, and was approximately 30 to 45 minutes from the Ramona paving sites (the distance traveled by the asphalt delivery trucks varied somewhat depending on which San Diego County road was currently being paved). The HMA was hauled to the paving site by belly dump trailer trucks (each trailer averaged approximately 23 metric tons [25 short tons]).

The conventional asphalt was used as a surface overlay for two-lane county residential streets located in Ramona (April 24–25). The CRM asphalt was used as a surface overlay for two-lane rural county roads located near Ramona on April 29–30. Approximately 2926 metric tons of conventional

asphalt were applied on April 24–25, compared to 3474 metric tons of CRM asphalt placed on April 29–30. The asphalt laydown temperature was 138°C (280°F) for the conventional paving while the laydown temperatures during CRM asphalt paving ranged from 160 to 163°C (320 to 325°F). The uncompacted depth of both the conventional asphalt and CRM asphalt overlays was approximately 4.5 cm (1.8 inches); the width of the paving was approximately 7.3 meters (24 feet).

The bottom dump trailers placed the hot asphalt material onto the road in a windrow channel approximately 1.2 meters (4 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 place 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 particulate (TP) and the benzene soluble particulate fraction (BSF). 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 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 TP levels. In an effort to address this situation, new or modified sampling and analytical methods were developed and included in this study. Polycyclic aromatic compounds (PACs) which may be present in asphalt fume were measured using a new analytical method. Some of the PACs may 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 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, xylene, benzene, and methyl isobutyl ketone [MIBK]) and total hydrocarbons (quantified as either n-hexane or 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 respirable particles. Direct-reading instruments were used to measure carbon monoxide (CO) and hydrogen sulfide (H₂S). 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 Transportable Automated Meteorological Station (TAMS) manufactured by Qualimetrics. Environmental measurements were obtained at 20-minute intervals using a Reuter Stokes RSS 214 Wibget[®] 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. Background area air samples were collected from locations adjacent to the roads being paved to evaluate the ambient air and possible impact from vehicle emissions. Area samples were collected for TP, 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), and elemental and organic carbon. Direct reading instruments were used to measure CO and H₂S.

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[®] tubing. The area and personal breathing-zone (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 most members of the paving crew for the following compounds: TP (along with the benzene soluble fraction), total PACs, and other sulfur–containing compounds (including benzothiazole).

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

Beginning on April 23, NIOSH investigators recruited 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. The 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 workers with direct exposure to the paving operation (pavers) were asked to participate in the study. Seven pavers volunteered and were included in the health assessment. NIOSH investigators also recruited an additional eight workers employed at the same construction site, but not in proximity to the asphalt paving operation (non–pavers), to participate in the health assessment for comparison purposes. Two of the non–pavers, however, performed traffic control for the paving operation and thus potentially received intermittent low–level exposure to asphalt fumes.

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

Acute symptom questionnaires were periodically administered to all study participants during their workshift to determine if eye, nose, throat, skin, or respiratory symptoms (including cough, chest tightness, or wheezing) were associated with their job tasks. 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.

The 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 1992], 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 1996]. 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 lowest of either the 1989 OSHA PEL, ACGIH TLV, or NIOSH REL.

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 ($\mu\text{g}/\text{m}^3$). 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 and Corbett 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 [1996].

In a 1977 criteria document, NIOSH established a REL of 5 mg/m³ (as a 15-minute ceiling limit) for asphalt fumes, measured as a TP. 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/m³ (as TP) 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/m³ as an 8-hour TWA [ACGIH 1996]. 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 TP, 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. With the exception of the second day of conventional paving (April 25), the ambient temperatures during the investigation were fairly consistent with the low temperatures ranging from 24 to 27°C (76 to 81°F). The ambient

temperature on April 25 was cooler, with a low temperature of 22°C (71°F) and a high temperature of 30°C (86°F). Also, the relative humidity on April 25 was higher (32%) than the other three days of paving (range 11 to 19%). All four days of the survey were sunny and warm, with no rain.

Wind speed and direction are particularly important factors that may influence the air sampling results. As shown in Table 4, the wind direction was generally from the southwest and the northeast (210° to 290°). The strongest winds, with gusts up to 12 miles per hour (mph), were observed during the two days of CRM asphalt paving, although on all days at least a slight wind was detected. The traffic density was low during all four paving days. There were no extended periods of constant traffic passing near the paving operations due to the type of roads being paved.

Process Information

For the two days of conventional asphalt paving, the terrain was mostly flat, and the county rural/residential roads being paved were primarily straight. In contrast, the county roads being paved with the CRM asphalt were located in the foothills surrounding Ramona. Therefore, the terrain was mostly hilly with the roads having numerous sharp curves which made paving more difficult. There were only two sections during the CRM asphalt paving phase where the road was relatively straight and level.

With the exception of the first day of conventional paving, the average production rate (number of tons of asphalt paved per hour) remained consistent, ranging from approximately 175 to 200 metric tons/hour. During the first day of conventional paving, the average production rate (290 metric tons/hour) was much higher than the other three days. A total of 1905 metric tons of asphalt were applied in 6.5 hours during the first day of conventional paving. On the second day, only 1021 metric tons of asphalt were laid in 5 hours. Several factors contributed to the lower average production rate on the second day of conventional paving. Although there was a slight delay before the paving actually started on the first

day, the flat terrain and the well-planned asphalt conveyance resulted in nearly continuous paving with very little down time. However, the following three reasons led to the lower production rate and shorter duration on the second day of conventional paving: (1) an approximately one hour break in the paving to transfer paving activities to another planned location approximately ¼ mile from the original paving site, (2) the difficulties encountered during the paving of an inclined three-way intersection, and (3) the greater than anticipated production rate on the first day resulting in the early completion of this two day project.

During the CRM asphalt phase of the project, a total of 1814 metric tons were applied on the first day (April 29) and 1660 metric tons on the second day (April 30). However, because of several difficulties encountered during the CRM phase, the job durations were much longer, 9.5 hours on both days, in order to complete this phase of the project. This resulted in the lower average production rates of 190 and 175 metric tons/hour on the first and second days of the CRM phase, respectively. Because the terrain was hilly and the roads contained several curves, the paving operations proceeded at a slower pace than what would be expected for level terrain and straight roads. In addition, difficulties in the conveyance of the CRM asphalt to the paving site and two significant breaks to move the paving activities to different locations resulted in lengthy delays. Because paving operations are easier when performed in a downhill direction and only one lane is paved at a time, one delay occurred to transfer the paver to the initial starting point of the road so that a second lane could be paved in the predominantly downhill direction. The other break occurred to transfer paving activities to another planned location several miles from the end of the original paving site.

On the two days of conventional asphalt paving the contractor placed a “petromat” prior to the asphalt overlay. A petromat, however, was not used on the CRM paving sections.

Area Air Samples

Total Particulate and Respirable Particulate

Tables 5 and 6 provide the concentrations for the total and respirable particulate samples, respectively. Four of the TP concentrations were above 5 mg/m³ and were all collected during one day of the CRM asphalt paving. At the paver screed, the TP concentrations ranged from 1.7 to 3.0 mg/m³ and from 1.4 to 6.3 mg/m³ for conventional and CRM asphalt paving, respectively. The highest TP concentrations for both asphalt types were observed above the screed auger. The TP background concentrations measured during this survey ranged from 0.01 to 0.09 mg/m³.

The highest respirable particulate concentration (9.0 mg/m³) was obtained over the screed during CRM asphalt paving. All of the respirable particulate sample concentrations collected near asphalt fume emission areas ranged from 0.20 to 1.3 mg/m³ (conventional asphalt paving) and 0.94 to 9.0 mg/m³ (CRM asphalt paving). The background respirable particulate sample concentrations ranged from not detected (<0.02 mg/m³) to 0.03 mg/m³.

Benzene Soluble Particulate Fraction

As summarized in Table 5, BSF concentrations at the paver screed ranged from 1.1 to 2.4 mg/m³ during conventional paving and from 1.2 to 5.6 mg/m³ during CRM asphalt paving. Overall, the highest average BSF concentrations were measured during CRM asphalt paving (5.6 mg/m³) versus the conventional paving (1.7 mg/m³). Presently, there are no occupational exposure criteria from NIOSH or OSHA for the benzene soluble particulate fraction of asphalt fume.

Polycyclic Aromatic Compounds

(PACs), Sulfur-containing Compounds, and Benzothiazole

Four 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 (a large number of compounds which have similar chromatographic elution times). This prevents 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 7 summarizes the total PACs area concentrations collected at emission and background locations. More PACs were measured during CRM rather than conventional asphalt paving. For example, the concentration for the total PAC₃₇₀ at the paver screed ranged from 65 to 136 µg/m³ for conventional and from 103 to 233 µg/m³ for CRM asphalts. The total PAC₄₀₀ concentrations from these same samples ranged from 8.9 to 22 and from 15 to 41 µg/m³, respectively, for conventional and CRM asphalt paving. In every sample the PAC₃₇₀ concentration was greater than the corresponding PAC₄₀₀ 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 7 also presents the benzothiazole and other sulfur-containing compound concentrations obtained from hexane extracts of PAC samples which were analyzed by gas chromatography with sulfur chemiluminescence detection. With the exception of one sample, benzothiazole was only detected during the CRM paving, with concentrations ranging from 26 to 52 µg/m³. Benzothiazole, an additive used in

tire manufacturing, was unexpectedly detected at a trace concentration (between 1.1 and 4.6 $\mu\text{g}/\text{m}^3$) in one sample collected during the conventional asphalt paving. The background benzothiazole concentrations were all not detected ($<1.1 \mu\text{g}/\text{m}^3$). Based on this information, the crumb rubber in the CRM asphalt formulation appears to be more important than the rest of the asphalt components as a source of benzothiazole.

The highest concentrations of sulfur compounds were measured during the first day of conventional paving. The concentrations measured on the second day of conventional asphalt paving were comparable to the concentrations measured during the CRM paving. The concentrations of sulfur compounds measured during conventional asphalt paving ranged from 26 to 144 $\mu\text{g}/\text{m}^3$ while the concentrations measured during CRM asphalt paving ranged from 25 to 65 $\mu\text{g}/\text{m}^3$. The average concentration of sulfur compounds over the screed auger during CRM asphalt paving was 49 $\mu\text{g}/\text{m}^3$; the average during conventional asphalt paving was approximately twice as high (90 $\mu\text{g}/\text{m}^3$). However, the concentrations of sulfur-containing compounds during the first day of conventional paving were almost three times higher than the similar concentrations obtained during the other three days. The concentrations of sulfur compounds obtained during the first day of conventional paving ranged from 113 to 144 $\mu\text{g}/\text{m}^3$, while the concentrations ranged from 25 to 88 $\mu\text{g}/\text{m}^3$ during the remaining three days.

Elemental and Organic Carbon

Elemental and organic carbon analytical results are provided in Table 8. All of the air samples collected for EC above the screed auger on the paver vehicle were above the background concentrations, suggesting that some diesel exhaust was present. However, the EC:TC ratios ranged from only 0.2 to 2.0% above the screed auger. Since diesel exhaust has been reported to contain EC levels between 60 to 80% of the TC [Blade et al. 1989], the much lower EC:TC ratios measured during this survey imply that diesel exhaust was not substantially contributing to these air sampling results.

Volatile Organic Compounds (VOCs)

Table 9 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, MIBK, and total hydrocarbons) were quantitatively analyzed by GC/FID. Although higher VOC concentrations were measured during CRM asphalt paving, the quantities of VOCs detected at emission sources during both types of paving were orders of magnitude below their respective occupational exposure limits published by NIOSH, OSHA, or ACGIH. One air sample had a quantifiable concentration of benzene (0.02 ppm) with the remaining samples having only non-detected ($<0.01 \text{ ppm}$) or trace concentrations (between 0.01 and 0.02 ppm). NIOSH classifies benzene as an occupational carcinogen and recommends that exposure be reduced to the lowest feasible concentration. The OSHA PEL for benzene is an 8-hour TWA of 1 ppm. Only trace concentrations (between 0.01 and 0.03 ppm) of toluene were detected for six of the eight area VOC samples. Xylene and MIBK concentrations ranged from 0.03 to 0.18 ppm and from trace (between 0.02 and 0.06 ppm) to 0.08 ppm, respectively, with the higher concentrations all being detected during the CRM asphalt paving. Total hydrocarbons quantified as either n-hexane or as Stoddard solvent averaged 0.66 mg/m^3 and 20 mg/m^3 , respectively. Both of these average concentrations are well below the occupational exposure limits for n-hexane and Stoddard solvent.

Hydrogen Sulfide (H_2S) and Carbon Monoxide (CO)

During the second day of CRM asphalt paving, H_2S and CO concentrations were measured using direct reading instrumentation. Hydrogen sulfide was not detected ($<1 \text{ ppm}$) while instantaneous CO concentrations ranged from 14 to 40 ppm. The highest CO concentrations were measured on the paver deck. The NIOSH REL for CO is an 8-hour

TWA of 35 ppm and a ceiling limit (never to be exceeded even momentarily) of 200 ppm.

Personal Breathing Zone Air Samples

Table 10 presents the PBZ monitoring results for TP and BSF collected during conventional and CRM asphalt paving operations. All of the PBZ TP exposures were well below the NIOSH REL for asphalt fume of 5 mg/m³. The TWA PBZ exposure to TP ranged from 0.14 to 1.0 mg/m³ and from 0.19 to 1.4 mg/m³ during conventional and CRM asphalt paving, respectively. As expected, the average TP concentrations measured on the truck dumper, paver operator, and screed operator (jobs in closest proximity to fume emissions from either the paver or the asphalt delivery trucks) were among the highest exposures, averaging 0.68 mg/m³ on conventional asphalt days and 0.83 mg/m³ on CRM asphalt paving days. Overall, the TP concentrations appeared to be slightly higher during CRM asphalt paving than during conventional asphalt paving.

The BSF results followed a similar pattern, with PBZ concentrations consistently higher during CRM asphalt paving as compared to conventional asphalt application. For example, the average BSF concentrations of the jobs in closest proximity to fume emissions from either the paver or the asphalt delivery trucks (truck dumper, paver operator, and screed operator) were approximately two times higher on CRM asphalt paving days than during conventional asphalt paving (0.51 mg/m³ versus 0.27 mg/m³, respectively).

Table 11 contains the PBZ results for PACs, benzothiazole, and sulfur compounds. In every sample, regardless of the type of asphalt being applied, the PAC₃₇₀ concentration was greater than the corresponding PAC₄₀₀ concentration, implying that the 2–3 ring PACs may be more abundant. The smaller ring number PACs are associated with more irritative effects, whereas more concern exists for suspect carcinogenicity of the 4–7 ring PACs. Although PAC₃₇₀ concentrations varied daily, they were generally higher during CRM (range: 4.2 to

58 µg/m³) versus conventional (range: 0.95 to 26 µg/m³) asphalt paving. Occupational exposure criteria for total PACs, as a class, are presently unavailable from either NIOSH, OSHA, or ACGIH.

Benzothiazole was detected only during CRM asphalt paving, ranging up to 94 µg/m³. This was anticipated since benzothiazole is a sulfur-containing compound present in rubber tires. Personal breathing-zone exposures to *other* sulfur-containing compounds during conventional and CRM asphalt paving ranged from not detected (<1.2 µg/m³) to 7.3 µg/m³ and not detected (<1.2 µg/m³) to 7.6 µg/m³, respectively.

MEDICAL RESULTS

The eight non-pavers recruited for the health assessment included four equipment operators, two traffic controllers, one laborer, and one construction services worker (this person operated a variety of delivery trucks, road graders, and sweepers during the work day). Six of the eight non-pavers participated in the study for all four survey days. The remaining two non-pavers (a laborer and an equipment operator) were absent on the third survey day (the first day of CRM asphalt paving). The seven pavers recruited for the health assessment included one paver operator, two screed operators, two rakers/laborers, one truck dumper, and one roller operator. These seven pavers participated in the study for all four survey days.

Four of the eight non-pavers were male, and the average age of this group was 39 years (range 27–51 years). All seven pavers were male, and the average age of this group was also 39 years (range 30–48 years). Three of the non-pavers currently smoked cigarettes (all smoked during work), one was a former smoker, and four never smoked. Among pavers, one currently smoked cigarettes and smoked during work, one infrequently smoked cigars and did not smoke during work, two never smoked, and three were former smokers.

The number of acute symptom questionnaires completed (i.e., the number of opportunities a worker

had to report a health symptom) varied among the non-pavers and pavers (Table 12). For the non-pavers a maximum of 40 (eight workers times five questionnaires/day) questionnaires could have been completed during each survey day. For the pavers, a maximum of 35 questionnaires (seven workers times five questionnaires/day) could have been completed during each survey day. There was only enough time on the second survey day for the pavers to complete four rounds of acute questionnaires, due to a shortened paving workshift (five hours). Two non-pavers were absent on the third survey day (one non-paver off on sick leave and one off on regular leave). The non-pavers completed 98% (78/80) of the questionnaires during the first two study days and 97% (68/70) during the last two study days. In comparison, the pavers completed 100% (63/63) of the questionnaires during the first two days and 100% (70/70) during the last two survey days.

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, they would have 35 symptom occurrences for that survey day.

Table 13 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, there were 48 symptom occurrences reported during the entire survey period (83% of these symptom occurrences were reported by three non-pavers). Four non-pavers reported 21 symptom occurrences during the first two survey days (conventional asphalt paving) and five non-pavers reported 27 symptom occurrences during the last two survey days (CRM asphalt paving). Among the non-pavers, the most frequently reported symptoms (as a percentage of occurrences over all four days) were nasal irritation (35%); burning, itching, or irritated skin (21%); eye irritation (21%); and throat irritation (15%). Among

pavers, there were 181 symptom occurrences reported during the entire survey period (76% of these symptom occurrences were reported by three pavers). Six pavers reported 70 (39%) symptom occurrences during the first two survey days (conventional asphalt paving) compared with 7 workers reporting 111 (61%) symptom occurrences during the last two survey days (CRM asphalt paving). Among the pavers, the most frequently reported symptoms (as a percentage of occurrences over all four days) were throat irritation (33%), eye irritation (24%), nasal irritation (24%), and cough (15%). Non-pavers reported an appreciably higher number of occurrences of skin irritation (none reported by pavers) and nasal irritation, while pavers reported an appreciably higher number of occurrences of throat irritation and cough. Eighty-seven percent (157/181) of the pavers' symptoms were reported during ongoing or recent exposure to asphalt fumes and were rated by the pavers as "mild" in severity (the choices were "mild," "moderate," or "severe"). Of note, the California Air Pollution Advisory Board issued a smoke alert warning of potential respiratory irritation due to area wildfires on April 30, 1996. For pavers, there was no noticeable change in the pattern of symptom reporting or environmental measurements on this day. Non-pavers (who were working in a different area) did have noticeably increased symptom reporting on April 30, 1996, however, it is unclear if this finding was related to environmental conditions.

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 14. The symptom reporting rate was 45% higher during the CRM paving period (1.6 symptoms per completed questionnaire) as compared to the conventional paving period (1.1 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. 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 15 shows each paver's estimated exposure time to asphalt paving for each survey day. The average estimated hours of exposure to asphalt paving increased during the CRM asphalt paving period. Workers had a combined average of 5.4 hours of exposure/day to the paving operation during the conventional asphalt paving period, compared to a combined average exposure of 7.3 hours/day during the CRM asphalt paving period.¹

Two non-pavers (traffic controllers) reported 2.5 hours and 1.0 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 16). There was little difference in the rate of symptom occurrences per hour of exposure among pavers between the CRM asphalt paving period (1.1 symptom occurrences per hour of exposure) and the conventional asphalt paving period (0.9 symptom occurrences per hour of exposure).

Two workers (both pavers) demonstrated PEFR changes consistent with significant bronchial lability (i.e., difference between the minimum and the maximum PEFR on at least one day exceeded 20% of the day's maximum PEFR). One worker had significant bronchial lability on three survey days (days 1, 2, and 4), and the other worker had significant bronchial lability on 1 survey day (day 3). Both workers showed a worsening in PEFR over the course of the workday, a pattern that is often seen with work-related bronchial lability. One worker

¹ The combined average of 5.4 hours of exposure/day during the conventional asphalt paving period was influenced by the short (3.6 hours) paving time on April 25, 1996.

reported symptoms of eye irritation on survey day 1, no symptoms on survey day 2, and eye irritation plus shortness of breath on survey day 4, in temporal association with the PEFR decreases. The other worker reported symptoms of throat irritation and cough during the single day of PEFR decrease.

DISCUSSION

Weather

The ambient temperatures and wind conditions may affect air sampling measurements obtained outdoors during this (or any) construction project. The ambient temperatures on the second day of conventional asphalt paving (30°C [86°F]) was cooler than the air temperatures recorded during the other three days of asphalt paving (33 to 35°C [91 to 95°F]). The average relative humidity was also higher on the second day (32%) than the other days (11 to 19%). Based on the limited number of air samples collected during this site survey, however, it is uncertain what effect(s), if any, the ambient temperatures or relative humidity may have had on asphalt fume generation.

The wind speed, and to a lesser extent the wind direction, varied between the two types of asphalt paving. During the conventional paving on the first two days of sampling, the wind was predominantly from the northwest to southwest at variable speeds up to 8 miles per hour (mph). During the CRM paving, the wind direction was more variable with winds from the northeast to the southwest while the wind speeds were consistently higher than the first two days, with gusts up to 12 mph. Although it is uncertain the extent that these weather conditions influenced the air sampling results, based on the greater wind speeds encountered during the CRM asphalt paving, the asphalt fumes may have been more quickly dispersed during this phase of the survey.

Process Information

The average production rate (number of tons of asphalt paved per hour) was the highest for the first day of the conventional asphalt paving while the average production rates for the remaining three days were very consistent. The average production rate for the first day was 290 metric tons/hour while the rate ranged from approximately 175 to 200 metric tons/hour for the remaining three days. In addition, the average production rates for both days of conventional paving were higher than the rates measured during both days of CRM asphalt paving. This was most likely due to the differences in the terrain and roads encountered during the two types of paving. The terrain was mostly flat and the roads were straight during the conventional paving, while the terrain was very hilly and the roads had numerous curves during the CRM paving. Therefore, paving operations were much more difficult during the CRM asphalt phase of the project which resulted in several delays and lower average production rates.

Air Sampling

The current occupational criterion for asphalt fume is 5 mg/m³, measured as TP. All of the PBZ samples were below this concentration, although four of 16 (25%) area samples collected adjacent to emission sources exceeded this concentration. 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 paver operator, screed operators, and laborers' PBZ exposure probably represents the highest asphalt fume exposure among workers on the paving crew. However, it is important to realize that exposure criteria are presently unavailable for several groups of compounds (such as total PACs, sulfur compounds, and benzothiazole) which are also present in asphalt fume. All the VOCs detected above the screed auger (i.e, benzene, toluene, xylene, MIBK, petroleum distillates, etc.) were also well below any existing occupational exposure criteria. During CRM asphalt paving, one sample had a benzene concentration of 0.02 ppm. NIOSH considers benzene to be an occupational carcinogen and recommends that exposure be reduced to the lowest feasible concentration.

Table 17 contains a summary of the results from the area air samples included in Tables 5 through 9, arranged by location, while the results for the PBZ samples are included in Tables 10 and 11. Although there were many inconsistent factors that could affect results, the following descriptive observations are presented:

- Total particulate and BSF area concentrations were typically higher during the CRM asphalt paving than the conventional paving.
- Total particulate and BSF PBZ concentrations were typically higher during CRM versus conventional asphalt paving, although all PBZ exposures were well below the criteria of 5 mg/m³, measured as total particulate, currently proposed by NIOSH for asphalt fume exposure.
- As may be expected, the average TP PBZ concentrations measured on the truck dumper, paver operator, and screed operator (those jobs in closest proximity to fume emissions from either the paver or the asphalt delivery trucks) were among the highest exposures, averaging 0.68 mg/m³ on conventional asphalt days and 0.83 mg/m³ on CRM asphalt paving days.
- The ratio of elemental to total carbon suggests that diesel exhaust was not excessively contributing to the air sampling results obtained on area and PBZ samples collected on the paving crew.
- Two detector emission wavelengths were used to provide greater sensitivity either to 2–3 ring PACs (370 nm) or to 4+ ring PACs (400 nm). Regardless of the asphalt composition or whether it was a PBZ or area air sample, greater PAC concentrations were detected using the 370 nm wavelength, 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.
- Higher concentrations of sulfur–containing compounds (not including benzothiazole) were measured in area air samples collected on the first day

of conventional asphalt paving (range 113 to 144 $\mu\text{g}/\text{m}^3$) than during either the second day of conventional asphalt paving or both days of CRM asphalt paving (range 25 to 88 $\mu\text{g}/\text{m}^3$). Although the average concentration of sulfur compounds measured over the screed auger during the first day of conventional asphalt paving was approximately three times higher than the similar concentrations obtained during the other three paving days, a definitive conclusion regarding this difference cannot be determined due to the limited number of samples. However, one possible explanation may be because the highest average production rate (number of tons of asphalt paved per hour) also occurred on the first day of conventional asphalt paving. Another factor which may have influenced the air sampling results may have been the placement of a petromat by the contractor prior to the overlay during the conventional asphalt paving (a petromat was not used on the CRM paving sections).

- Personal breathing-zone concentrations of other sulfur-containing compounds (not including benzothiazole) measured during conventional and CRM asphalt paving were similar.
- Except for one area air sample, benzothiazole was only detected during CRM asphalt paving. This was anticipated since benzothiazole is a sulfur-containing compound present in rubber tires. It also suggests that the crumb rubber in the CRM asphalt formulation is the primary source of the benzothiazole.

Medical

The results of the acute symptom survey revealed that among the pavers, the *number of reported health symptoms* and *rate of symptom occurrences per completed questionnaire* was approximately 50% 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 eye irritation and cough during the CRM asphalt paving period. There was little difference in the *rate of symptom occurrences per self-reported hour of asphalt paving* between the conventional and CRM paving periods.

Acute symptoms in combination with peak flow testing were evaluated to determine whether acute respiratory symptoms were associated with intermittent or reversible bronchospastic responses. Typically, acute irritant symptoms were reported by workers in association with worksite exposures. Two workers (both pavers) demonstrated significant bronchial lability, associated with respiratory symptoms, on at least one survey day. Various occupational and non-occupational conditions can cause acute PEFV changes. The few studies that have examined the respiratory effects from exposure to asphalt fumes have not reported any exposure-related changes in pulmonary function. The extent, if any, to which occupational exposures, specifically asphalt fumes, may have contributed to the PEFV changes in these two pavers is unknown. Continuing evaluation of the relationship between reported symptoms, measured bronchoreactivity, and any environmental measurements indicative of workers' asphalt fume exposure will be conducted as additional data become available from other study sites. Additionally, information concerning chronic health symptoms collected on the general health questionnaires at each site will be examined with respect to workers' occupation and responses on acute symptom questionnaires.

CONCLUSIONS

Results presented here apply only to this survey and cannot be generalized to indicate the exposures or health effects associated with CRM asphalt paving. This study showed that PBZ exposures to asphalt fume emissions, as well as to other substances, were below current NIOSH RELs, OSHA PELs, and other relevant exposure limits for those substances that have them. Concentrations of TP, respirable particulate, BSF, and PACs in area samples were higher during CRM asphalt paving than during conventional asphalt paving. In contrast, the differences in PBZ concentrations of TP, BSF, and total PACs were not as large as with the area samples, although generally higher concentrations were measured during CRM asphalt paving than during conventional asphalt paving. For pavers, the symptom survey revealed a *higher rate of symptom*

occurrences per completed questionnaire during the CRM asphalt paving period than during the conventional asphalt paving period. Two pavers had PEFIR changes indicative of bronchoreactivity, but the occupational contribution to this finding is unclear at this time. Although the higher symptom rates associated with CRM asphalt paving coincide with the higher area air concentrations measured during the CRM asphalt paving periods, the limited number of both area and PBZ air samples obtained from this one evaluation makes further interpretation of this association difficult. Presently, NIOSH investigators feel it is premature to draw definitive conclusions from this single site evaluation. 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. A final composite report will be issued after these additional site evaluations are completed.

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. Any additional recommendations specifically concerning asphalt fume exposure will be included in a final composite report.

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 provided with adequate washing facilities (i.e., portable hand washes) for use prior to eating. Additionally, workers should avoid consuming food and beverages in close proximity to asphalt fume emissions.
3. Until the long term health effects of exposure to asphalt fume can be determined, workers should consider the combined exposure to asphalt fume and tobacco smoke to have potentially increased health risks and should be strongly urged to avoid smoking in close proximity to asphalt fume emissions.
4. In order to reduce skin contamination and potential contamination of workers' homes and vehicles, workers should be provided with adequate washing and changing facilities for use prior to leaving work.
5. The use of, and therefore exposure to, diesel fuel for the routine cleaning of equipment should be minimized.
6. All workers should wear protective clothing or appropriate sunscreen to shield exposed skin surfaces from the harmful ultraviolet component of sunlight.
7. 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	IH	Industrial hygiene
BSF	Benzene soluble (particulate) fraction	ISTEA	Intermodal Surface Transportation Efficiency Act
C	Ceiling, an exposure that shall not be exceeded during any part of the workday	LC	Liquid chromatography
CFR	Code of Federal Regulations	LOD	Limit of detection (analytical method)
cm ²	Square centimeters	LOQ	Limit of quantitation (analytical method)
CO	Carbon monoxide	Lpm	Liters per minute
Control	A person working in road construction but not exposed to hot asphalt fume.	MCE	Mixed cellulose–ester filter
CRM	Crumb rubber modified	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.
DOT	Department of Transportation	mg	Milligrams
EC	Elemental carbon	mg/m ³	Milligrams per cubic meter of air
EPA	Environmental Protection Agency	MIBK	Methyl isobutyl ketone
FHWA	Federal Highway Administration	mL	Milliliter
FID	Flame ionization detector	mm	Millimeter
GC–MS	Gas chromatography–Mass Spectrometry	MQC	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 volume.
H ₂ S	Hydrogen sulfide	ND	Not detected
HHE	Health hazard evaluation	NIOSH	National Institute for Occupational Safety and Health
HMA	Hot mix asphalt	nm	Nanometer
IARC	International Agency for Research on Cancer		
ICP–AES	Inductively coupled (argon) plasma–atomic emission spectroscopy		

OC	Organic carbon	TWA	Time-weighted average
OSHA	U.S. Occupational Safety and Health Administration	VOCs	Volatile organic compounds
PAC ₃₇₀	PACs monitored at an emission wavelength of 370 nanometers (representative of 2-ring and 3-ring compounds)	WBGT	Wet bulb globe temperature
PAC ₄₀₀	PACs monitored at an emission wavelength of 400 nanometers (representative of 4-ring and higher compounds)	°C & °F	Degrees Celsius and Degrees Fahrenheit
PACs	Polycyclic aromatic compounds	µg	Microgram (10 ⁻⁶), a unit of weight
PAHs	Polynuclear aromatic hydrocarbons	µg/m ³	Micrograms of contaminant per cubic meter of air (a unit of concentration)
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)		

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APPENDIX A

MODIFIED ANALYTICAL METHOD FOR POLYCYCLIC AROMATIC COMPOUNDS

Larry Jaycox, Charles Neumeister, and Larry Olsen

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 polycyclic aromatic compounds (PACs) 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 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 µm 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 were utilized. One set of 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 co-elution 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)

5040

C

MW: 12.01

CAS: none

RTECS: none

METHOD: 5040, Issue 1

EVALUATION: 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 particles, diesel particulate matter

SAMPLING

MEASUREMENT

SAMPLER: FILTER
(quartz fiber, 37-mm; size-selective impactor may be required, see INTERFERENCES)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 106 L @ 40 µg/m³
-MAX: 4300 L (for filter load ~ 20 µg/cm²)

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

TECHNIQUE: EVOLVED GAS ANALYSIS (EGA) by thermal-optical analyzer

ANALYTE: elemental carbon (EC)

FILTER PUNCH SIZE: 1.54 cm²

CALIBRATION: methane injection [1]

RANGE: 0.76 to 54 µg per filter portion

ESTIMATED LOD: 0.2 µg per filter portion

PRECISION (S_r): 0.10 @ 1 µg C,
0.01 @ 10–72 µg C

ACCURACY

RANGE STUDIED: 4.0 mg/m³
(60-L sample) [1]

BIAS: none [1]

OVERALL PRECISION (S_r): see EVALUATION OF METHOD

ACCURACY: see EVALUATION OF METHOD

APPLICABILITY: The working range is 4.4 to 312 µg/m³ with an LOD of ~1.3 µg/m³ for a 960-L air sample collected on a 37-mm filter with a 1.54 cm² punch from the sample filter. If a lower LOD is desired, a larger sample volume and 25-mm filter may be used (e.g., a 1920-L 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/cm² 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:

1. 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 ≥ 0.5 cm² with diameter or width of ≤ 1 cm is recommended.
5. Syringe, 10– μ L

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 CH₄ 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: 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 H₂O 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.

11. Determine EC (and OC) mass, μg , as provided by analyzer and divide by sample punch area, cm^2 , to report result in terms of $\mu\text{g C per cm}^2$ of filter.

CALCULATIONS:

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

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

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 [$m = 0.99 (\pm 0.01)$, $r^2 = 0.999$, $n = 43$]. 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., $\approx 0.24 \mu\text{g C}$ or $0.15 \mu\text{g C/cm}^2$), ethylenediaminetetraacetic acid (EDTA) calibration standards covering a range from 0.23 to $2.82 \mu\text{g C}$ (or from 0.15 to $1.83 \mu\text{g C per cm}^2$ of filter) were analyzed. Results of linear regression of the low-level calibration data (i.e., $\mu\text{g C}$ reported vs. actual) were then used to calculate the LOD as $3 \sigma_y/m$ (where σ_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 $\text{LOD} = (\text{blank} + 3\sigma_{\text{blank}})$, which gives a value of $\approx 0.22 \mu\text{g C}$. The mean ($n = 40$) instrumental blank was $\approx .02 (\pm 0.07) \mu\text{g C}$.

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_p of the mean EC concentration (4 mg/m^3) 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 ($240 \mu\text{g per sample}$) would be equivalent to sampling an EC level of $250 \mu\text{g/m}^3$ 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/m³ 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°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 µg/cm² 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 CO₂ in a bed of granular MnO₂ (at 950°C), CO₂ is reduced to CH₄ in a Ni/firebrick methanator (at 450°C), and CH₄ is quantified by an FID. In the second stage of the analysis, the oven temperature is reduced, an oxygen-helium mix (2% O₂ 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 CH₄ 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.

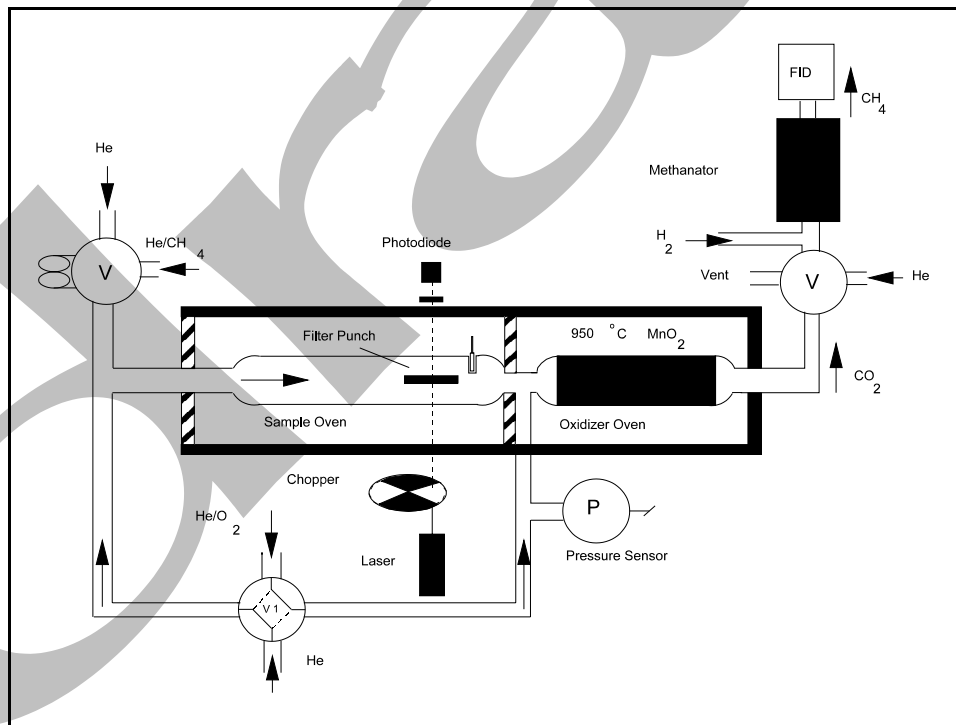


Figure 1. Schematic of Thermal-Optical Analyzer.

Table 1
Production and Equipment Information for Ramona, California Project
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Description	4/24/96 Conventional Asphalt	4/25/96 Conventional Asphalt	4/29/96 CRM Asphalt	4/30/96 CRM Asphalt
Pavement Function	Overlay of two lane county streets (rural residential)	Overlay of two lane county streets (rural residential)	Surface overlay of two lane road (rural)	Surface overlay of two lane road (rural)
Hot Mix Asphalt Type	Type 2C3, 13 mm (½") size medium gap grade mix	Type 2C3, 13 mm (½") size medium gap grade mix	Rubber 13 mm (½") size maximum gap grade mix	Rubber 13 mm (½") size maximum gap grade mix
Crude Supplier	Paramount	Paramount	Paramount	Paramount
Asphalt Cement Grade	AR 4000	AR 4000	AR 4000	AR 4000
%Binder Content	5.3%	5.3%	8.0%	8.0%
% Rubber (total weight of rubber by total weight of asphalt/rubber blend)	Not Applicable	Not Applicable	20% (Supplier: Baker Rubber Company)	20% (Supplier: Baker Rubber Company)
Rubber Blending	Not Applicable	Not Applicable	Wet	Wet
Production, in metric tons	1905 (2100 short tons)	1021 (1125 short tons)	1814 (2000 short tons)	1660‡ (1830 short tons)
Asphalt Laydown Temperature (estimated)	138°C (280°F)	138°C (280°F)	163°C (325°F)	160°C (320°F)
Mat Thickness (uncompacted)	4.5 centimeters	4.5 centimeters	4.5 centimeters	4.5 centimeters
Laydown Width (approximation)	7.3 meters (24')	7.3 meters (24')	7.3 meters (24')	7.3 meters (24')
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	6.5 hours	5.0 hours	9.5 hours	9.5 hours‡
Transport	Double (tandem) bottom dump trailers (approx. 25 long ton capacity per truck)	Double (tandem) bottom dump trailers (approx. 25 long ton capacity per truck)	Double (tandem) bottom dump trailers (approx. 25 long ton capacity per truck)	Double (tandem) bottom dump trailers (approx. 25 long ton capacity per truck)
Windrower Pick-up	Yes	Yes	Yes	Yes
Paver	Blaw Knox Model PF200B	Blaw Knox Model PF200B	Blaw Knox Model PF200B	Blaw Knox Model PF200B
Roller (joint pinch)	No	No	No	No
Roller (breakdown)	Yes	Yes	Yes	Yes
Roller (finishing)	Yes	Yes	Yes	Yes
Average Production Rate	290 metric tons/hr	200 metric tons/hr	190 metric tons/hr	175 metric tons/hr‡

Conventional = Conventional hot mix asphalt

CRM = Crumb rubber modified hot mix asphalt

‡ The crew, after completing the two-lane mountain road which they had begun on 4/29/96 at approximately 1:00 pm on 4/30/96, switched to a new paving location (a two-lane road in a valley about 15 minutes from the original site). This change disrupted the sampling times on several members of the paving crew (paver operator, screed operator, and a laborer). The total tons paved, as well as the job duration, is estimated between these two locations.

Table 2
Summary of Sampling and Analytical Methods
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Substance	Flow Rate (Lpm)	Sample Media	Analytical Method	Comments
Total Particulate[‡]	2.0	Tared Zefluor filter (37 mm diameter, 1 µm pore size)	NIOSH Method No. 0500, with modifications Gravimetric analysis	The modification to this method involved substituting a tared Zefluor filter in place of a tared PVC filter for sample collection. 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 42 sorbent tube	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	Tared Zefluor filter (37 mm diameter, 1 µm pore size) Note: In three NIOSH asphalt paving surveys conducted prior to this evaluation, a glass fiber filter was used.	OSHA Method No. 58, with modifications. The filters were rinsed with benzene, the leachate collected and evaporated, and the residue weighed to report the benzene soluble fraction. 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 ²) 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.
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.

Table 2
Summary of Sampling and Analytical Methods
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Substance	Flow Rate (Lpm)	Sample Media	Analytical Method	Comments
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.	Specific VOCs that were quantified included benzene, toluene, MIBK, and petroleum distillates (other hydrocarbons with retention times greater than toluene).
H₂S, SO₂, CO	Diffusion	Toxilog® diffusion monitors for H ₂ S, SO ₂ , CO.	Toxilog® diffusion monitors use individual electrochemical sensors specific for H ₂ S, SO ₂ , CO.	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. [Houk et al. 1991; Mut. Res. 1989].	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.

‡ In this evaluation a new sampling and analytical technique was used to measure both total particulate and the benzene soluble particulate fraction from the same sample filter. The advantage to this approach is that additional personal breathing-zone information may be obtained. The most significant modification involved using a 37 millimeter, 1.0 µm pore size tared Zefluor filter in place of a tared PVC filter typically used for total particulate sampling. Used previously in HETA 95-0307-XXXX, this new combination method has yet to be assigned a NIOSH sampling and analytical method number .

The following are abbreviations which were not spelled out in the table.

PVC	=	Polyvinyl chloride	SO ₂	=	Sulfur dioxide
mm	=	millimeter	CO	=	Carbon monoxide
µm	=	micrometer	Lpm	=	Liters per minute
GC-FID	=	Gas chromatography-flame ionization detector	MIBK	=	Methyl isobutyl ketone
H ₂ S	=	Hydrogen sulfide	Zefluor	=	Teflon® sampling filter
HPLC	=	High pressure liquid chromatography	nm	=	Nanometer

**Table 3
Toxicity and Exposure Criteria Information
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)**

Compound	Toxicity Review	Exposure Criteria
<p>Asphalt Fume (As Total Particulate)</p>	<p>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.</p>	<p>The NIOSH REL is 5 mg/m³ for a 15-minute ceiling exposure.</p> <p>There is no current OSHA PEL for asphalt fume.</p> <p>The ACGIH TLV is 5 mg/m³ as an 8-hour TWA to total particulate.</p>
<p>Respirable Particulate</p>	<p>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.</p> <p>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.</p>	<p>No NIOSH REL</p> <p>The OSHA PEL is 5 mg/m³, 8-hour TWA.</p> <p>The ACGIH TLV for particulates not otherwise classified is 10 mg/m³ for inhalable particulate and 3 mg/m³ for respirable particulate. Both are 8-hour TWAs.</p>
<p>Benzene Soluble Particulate</p>	<p>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.</p> <p>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).</p>	<p>None established for BSF associated with asphalt fume</p>
<p>Polynuclear Aromatic Hydrocarbons and Polycyclic Aromatic Compounds</p>	<p>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.</p> <p>Polycyclic aromatic compounds refers 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.</p> <p>NIOSH investigators have hypothesized that PACs with 2 to 3 rings (referred to in this report as PAC₃₇₀) are associated with more irritative effects, while the 4 to 7 ring PACs (termed PAC₄₀₀) may have more carcinogenic and/or mutagenic effects. It is not currently possible 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.</p>	<p>None established for PAHs and PACs as a class.</p>

Table 3
Toxicity and Exposure Criteria Information
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Compound	Toxicity Review	Exposure Criteria
Benzothiazole	In its pure form, benzothiazole is a yellow liquid with an unpleasant odor [Sax et al. 1987]. It is used as a rubber vulcanization accelerator [ILO 1971], as an antimicrobial agent [Ito 1978], and in dyes [Kirk 1978]. Benzothiazole was identified in the air during rubber vulcanization [Rappaport et al. 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
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. No specific occupational exposure limits exist for this group of sulfur compounds, but it was hypothesized that some compounds 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 et al. 1989]. A copy of the draft NIOSH Method 5040 is provided in Appendix B.	None established
MIBK	Tire rubber may be a source for methyl isobutyl ketone (MIBK) since this organic compound can be used as an antioxidant in the tire manufacturing process. In its pure form, MIBK is a colorless, flammable organic solvent that is typically used 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 [Hathaway 1991]. At air concentrations much higher than were measured in this asphalt study, MIBK has caused central nervous system depression [Hathaway 1991]. Continued or prolonged skin contact with the liquid can cause dermatitis [Hathaway 1991].	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 1996].	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 irritation 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 [Hathaway 1991, 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 1996].	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).

**Table 3
Toxicity and Exposure Criteria Information
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)**

Compound	Toxicity Review	Exposure Criteria								
Xylene	Structurally similar to toluene, xylene can also cause acute irritation of the eyes, respiratory tract, and skin [Hathaway 1991]. 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 [Hathaway 1991].	<p>NIOSH REL is 100 ppm, 8-hour TWA.</p> <p>OSHA PEL is 100 ppm, 8-hour TWA.</p> <p>ACGIH TLV is 100 ppm for an 8-hour TWA and 150 ppm for a 15-minute STEL</p>								
<p align="center">Total Hydrocarbons</p> <p>(as either n-hexane or Stoddard solvent)</p>	In this study, total hydrocarbons (HC) were quantified as either n-hexane or as Stoddard solvent, a petroleum distillate mixture. Effects from exposure to either n-hexane or Stoddard solvent are primarily acute (such as upper respiratory irritation, nausea, headaches, and irritation of the eyes and nose), unless significant amounts of substances that have chronic toxicity are present, such as benzene or glycol ethers[Hathaway 1991]. 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 either n-hexane or Stoddard solvent).	<p>NIOSH REL is 350 mg/m³, 10-hour TWA (for all petroleum distillate mixtures, including Stoddard solvent). The NIOSH ceiling limit is 1800 mg/m³, 15 minutes.</p> <p>OSHA PEL for Stoddard solvent is 2,900 mg/m³, 8-hour TWA.</p> <p>ACGIH TLV for Stoddard solvent is 525 mg/m³, 8-hour TWA.</p> <p>NIOSH REL for n-hexane is 180 mg/m³ for up to a 10-hour TWA.</p> <p>OSHA PEL for n-hexane is 1,800 mg/m³, 8-hour TWA.</p> <p>ACGIH TLV for n-hexane is 176 mg/m³, 8-hour TWA.</p>								
<p>Abbreviations:</p> <table border="0"> <tr> <td>REL = recommended exposure limit (NIOSH)</td> <td>PEL = permissible exposure limit (OSHA)</td> </tr> <tr> <td>TLV = Threshold Limit Value (ACGIH)</td> <td>TWA = Time-weighted average</td> </tr> <tr> <td>STEL = Short-term exposure limit</td> <td>ppm = parts per million</td> </tr> <tr> <td>µm = micrometers</td> <td>mg/m³ = milligrams per cubic meter</td> </tr> </table>			REL = recommended exposure limit (NIOSH)	PEL = permissible exposure limit (OSHA)	TLV = Threshold Limit Value (ACGIH)	TWA = Time-weighted average	STEL = Short-term exposure limit	ppm = parts per million	µm = micrometers	mg/m ³ = milligrams per cubic meter
REL = recommended exposure limit (NIOSH)	PEL = permissible exposure limit (OSHA)									
TLV = Threshold Limit Value (ACGIH)	TWA = Time-weighted average									
STEL = Short-term exposure limit	ppm = parts per million									
µm = micrometers	mg/m ³ = milligrams per cubic meter									

Table 4
Summary of Environmental Conditions
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Description	4/24/96 Conventional Asphalt	4/25/96 Conventional Asphalt	4/29/96 CRM Asphalt	4/30/96 CRM Asphalt
Summary	Sunny, warm, and dry	Sunny, warm, and dry	Sunny, warm, and dry	Sunny, warm, and dry
Minimum Temp.	27°C (81°F)	22°C (71°F)	25°C (77°F)	24°C (76°F)
Maximum Temp.	34°C (94°F)	30°C (86°F)	35°C (95°F)	33°C (91°F)
Average Humidity	19%	32%	11%	15%
Minimum WBGT	58°F	61°F	49°F	*
Maximum WBGT	64°F	66°F	70°F	*
Wind Speed	variable breeze 0 to 7 mph	variable breeze 2 to 8 mph	steady breeze with gusts up to 12 mph	moderate breeze with gusts up to 12 mph in the afternoon
Wind Direction	210° to 270° (winds from SW-W)	210° to 290° (winds from SW-NW)	30° to 240° (variable winds from NE- SW)	230° to 290° (winds from SW-NW)
Traffic Density	Low	Low	Low	Low

WBGT = Wet bulb globe temperature, a heat stress index
 Conventional = Non-rubber hot mix asphalt
 Crumb Rubber = Crumb rubber modified hot mix asphalt

* Not Applicable, low battery in the WBGT meter prevented data logging.

Note:

Wind direction is expressed in degrees, ranging from 0° to 360°. Zero degrees (0°) refers to wind from the north (N); 90° describes wind from the east (E); 180° refers to wind from the south (S); and 270° is wind from the west (W).

Table 5
Total Particulate Concentration and Benzene Soluble Fraction Concentration: Area Samples
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m ³)	
				Total Particulate	Benzene Soluble Fraction
Conventional Asphalt 4/24/96	Screed Left	399	798	1.7	1.2
	Screed Left	399	798	2.9	2.4
	Screed Right	404	808	2.9	2.1
	Screed Right	404	808	2.9	2.1
	Highway Background 1	365	730	0.01	ND
	Highway Background 2	290	566	0.06	ND
	Highway Background 3	383	747	0.05	ND
Conventional Asphalt 4/25/96	Screed Left	315	630	1.7	1.1
	Screed Left	315	630	1.9	1.1
	Screed Right	317	634	2.9	1.9
	Screed Right	317	618	3.0	2.0
	Highway Background 1	308	616	0.04	ND
	Highway Background 2	310	597	0.05	ND
	Highway Background 3	288	576	0.09	ND
CRM Asphalt ¹ 4/29/96	Screed Left	602	1174	5.7	5.4
	Screed Left	602	1204	5.2	4.7
	Screed Right	588	1176	6.3	5.6
	Screed Right	588	1176	6.1	5.5
	Highway Background 1	548	1096	0.03	ND
	Highway Background 2	548	1069	0.03	ND
	Highway Background 3	534 [■]	1068	0.04	ND
CRM Asphalt ² 4/30/96	Screed Left	544	1088	2.1	1.7
	Screed Left	544	1088	3.0	2.8
	Screed Right	540	1080	1.8	1.6
	Screed Right	540	1080	1.4	1.2
	Highway Background 1	553	1106	0.06	ND
	Highway Background 2 [•]	306	612	0.03	ND
	Highway Background 3	620	1240	0.04	ND

mg/m³ = Concentration, milligrams per cubic meter
 ND = Not Detected; value was below the Minimum Detectable Concentration (MDC). The analytical Limit of Detection was 0.03 mg which equates to a MDC of 0.04 mg/m³, assuming a sampling volume of 835 Liters.

■ Actual sampling time was estimated due to a recording error.
 • For approximately 1 hour at the end of the sampling period, this sample was located in the pilot car.
¹ No paving occurred between 2:20 pm to 3:00 pm due to transfer of paving equipment to a new site.
² All samples except Background 2&3 were transferred to a second paving site between 1:40 pm and 2:40 pm. Screed samples were shut off during transfer, while Background 1 was not shut off during the transfer.

Table 6
Respirable Particulate Concentrations: Area Samples
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m ³)
Conventional Asphalt 4/24/96	Screed (Left)	399	678	1.2
	Screed (Right)	404	687	1.2
	Highway Background	365	620	0.03
Conventional Asphalt 4/25/96	Screed (Left)	315	536	0.20
	Screed (Right)	317	523	1.2
	Highway Background	308	524	ND
CRM Asphalt ¹ 4/29/96	Screed (Left) [■]	128	218	9.0
	Screed (Right) [■]	516	877	2.3
	Highway Background	548	932	0.03
CRM Asphalt ² 4/30/96	Screed (Left)	544	925	1.3
	Screed (Right)	540	918	0.9
	Highway Background	553	940	0.02

mg/m³ = Concentration, milligrams per cubic meter
 ND = Not Detected; value was below the Minimum Detectable Concentration (MDC). The analytical Limit of Detection was 0.02 mg, which equates to a MDC of 0.02 mg/m³, assuming a sampling volume of 940 Liters.

■ Sampling pumps faulted during the sampling period; therefore, sampling times and volumes were estimated using the internal timers on the sampling pumps.

¹ No paving occurred between 2:20 pm to 3:00 pm due to transfer of paving equipment to a new site.

² All samples were transferred to a second paving site between 1:40 pm and 2:40 pm. Screed samples were shut off during transfer, while the Background sample was not shut off during the transfer.

Table 7
Concentrations of Polycyclic Aromatic Compounds (PACs): Area Samples
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, micrograms per cubic meter			
				PACs @ 370 nm	PACs @ 400 nm	Other SulCom	Benzothiazole
Conventional Asphalt 4/24/96	Screed Left	399	798	102	16	139	ND
	Screed Left	399	798	130	20	123	ND
	Screed Right	404	808	132	22	113	ND
	Screed Right	404	808	136	22	144	trace
	Highway Background	365	712	1.2	0.11	ND	ND
Conventional Asphalt 4/25/96	Screed Left	315	630	65	8.9	48	ND
	Screed Left	315	630	65	9.0	41	ND
	Screed Right	317	634	116	17	88	ND
	Screed Right	317	634	119	15	26	ND
	Highway Background	308	616	ND	ND	ND	ND
CRM Asphalt ¹ 4/29/96	Screed Left [■]	471	942	228	41	65	44
	Screed Left [■]	577	1154	222	39	48	31
	Screed Right	588	1176	224	40	62	52
	Screed Right	588	1147	233	40	58	51
	Highway Background	548	1096	0.2	trace	ND	ND
CRM Asphalt ² 4/30/96	Screed Left	544	1088	140	23	47	39
	Screed Left	544	1088	151	26	58	40
	Screed Right	540	1080	103	15	25	28
	Screed Right	540	1053	105	17	29	26
	Highway Background	553	1106	trace	ND	ND	ND

PACs = Polycyclic Aromatic Compounds
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)
ND = Not Detected; value was below the Minimum Detectable Concentration (MDC)
Trace = Concentration is between the MDC and Minimum Quantifiable Concentration (MQC)

Note: The MDC and MQC are calculated by dividing the analytical Limit of Detection and Limit of Quantification, respectively, by the air sample volume. The respective MDCs and MQCs for these analytes were 0.02 and 0.05 µg/m³ for PACs@370 nm, 0.03 and 0.10 µg/m³ for PACs@400 nm, and 1.1 and 4.6 µg/m³ for both benzothiazole and other SulCom assuming an average air sample volume of 900 Liters.

■ Sampling pumps faulted during the sampling period; therefore, sampling times and volumes were estimated.

¹ No paving occurred between 2:20 pm to 3:00 pm due to transfer of paving equipment to a new site.

² All samples were transferred to a second paving site between 1:40 pm and 2:40 pm. Screed samples were shut off during transfer, while the Background sample was not shut off during the transfer.

Other Comments:

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

Table 8
Elemental Carbon Concentrations: Area Samples
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, micrograms per cubic meter			EC/TC
				Organic Carbon (OC)	Elemental Carbon (EC)	Total Carbon (TC)	
Conventional Asphalt 4/24/96	Screed (Left)	399	798	1973	14	1987	0.7%
	Screed (Right)	404	808	2282	13	2295	0.6%
	Highway Background	365	712	41	2.7	44	6.1%
Conventional Asphalt 4/25/96	Screed (Left)	315	630	916	9.8	926	1.1%
	Screed (Right)	†	†	†	†	†	†
	Highway Background	308	616	8.8	0.8	9.6	8.3%
CRM Asphalt ¹ 4/29/96	Screed (Left)	602	1204	6021	21	6042	0.3%
	Screed (Right)	588	1176	6547	14	6561	0.2%
	Highway Background	548	1151	9.2	1.0	10	10%
CRM Asphalt ² 4/30/96	Screed (Left)	544	1088	2253	45	2298	2.0%
	Screed (Right)	540	1080	1532	16	1548	1.0%
	Highway Background	553	1106	26	2.7	29	9.3%
EC/TC = Ratio of Elemental Carbon to Total Carbon † Sample was lost during collection (filter was dislodged from sampling equipment). No paving occurred between 2:20 pm to 3:00 pm due to transfer of paving equipment to a new site. ² All samples were transferred to a second paving site between 1:40 pm and 2:40 pm. Screed samples were shut off during transfer, while the Background sample was not shut off during the transfer.							

**Table 9
Concentrations of Selected Volatile Organic Compounds (VOCs): Area Samples
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)**

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, expressed in parts per million				Concentration, expressed in mg/m ³	
				Benzene	Toluene	Xylene	MIBK	Total HC < Toluene [†]	Total HC > Toluene [‡]
Conventional Asphalt Paving 4/24/96	Screed (Left)	399	79.8	trace	trace	0.08	trace	0.70	25
	Screed (Right)	404	80.8	trace	trace	0.07	trace	1.1	21
Conventional Asphalt Paving 4/25/96	Screed (Left)	315	63.0	ND	ND	0.03	trace	0.27	6.3
	Screed (Right)	317	63.4	ND	ND	0.04	trace	0.49	8.4
CRM Asphalt Paving 4/29/96	Screed (Left)	602	120	0.02	trace	0.18	0.08	0.92	34
	Screed (Right)	588	118	trace	trace	0.16	0.07	0.58	20
CRM Asphalt Paving 4/30/96	Screed (Left)	544	109	trace	trace	0.18	0.07	0.69	26
	Screed (Right)	540	108	trace	trace	0.13	trace	0.56	18

mg/m³ = Concentration, milligrams per cubic meter.
MIBK = Methyl isobutyl ketone.
Trace = Concentration is between the Minimum Detectable Concentration (MDC) and Minimum Quantifiable Concentration (MQC).
ND = Not Detected; value was below the MDC.

Note: The MDC and MQC are calculated by dividing the analytical Limit of Detection and Limit of Quantification, respectively, by the air sample volume. The respective MDCs and MQCs for these analytes were 0.01 and 0.02 ppm for benzene, 0.01 and 0.03 ppm for toluene, and 0.02 and 0.06 ppm for MIBK assuming average air sample volumes of 92.8 Liters for benzene and toluene and 120 Liters for MIBK.

[†] Total hydrocarbons with a gas chromatograph retention time less than (<) toluene. These concentrations are expressed in milligrams per cubic meter (mg/m³).
[‡] Total hydrocarbons with a gas chromatograph retention time greater than (>) toluene. These concentrations are expressed in milligrams per cubic meter (mg/m³).
¹ No paving occurred between 2:20 pm to 3:00 pm due to transfer of paving equipment to a new site.
² All samples were transferred to a second paving site between 1:40 pm and 2:40 pm. Screed samples were shut off during transfer.

Table 10
Total Particulate and Benzene Soluble Particulate Concentrations: Personal Breathing-Zone Samples
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Sampling Date	Activity	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m ³)	
				Total Particulate	Benzene Soluble
Conventional Asphalt 4/24/96	Truck Dumper†	408	816	0.63	0.32
	Truck Dumper‡	392	725	0.50	0.21
	Paver Operator	422	823	0.70	0.46
	Screed Operator (Left)	393	786	0.67	0.17
	Screed Operator (Right)	402	784	0.47	0.22
	Raker	403	806	0.22	0.07
	Raker	407	814	0.36	0.12
	Breakdown Roller Operator	410	800	0.22	0.02
Conventional Asphalt 4/25/96	Truck Dumper†	297	594	0.89	0.14
	Truck Dumper‡	252■	479	0.60	0.14
	Paver Operator	328	656	0.55	0.23
	Screed Operator (Left)	315	614	0.76	0.15
	Screed Operator (Right)	285	606	1.0	0.21
	Raker	318	588	0.42	0.06
	Raker	320	608	0.51	0.11
	Breakdown Roller Operator	313	626	0.14	0.01
CRM Asphalt¹ 4/29/96	Truck Dumper†	590	1180	0.84	0.51
	Truck Dumper‡	613	1226	0.91	0.50
	Paver Operator	572	1144	0.91	0.75
	Screed Operator (Left)	570	1140	1.4	0.88
	Screed Operator (Right)	573	1117	1.4	1.1
	Raker●	575	1093	0.28	0.07
	Raker	571	1085	0.68	0.36
	Breakdown Roller Operator	568	1136	0.22	0.06
CRM Asphalt 4/30/96	Truck Dumper†	574	1148	0.51	0.22
	Truck Dumper‡	582	1164	0.77	0.40
	Paver Operator	440	880	0.33	0.21
	Screed Operator (Left)	299	598	0.85	0.31
	Screed Operator (Left) ²	238	476	1.0	0.67
	Screed Operator (Right)	451	879	0.28	0.10
	Raker	422	823	0.34	0.16
	Raker	541	1028	0.45	0.18
	Breakdown Roller Operator	268	536	0.19	0.03

mg/m³ = Concentration, milligrams per cubic meter

† This truck dumper was situated **nearer** to the paving vehicle than the other truck dumper.

‡ This truck dumper was situated **farther** from the paving vehicle than the other truck dumper.

■ Sampling period reduced by 60 minutes because the tubing connecting the pump to the filter was inadvertently disconnected.

● Tubing connecting the sampler to the pump was reconnected at 3:30 pm.

¹ No paving occurred between 2:20 pm to 3:00 pm due to the transfer of paving equipment to a new site.

² Sample collected at the second paving site. At this location the employee worked as paver operator and screed operator.

Table 11
Concentrations of Polycyclic Aromatic Compounds (PACs): Personal Breathing-Zone Samples
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Sampling Date	Work Activity	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, micrograms per cubic meter			
				PACs @ 370 nm	PACs @ 400 nm	Other SulCom†	Benzothiazole
Conventional Asphalt 4/24/96	Truck Dumper†	408	796	9.9	1.4	ND	ND
	Truck Dumper‡	392	745	12	1.6	ND	ND
	Paver Operator	422	823	24	3.3	7.2	ND
	Screed Operator (Left)	393	766	20	2.7	trace	ND
	Screed Operator (Right)	402	804	26	3.5	7.3	ND
	Raker	403	767	5.7	0.78	ND	ND
	Raker	407	814	10	1.2	ND	ND
Breakdown Roller Operator	410	779	1.3	0.15	ND	ND	
Conventional Asphalt 4/25/96	Truck Dumper†	297	579	8.3	1.1	ND	ND
	Truck Dumper‡	312	593	9.1	1.2	ND	ND
	Paver Operator	328	640	13	1.7	ND	ND
	Screed Operator (Left)	315	599	11	1.4	ND	ND
	Screed Operator (Right)	285	556	16	2.1	trace	ND
	Raker	318	620	5.0	0.61	ND	ND
	Raker	320	608	7.2	0.92	ND	ND
Breakdown Roller Operator	313	610	0.95	0.16	ND	ND	
CRM Asphalt ¹ 4/29/96	Truck Dumper†	590	1151	23	3.0	trace	19
	Truck Dumper‡	613	1226	28	4.1	ND	16
	Paver Operator	572	1144	37	5.3	trace	27
	Screed Operator (Left)	570	1112	43	6.4	ND	6.8
	Screed Operator (Right)	573	1146	58	8.1	5.7	40
	Raker	575	1121	5.6	0.70	ND	trace
	Raker	571	1142	15	2.2	ND	16
Breakdown Roller Operator	568	1051	4.2	0.57	ND	ND	
CRM Asphalt 4/30/96	Truck Dumper†	574	1148	12	1.5	ND	14
	Truck Dumper‡	582	1106	14	1.7	ND	19
	Paver Operator	440	858	15	1.9	ND	23
	Screed Operator (Left)	299	598	24	3.6	ND	43
	Screed Operator (Left) ²	238	476	46	6.6	7.6	94
	Screed Operator (Right)	451	879	11	1.4	ND	20
	Raker	422	844	11	1.5	ND	21
	Raker	541	1055	12	1.6	ND	19
Breakdown Roller Operator	268	523	*	*	*	*	

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)
ND = Not Detected; value is below the Minimum Detectable Concentration (MDC)
trace = Concentration is between the MDC and Minimum Quantifiable Concentration (MQC)
Note: The MDC and MQC are calculated by dividing the analytical Limit of Detection and Limit of Quantification, respectively, by the air sample volume. The respective MDCs and MQCs for both benzothiazole and other SulCom were 1.2 and 4.9 µg/m³ assuming an average air sample volume of 839 Liters.
† This truck dumper was situated **nearer** to the paving vehicle than the other truck dumper.
‡ This truck dumper was situated **farther** from the paving vehicle than the other truck dumper.
¹ No paving occurred between 2:20 pm to 3:00 pm due to the transfer of paving equipment to a new site.
² Sample collected at the second paving site. At this location the employee worked as paver operator and screed operator.
* sample lost during analysis

Table 12
Number of Acute Symptom Questionnaires Completed by Workers
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Work Group		Acute Questionnaires Completed			
		4/24/96 Day 1 Conventional Asphalt	4/25/96 Day 2 Conventional Asphalt	4/29/96 Day 3 CRM Rubber Asphalt	4/30/96 Day 4 CRM Rubber Asphalt
Pavers■ (n= 7)		35/35	28/28 *	35/35	35/35
Non-pavers◆ (n=8)		40/40	38/40	28/30**	40/40
Paving Period Totals	Pavers	63/63		70/70	
	Non-pavers	78/80		68/70	

* = Short paving workshift (five hours) provided only enough time to complete four rounds of acute questionnaires.
** = One non-paver off on sick leave and one off on regular leave.
■ = All seven pavers participated in the study for all four survey days.
◆ = All eight non-pavers participated in the study for all four survey days, except for two workers who were off on day three.

Table 13
Number of Workers Reporting Symptoms and Number of Symptom Occurrences by Survey Day
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Symptoms	Work Groups	Number of workers reporting symptoms (Number of symptom occurrences reported)			
		4/24/96 Day 1 Conventional Asphalt	4/25/96 Day 2 Conventional Asphalt	4/29/96 Day 3 CRM Asphalt ‡	4/30/96 Day 4 CRM Asphalt
Dry, itching, or irritated eyes	Pavers	3(7)	1 (4)	5 (20)	5 (13)
	Non-pavers	2 (3)	1 (1)	0	3 (6)
Stuffy, burning, or irritated nose	Pavers	4 (12)	2 (7)	4 (16)	2 (8)
	Non-pavers	2 (6)	3 (6)	1 (1)	1 (4)
Sore, dry, scratchy, or irritated throat	Pavers	4 (16)	3 (12)	4 (18)	4 (14)
	Non-pavers	0	1 (1)	0	2 (6)
Skin burning, rash, itching, or irritated	Pavers	0	0	0	0
	Non-pavers	1 (1)	0	1 (3)	2 (6)
Bothered by coughing	Pavers	1 (5)	1 (4)	2 (8)	2 (10)
	Non-pavers	1 (1)	1 (1)	0	1 (1)
Chest tightness or shortness of breath	Pavers	1 (2)	1 (1)	0	1 (1)
	Non-pavers	1 (1)	0	0	0
Wheezing or whistling in chest	Pavers	0	0	0	1 (3)
	Non-pavers	0	0	0	0
Totals	Pavers (n=7)	6 (42)	3 (28)	6 (62)	7 (49)
	Non-pavers (n=8)	3 (12)	3 (9)	2 (4)	4 (23)

‡ = Two non-pavers were absent from work on survey day three

Table 14
Rate of Symptoms Occurrence Per Questionnaire Among Pavers by Survey Day
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Pavers (n=7)	4/24/96 Day 1 Conventional Asphalt	4/25/96 Day 2 Conventional Asphalt	4/29/96 Day 3 CRM Rubber Asphalt	4/30/96 Day 4 CRM Rubber Asphalt
	Completed Questionnaires	35	28	35
Symptom Occurrences	42	28	62	49
Rate symptom occurrence per questionnaire	1.2	1.0	1.8	1.4
	1.1 ‡		1.6 ‡	

‡ Average rate (over two days) of symptom occurrence per questionnaire

Table 15
Estimated Hours of Exposure to Asphalt Fume Among Pavers by Job Title and Survey Day
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Job Title (n=7)	Estimated hours exposure to asphalt fume			
	4/24/96 Day 1 Conventional Asphalt	4/25/96 Day 2 Conventional Asphalt	4/29/96 Day 3 CRM Rubber Asphalt	4/30/96 Day 4 CRM Rubber Asphalt
Paver Operator	6.75	4.5	7.75	6.5
Screed Operator	6.5	4.25	7.75	7.75
Screed Operator	6.75	4.5	7.75	6.75
Raker / Laborer	6.5	2.5	7.5	6.25
Raker / Laborer	6.75	4.0	7.75	8.0
Dumpman	6.75	4.0	7.25	7.5
Roller Operator	6.75	4.5	8.0	6.0
Daily Total Hours (Average)	46.75 (6.7)	28.25 (4.0)	53.75 (7.7)	48.75 (7.0)
Total Hours by Asphalt Paving Material (Average)	75.0 (5.4)		102.5 (7.3)	

Table 16
Rate of Symptoms Per Hour of Exposure Among Pavers by Survey Day
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

Pavers (n=7)	4/24/96 Day 1 Conventional Asphalt	4/25/96 Day 2 Conventional Asphalt	4/29/96 Day 3 CRM Rubber Asphalt	4/30/96 Day 4 CRM Rubber Asphalt
Estimated Exposure to Asphalt (total hours)	46.75	28.25	53.75	48.75
Number Symptom Occurrences	42	28	62	49
Rate (symptom occurrence/hr exposure)	0.9	1.0	1.2	1.0
	0.9		1.1	

Table 17
Summary of Area Concentrations of Air Contaminants
Paving Site: Sim J. Harris Company, San Diego, California (HETA 96-0130)

	Analyte	TWA Concentration, expressed in micrograms per cubic meter								
		4/24/96 Conventional		4/25/96 Conventional		4/29/96 Crumb Rubber		4/30/96 Crumb Rubber		
Air Sample Position at Screenshot →		Left	Right	Left	Right	Left	Right	Left	Right	
Paver Screenshot	Total Particulate	1730	2920	1740	2900	5740	6260	2080	1820	
	Benzene Soluble Fraction	1230	2070	1090	1940	5420	5580	1680	1640	
	Total Particulate	2900	2870	1850	2970	5200	6110	3040	1400	
	Benzene Soluble Fraction	2350	2080	1070	1980	4700	5490	2830	1230	
	PAC ₃₇₀ (vapor & particulate)	102	132	65	116	228	224	140	103	
	PAC ₄₀₀ (vapor & particulate)	16	22	8.9	17	41	40	23	15	
	PAC ₃₇₀ (vapor & particulate)	130	136	65	119	222	233	151	105	
	PAC ₄₀₀ (vapor & particulate)	20	22	9.0	15	39	40	26	17	
	Benzothiazole	ND	ND	ND	ND	44	52	39	28	
	Other Sulfur Compounds	139	113	48	88	65	62	47	25	
	Benzothiazole	ND	trace	ND	ND	31	51	40	26	
	Other Sulfur Compounds	123	144	41	26	48	58	58	29	
	Total Hydrocarbons with a retention time < toluene	700	1100	270	490	920	580	690	560	
	Total Hydrocarbons with a retention time > toluene	25000	21000	6300	8400	34000	20000	26000	18000	
	Respirable Particulate	1190	1280	200	1210	9010	2280	1310	940	
	Highway Background	Total Particulate	40		60		30		40	
		Benzene Soluble Fraction	ND		ND		ND		ND	
		PAC ₃₇₀ (vapor & particulate)	1.2		ND		0.2		trace	
PAC ₄₀₀ (vapor & particulate)		0.11		ND		trace		ND		
Benzothiazole		ND		ND		ND		ND		
Other Sulfur Compounds		ND		ND		ND		ND		
Respirable Particulate		30		ND		30		20		

PAC₃₇₀ = Polycyclic aromatic compound measured with 370 nanometer wavelength detector
PAC₄₀₀ = Polycyclic aromatic compound measured with 400 nanometer wavelength detector
ND = Not Detected; value is below the Minimum Detectable Concentration (MDC). MDCs are calculated by dividing the analytical Limit of Detection by the air sample volume.
trace = Concentration was between the MDC and Minimum Quantifiable Concentration (MQC). MQCs are calculated by dividing the analytical Limit of Quantification by the air sample volume.

The respective MDCs were 1.1 µg/m³ for benzothiazole and other sulfur compounds, 40 µg/m³ for benzene solubles, 0.02 µg/m³ for PAC₃₇₀, 0.03 µg/m³ for PAC₄₀₀, and 20 µg/m³ for respirable particulates. The MDCs for benzothiazole, other sulfur compounds, PAC₃₇₀, and PAC₄₀₀ were calculated assuming an average sample volume of 900 Liters, while the MDCs for benzene solubles and respirable particulates were calculated assuming average sample volumes of 835 and 940 Liters, respectively.

Concentrations were between the respective MDCs and MQCs of 1.1 and 4.6 µg/m³ for benzothiazole, 0.02 and 0.06 µg/m³ for PAC₃₇₀, and 0.03 and 0.10 µg/m³ for PAC₄₀₀. All values were calculated assuming an average sample volume of 900 Liters.